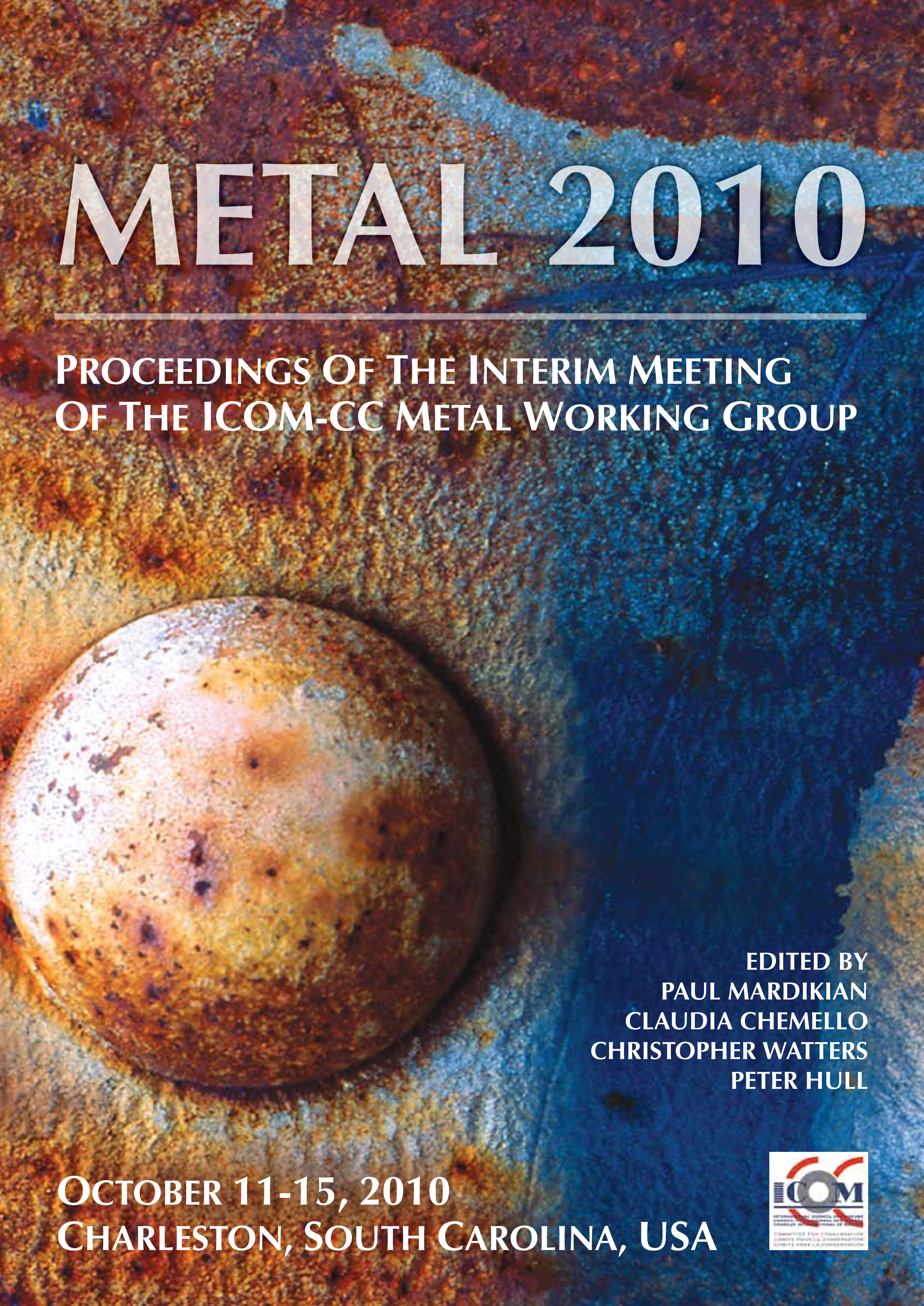

METAL 2010

PROCEEDINGS OF THE INTERIM MEETING OF THE ICOM-CC METAL WORKING GROUP

EDITED BY
PAUL MARDIKIAN
CLAUDIA CHEMELLO
CHRISTOPHER WATTERS
PETER HULL

OCTOBER 11-15, 2010
CHARLESTON, SOUTH CAROLINA, USA

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DEDICATION

The Editors and Organizing Committee for METAL 2010 dedicate this volume to our dear friend and mentor Ian Donald MacLeod.

Ian, we acknowledge your outstanding contribution to the field of materials conservation and scientific research, and thank you for your constant support, good humor and passion. Your gifts of enthusiasm, wonder and curiosity have enriched our lives and continue to inspire us all.

Ian Donald MacLeod is Executive Director, Collections Management and Conservation, at the Western Australian Museum, an institution with which he has been affiliated for 32 years.

He received a PhD in chemistry studying the electrochemistry of metal fluorides in liquid anhydrous hydrogen fluoride from the University of Melbourne in 1974. His research taught him the experimental skills of dealing with highly corrosive, moisture and oxygen sensitive and toxic but delightful chemicals. His first post-doctoral position was a two-year position at the University of Glasgow in Scotland, where he studied organometallic chemistry and examined the intra-molecular bonding in the chlorination catalysts. During this period, he managed to blow up the laboratory and himself while developing new compounds with reactive intermediates!

Ian returned to Australia in 1976 and joined the team at Murdoch University in Perth, Western Australia, where he worked on the electrochemistry of copper and its minerals in mixed solvent systems, and taught the first electrochemistry course at that institution. After three years at Murdoch, he began working as a research officer in the Department of Materials Conservation at the Western Australian Museum in Fremantle.

Shortly after Ian began work at the museum, the wreck of the American China Trader *Rapid* (1811) was discovered, prompting him to learn how to scuba dive and take his instruments underwater to look at corrosion processes on the seabed with Neil North. Ian and Neil began a systematic study of corroding metal objects in their natural environment, and followed them through excavation and conservation to exhibition in Western Australian museums across the state. Over the last 32 years, Ian has applied his knowledge of chemistry to solve countless conservation problems, as well as developing new methods to stabilize shipwreck artifacts. He helped conserve large sections of the wooden hull timbers from the *Batavia* (1629) and also has worked on solving deterioration problems on a wide range of materials as diverse as aboriginal rock art sites, headstones in cemeteries, cathedrals and automobiles.

Ian's most significant projects have included the assessment, excavation and conservation of the engine of the SS *Xantho* (1872) and the analysis of the decay patterns on the HMS *Sirius* (1790) site on Norfolk Island off the East coast of Australia. This project included in situ treatment of anchors and cannon from the *Sirius*, the flagship of the First Fleet, the group of 11 ships that sailed from England to establish the first European colony in Australia. One of Ian's most far-reaching accomplishments has been learning how to read corrosion patterns and interpreting them for maritime archaeologists and conservators.

Dr. MacLeod has taught conservation programs in Finland, the Netherlands and in Australia, and his research, influence and knowledge extends around the world. He has written more than 120 papers about the corrosion of metals and the conservation of artifacts and has presented countless papers at national and international conferences. Few people could forget listening to one of his inspired lectures, always delivered with innate style, flair, humor, and the occasional sound effect.

Ian has been a Metal Working Group coordinator for ICOM-CC for three terms, a member of the Directory Board for two terms and a Program Committee member for several triennial meetings. He is currently a member of the advisory panel for the *H.L. Hunley* and USS *Monitor* projects, a member of the Royal Society of Chemistry, a Chartered Chemist, a Fellow of the International Institute for Conservation of Historic and Artistic Works, a Fellow of the Royal Australian Chemical Institute, a Fellow of the Australian Academy of Technological Sciences and Engineering, and a Fellow of the Society of Antiquaries of Scotland.

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INTERNATIONAL COUNCIL OF MUSEUMS
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COMMITTEE FOR CONSERVATION
COMITÉ POUR LA CONSERVATION
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FOREWORD

In 1997, when I was asked to serve as chairman of Friends of the Hunley Inc., I had only one question: “What’s the Hunley?” The answer has changed my life. Three years later, on a sunny day in August 2000, I stood on the deck of a barge off the coast of Charleston, fighting back tears. Below me, the Confederate submarine *H. L. Hunley* was surfacing for the first time in 136 years from the floor of the Atlantic Ocean, where it sat buried and undiscovered for more than a century. The recovery was a complex, inter-disciplinary operation designed and carried out by numerous engineers, scientists and volunteers. The lift was an amazing success and for the first time, a Civil War-era submarine had been recovered, intact, with its crew still onboard. That day, as Charleston and the rest of the world watched the *Hunley* barged to its new home at the Warren Lasch Conservation Center in North Charleston, everyone involved thought we had pulled off a miracle. In truth, the work had just begun.

No object of the *Hunley’s* size and structural complexity has ever been fully studied and conserved. For seven years, scientists at the Lasch Conservation Center, in collaboration with Clemson University, have worked to develop a new treatment for iron artifacts. The conservation and scientific team at the Lasch Conservation Center can explain it better (and do, in their paper included in this volume), but basically, the process allows for a greater penetration of corrosion layers, and decreases the density and viscosity of the treatment solution, which promotes a more effective and efficient increase in the chloride diffusion rate. The upshot is that this new technology will speed the conservation process and save countless dollars – making it more affordable to preserve the world’s treasures in a fraction of the time previously needed to preserve these objects. And that has been one of the goals of the *Hunley* project all along, and may be one of its greatest legacies.

It is fitting that Charleston, South Carolina, was chosen as the first North American city to host the triennial conference of the International Council of Museums Committee for Conservation Metal Working Group, METAL 2010. In the last decade, the work of the *Hunley* team to document, analyze and conserve this historic submarine has been nothing short of groundbreaking. METAL 2010 showcased the work on the *Hunley*, and these proceedings present the most recent innovative research concerning the scientific study and conservation of a diverse range of subjects. These include archaeological, fine art and industrial metal objects, scientific research and analysis, and investigation of new coatings and corrosion inhibitors.

I am honored to be associated with the *Hunley* project, and I have undeniably become, in the words of State Senate President Pro Tempore Glenn McConnell, “Hunleytized,” and sincerely hope you will be, also. I enjoyed welcoming all of you to Charleston and congratulations on the success of METAL 2010.

Warren Lasch

Warren Lasch, Past Chairman
Friends of the Hunley Inc.

PREFACE

This publication contains the proceedings of METAL 2010, the International Council of Museums Committee for Conservation Metal Working Group Conference. METAL 2010 was held in Charleston, South Carolina, USA, from October 11-15, 2010. The ICOM-CC Metal Working Group (MWG) is a triennial conference organized by a different local host institution each triennial. This meeting was the sixth international meeting of the MWG. Previous conferences have been held in France, Chile, Australia and the Netherlands. In 2010, the interim meeting was held for the first time in the United States and was hosted by Clemson University, South Carolina.

The MWG is the conservation community's peak body concerned with the conservation, restoration and preservation of all objects made of metal or metallic alloys of archaeological, indigenous, artistic, or historical origin. The MWG is one of the most significant within ICOM-CC with more than 800 members. The principle objective of the group is to provide a rich forum for exchange of knowledge and experiences on the conservation of metal artifacts, to promote conservation and to promote the conservation science of metals, to encourage the networking of conservators and metals experts, and to facilitate the dissemination of information on current conservation practice, research, and education.

The forty-nine papers presented in this volume provide an overview of the current state of research in the field of metals conservation worldwide. Authors from more than 15 countries presented papers at METAL 2010, with participants attending from more than 20 countries. Many of the papers are co-written by multiple authors of several national research laboratories, cultural institutions, those in private practice or joint research programs, and illustrate the truly multidisciplinary nature of this field. The papers gathered here are truly international in their scope and represent an ongoing dialogue between conservation practice, research and science.

These papers represent an extraordinary achievement for their authors, and were chosen from more than 100 submitted abstracts. Papers were initially selected through a double-blind peer review process and then independently peer reviewed by two program committee members before final editing. Forty-six papers were presented at the conference in Charleston with three authors unable to present.

In this volume, papers have been grouped into the relevant session in which they were presented at the conference. Each paper is followed by the questions and answers for that paper, and each session is followed by its transcribed panel discussion.

ACKNOWLEDGEMENTS

The proceedings were edited by Paul Mardikian, Claudia Chemello, Christopher Watters and Peter Hull. Vincent Blouin and Benjamin Rennison served as ad hoc reviewers for two of the papers. The editors would like to acknowledge the enormous effort made by all authors and reviewers to ensure the high quality of the papers presented here, and without whom this volume would not have come to fruition.

The Organizing Committee for METAL 2010 comprised Paul Mardikian, Christopher Watters, Claudia Chemello, Liisa Nasanen, Mike Drews, Stephanie Smith and David Hallam. Ian MacLeod also provided his wisdom and guidance in numerous matters and assisted Liisa Nasanen and Claudia Chemello with transcribing the question and answer sessions. The panel discussions were transcribed and compiled by Claudia Chemello. Stephanie Smith was responsible for the website and administrative support. The Poster Committee comprised Liisa Nasanen and Claudia Chemello.

Paul Mardikian served as the Program Chair for the conference. We thank David Hallam for his pivotal role as the Metal Working Group Coordinator, and for his thoughtful advice, guidance and patience during the planning and execution of METAL 2010.

METAL 2010 Program Committee members were:

Vasilike Argyropoulos – Technical Education Institute of Athens, Greece

Régis Bertholon – Université Paris 1 Panthéon-Sorbonne, France

Stefan Brueggerhoff – Deutsches Bergbau-Museum, Germany

Tom Chase – Chase Art Services, United States

Christian Degrigny – Haute école de Conservation-restauration Arc, Switzerland

David Hallam – National Museum of Australia, Australia

Andrew Lins – Philadelphia Museum of Art, United States

Ian Donald MacLeod – Western Australian Museum Collections and Research Centre, Australia

Paul Mardikian – Warren Lasch Conservation Center, Clemson University, United States

Jean-Bernard Memet – A-CORROS Expertises, France

Alice Boccia Paterakis – Kaman-Kalehöyük excavation, United States

Emma Schmuecker – Plowden and Smith Ltd, United Kingdom

David Scott – UCLA Conservation Program, United States

John Scott – New York Conservation Foundation, United States

Lyndsie Selwyn – Canadian Conservation Institute, Canada

Joseph Sembrat – Conservation Solutions, Inc., United States

Shelley Sturman – National Gallery of Art, United States

Johanna Theile – Facultad de Arte Universidad de Chile, Chile

David Thickett – English Heritage, United Kingdom

Robert Van Langh – Rijksmuseum Amsterdam, The Netherlands

David Watkinson – Cardiff University, United Kingdom

Session Chairs for METAL 2010 were: Lyndsie Selwyn, Paul Mardikian, Andrew Lins, David Thickett, Alice Paterakis, Tom Chase, Shelley Sturman, Ian MacLeod, Emma Schmuecker and David Hallam. The conference sessions benefitted from their expertise and wisdom, and we thank them sincerely for their support.

Our thanks are gratefully extended to Warren Lasch who generously contributed to a grant that enabled many international speakers to attend the conference. Warren's ongoing support is especially recognized. Robert Armentano of Total Energy is also greatly acknowledged for his conference assistance grant to also enable speakers to attend METAL 2010.

We would also like to thank the following institutions, sponsors, and individuals who have made this conference possible: Clemson University Restoration Institute, the International Council Of Museums Committee for Conservation (ICOM-CC), Brüker-AXS and Bruker Optics, Hitachi High Technologies, Applied Separations, Vashaw Scientific, Total Energy, Swagelok, Nancy Belanger, and Jon Tirpak. Special thanks is due to John Moore for allowing us to use his spectacular photographs for the conference. Lee Manigault graciously agreed to allow the program committee reception to be hosted at her incredible Antebellum house in Charleston, and we would like to acknowledge her generosity and kindness.

We especially thank Kit Menis from Kit Creative Marketing, Charleston, South Carolina, who was responsible for the wonderful design of this volume, in addition to the Program Book and CD-ROM of the conference.

The Editors and Organizing Committee have the pleasure of presenting these proceedings, and we hope that you enjoy reading them and are inspired by the stimulating papers. We were honored to work with all of you to bring METAL 2010 together.

For more information about ICOM-CC and the Metals Working Group, visit the MWG website at http://www.icom-cc.org/31/working-groups/metals.

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A NOTE FROM THE METAL WORKING GROUP COORDINATOR

METAL 2010, like previous Metal Working Group (MWG) conferences, is the result of a massive amount of unseen labor and planning. On behalf of the MWG, I would like to thank the Organizing Committee for the passion and effort they have put into organizing this conference. The conference was an enormous success and I sincerely thank all of the speakers and attendees for having contributed to its success.

The Organizing Committee strived to make this conference reflect a balance between the practice and science of metals conservation in all of its many flavors. We endeavored to include not only scientific research but also practical papers in the program. It was a difficult task to satisfy such a diverse group, but this was a specific aim of METAL 2010. As such, the conference was somewhat experimental, in that it took a different approach to previous years. This has resulted in much positive feedback and is a trend that we hope will be emphasized in future MWG conferences. A conscious effort was made to bring different, possibly contradictory, opinions to the table, and we have been encouraged by the results.

Another way that we tried to broaden the conference was by recording the questions and answers after each paper and introducing a panel discussion at the end of each session. These sessions are included in this volume, compiled and transcribed in full. The dialogue was stimulating, and provided a forum for discussion and sharing of information, helped vary the structure of the conference, and encouraged interaction between speakers and conference attendees. A post-conference survey, also a first, helped guide and critically evaluate our performance, an approach that can only strengthen the group and its goals.

Neither the practice nor the science of metals conservation can survive and grow without each other. Conservators enjoy treating objects and improving their stability, increasing our understanding of them and improving accessibility – be it a Roman coin, an outdoor sculpture or a spacecraft. We need to keep this final set of goals — analysis, stabilization, treatment and accessibility — paramount in our discussions. Conservators are practical people who are doing risky and amazing things in their everyday lives.

Nevertheless, metals conservators are a strange breed — ICOM-CC recently asked working group coordinators for a list of "professions" within each group. In the MWG, almost no one was 'just' a conservator. We have conservation educators, materials scientists, corrosion scientists, conservation scientists, archaeological conservators, silversmiths, goldsmiths, technological conservators, conservation engineers, engineers, mechanics…and the list goes on. With such a wide and diverse group of professionals, we need to be able to communicate and share knowledge in a free and open manner — this goal is primarily what this conference is about. My concern is ensuring that we can do the same throughout the time in between the conferences. Hence I have embraced more interactive and collaborative ways to connect, and been instrumental in trying many — some say too many — different ways of enabling better communication through the use of email, forums, online bibliographies, wikis and social networks. I know some of these initiatives will fail, but some are working wonderfully. Time will tell which are most useful, but we lose opportunities for growth if we are not willing to actually try them.

I encourage you to join ICOM-CC MWG, because it is only through sharing information and expertise that we can grow as a worldwide profession of metals conservators.

Communicate and share.

David Hallam
ICOM-CC Metal Working Group Coordinator

TREATMENT OF ARCHAEOLOGICAL IRON

Session Chair: Lyndsie Selwyn

RESIDUES OF ALKALINE SULPHITE TREATMENT AND THEIR EFFECTS ON THE CORROSION OF ARCHAEOLOGICAL IRON OBJECTS

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Abstract

The formation of chemical residues on archaeological iron following its treatment in aqueous alkaline sulphite ($NaOH/Na_2SO_3$) is simulated by evaporating selected ion mixtures to dryness. The residues are identified by X-ray diffraction (XRD) and their influence on iron corrosion is investigated by mixing them with iron powder and dynamically recording the weight change of these powder mixtures at fixed temperature and relative humidity (RH) in a climatic chamber. Ferrous chloride was dissolved in Na_2SO_4 to simulate Fe^{2+}/Cl^- contaminated Na_2SO_4 solution. This formed $FeSO_4 \cdot 4H_2O/FeSO_4 \cdot 7H_2O/NaCl$ upon evaporation. Evaporating a $FeCl_2/NaOH/Na_2SO_3$ solution produced either $Na_2SO_4/NaCl/\gamma$-FeOOH or $Na_6(CO_3)(SO_4)_2/Na_2SO_4/NaCl/\gamma FeOOH$ mixtures according to ion concentration in the initial solution. Iron powder and various residues were mixed and exposed at 75% RH and 20°C; Na_2SO_4/Fe did not corrode iron; $FeSO_4 \cdot 7H_2O/Fe$ produced minimal corrosion of iron; during the hydration phase of $FeSO_4 \cdot 4H_2O$ to $FeSO_4 \cdot 7H_2O$ iron corroded; a $NaCl/FeSO_4 \cdot 7H_2O/FeSO_4 \cdot 4H_2O$ mixture corroded iron rapidly. Overall, at 75% RH, soluble chloride residues offer a more immediate and significant corrosion risk to iron than Na_2SO_4, $FeSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 4H_2O$.

Keywords: archaeological iron, desalination, residues, iron sulphate, sodium sulphate

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Introduction

Archaeological iron objects often contain chlorides from their burial environment, which act as counter-ions in the electrochemical corrosion process (Turgoose 1985, Neff et al. 2005). Post-excavation corrosion delaminates objects and destroys their aesthetic, technological and heritage value. (Turgoose 1985, Selwyn et al. 1999). While desiccation can prevent this corrosion (Watkinson and Lewis 2005), an alternative is to attempt the removal of soluble chlorides using washing methods, such as aqueous alkaline sulphite ($NaOH/Na_2SO_3$) (North and Pearson 1975). Washing has been described as a stabilisation process, but this is an unproven and inaccurate statement, as the amount of chloride removed is unpredictable and residual chloride is unknown (Watkinson 1983, 1996, Watkinson and Al Zahrani 2008). Consequently, washing is better described as a stability enhancer, as it does not remove the need to control the storage environment (Watkinson 1996, Watkinson and Al Zahrani 2008). Nevertheless, quantitative data indicate that alkaline sulphite washing can remove a large percentage of the total chloride present in an object (Watkinson 1996, Al-Zahrani 1999, Watkinson and Al-Zahrani 2008) and qualitative studies indicate that such objects have increased longevity when compared with untreated objects (Keene and Orton 1985, Selwyn and Logan 1993, Keene 1994).

Despite these advantages, conservators in the UK now rarely use alkaline sulphite washing because it is time consuming and imparts an unknown level of stability. Also, there is a concern that treatment chemicals remain in the iron and pose a corrosion threat. Although post-treatment rinsing has been employed to combat this threat (Selwyn and Logan 1993; Keene 1994), this increases treatment time, causes iron to corrode in oxygenated aqueous wash solutions and has an unknown efficiency. Barium hydroxide rinsing has been suggested for immobilising SO_3^{2-}/SO_4^{2-} ions as $BaSO_4$ (North and Pearson 1975), but this produces white residues and its effectiveness is unknown (Keene 1994).

Our study examines the formation of chemical residues following alkaline sulphite treatment and investigates their influence on iron corrosion by:

- Modelling solutions to contain ions present during alkaline sulphite treatment of iron objects and evaporating these to dryness;
- Identifying the compounds formed upon drying using XRD;
- Mixing these compounds with iron powder and exposing them to controlled RH and temperature to determine if they corrode iron at selected RH values.

Formation of alkaline sulphite residues

The original alkaline sulphite treatment sequentially washed iron in sealed containers of aqueous 0.5M NaOH/0.5M Na_2SO_3 at 70°C (North and Pearson 1975). The SO_3^{2-} deoxygenates the solution and prevents cathodic reduction of oxygen, which stops iron corrosion and frees chloride from its counter ion role allowing it to diffuse into solution. Treatment modifications have included lower NaOH (0.1M) and Na_2SO_3 (0.05M) concentrations (Schmidt-Ott and Oswald 2006) and room temperature treatment (Al-Zahrani 1999). During treatment, Fe^{2+} ions present in the object react with OH^- ions to produce insoluble $Fe(OH)_2$ that later oxidises to rust. Therefore, upon completion of treatment, Cl^- and Fe^{2+} concentration within the NaOH/Na_2SO_3 solution and the corroded iron matrix are expected to be low. Drying treated iron objects without first washing them to remove chemical residues from treatment allows them to retain substantial amounts of Na^+, OH^-, SO_4^{2-} and SO_3^{2-}. The interactions between these ions will form new compounds that may pose corrosion risks to the iron.

Atmospheric oxygen will react with SO_3^{2-} to form SO_4^{2-}, or SO_3^{2-} will adsorb onto corrosion products during drying (Kaneko 1993). Fe^{2+} may form on objects if post-treatment corrosion occurs and hygroscopic iron sulphate could form and corrode archaeological iron above 60% RH (Turgoose 1993, Jones 1996). However, since Fe^{2+} precipitates as insoluble hydroxide during treatment the Fe^{2+} needed to form $FeSO_4$ must be supplied by renewed corrosion. This may not produce $FeSO_4$ as oxidation of Fe^{2+} in SO_4^{2-} containing solutions favors goethite (α-FeOOH) formation via an intermediate sulphate-containing Green Rust II (Refait and Genin 1994, Oh et al. 2002). Also, aggressive atmospheric corrosion of iron by iron sulphate (Schwarz 1965a, Schwarz 1965b, Stambolov 1985) has recently been questioned (Weissenrieder et al. 2004, Cai and Lyon 2005) and there is currently no evidence either that iron sulphate forms on alkaline sulphite treated iron or that it offers a corrosion risk. Additionally, post-treatment drying of objects may form sodium sulphate (Na_2SO_4), but this has not been confirmed nor has its potential for corroding iron been studied.

Experimental

Table 1 details the solutions used to simulate ion mixtures occurring in alkaline sulphite treatment of archaeological iron and on object surfaces following their removal from the treatment bath. These were evaporated to dryness over several days in an open container in the laboratory (35%-60% RH approximately 20°C). Throughout the experiments Analar grade reagents were dissolved in deionised water and products were analysed by X-ray diffraction (PANalytical X'Pert PRO at 40 kV/30 mA). Panalytical X'Pert High Score was used to identify and calculate approximate quantities of the principal products. All solutions in these tests are likely to contain more Fe^{2+} than occurs on iron treated in alkaline sulphite.

Solution composition (concentrations are the concentrations of each component in 200 mls of solution)	Products on drying	Approx. proportion (±10%)
1M Na_2SO_3	Na_2SO_4 Na_2SO_3	64 36
1M $FeCl_2{\cdot}4H_2O$ 1M Na_2SO_4	$FeSO_4{\cdot}7H_2O$ $FeSO_4{\cdot}4H_2O$ NaCl	52 17 30
0.1M NaOH 0.05M Na_2SO_3 0.05M $FeCl_2{\cdot}4H_2O$	Na_2SO_4 NaCl γ-FeOOH	49 47 4
1M NaOH 1M Na_2SO_3 0.1M $FeCl_2{\cdot}4H_2O$	$Na_6(CO_3)(SO_4)_2$ Na_2SO_4 NaCl γ-FeOOH	56 29 13 2

Table 1. Compounds formed by evaporation identified by XRD analysis.

Compound	RH (%)	Temp °C
Fe	75 and 90	20
Na_2SO_4	75 and 90	20
Na_2SO_4/Fe	75 and 90	20
$FeSO_4{\cdot}7H_2O$	75	20
$FeSO_4{\cdot}4H_2O$	75	20
$FeSO_4{\cdot}7H_2O$/Fe	75	20
$FeSO_4{\cdot}4H_2O$/Fe	75	20
$FeSO_4{\cdot}4H_2O$/$FeSO_4{\cdot}7H_2O$/NaCl/Fe	75	20

Table 2. Summary of climate chamber tests.

Potential reactions of iron with the residues identified from the solution evaporation tests were examined by mixing their powders with nitrogen-reduced iron powder and exposing them at 20°C (±0.5°C) and fixed RH values (±1%) in a Vötsch VC4018 climatic chamber (Table 2). A Mettler AJ100 balance (±0.0001 g) recorded weight change to file every five minutes to offer hydration, dehydration and corrosion data. The instability of the balance from chamber vibration produces reproducible weight fluctuation. All powders were mixed in the ratio 1:1 by weight except the $FeSO_4.4H_2O$/Fe hydration experiment. They were spread out in Petri dishes to provide maximum surface area for reaction. Controls of Na_2SO_4, $FeSO_4{\cdot}7H_2O$ and Fe were run. Visual examination of the samples was used to check for any signs of corrosion occurring.

Results

The nature and quantity of the compounds formed by the evaporation tests are shown in Table 1. After standing for several weeks in a closed volumetric flask in the laboratory a $FeCl_2$/Na_2SO_4 solution also formed natrojarosite ($NaFe_3(SO_4)_2(OH)_6$).

In solid phase tests at 75% RH and 20°C, neither anhydrous Na_2SO_4 nor iron powder showed detectable weight gain (see Figure 1a and b). A Na_2SO_4/Fe mixture showed a slight weight gain over a 16-day period with a few very small visible nodules of orange-brown corrosion products (see Figure 1c).

Anhydrous Na_2SO_4 exposed to 90% RH hydrated rapidly (see Figure 2a) producing a mixture of liquid and solid Na_2SO_4 in less than 24 hours. A Na_2SO_4/Fe mixture was slower to hydrate (see Figure 2b), but small quantities of iron corrosion product were observed within a day.

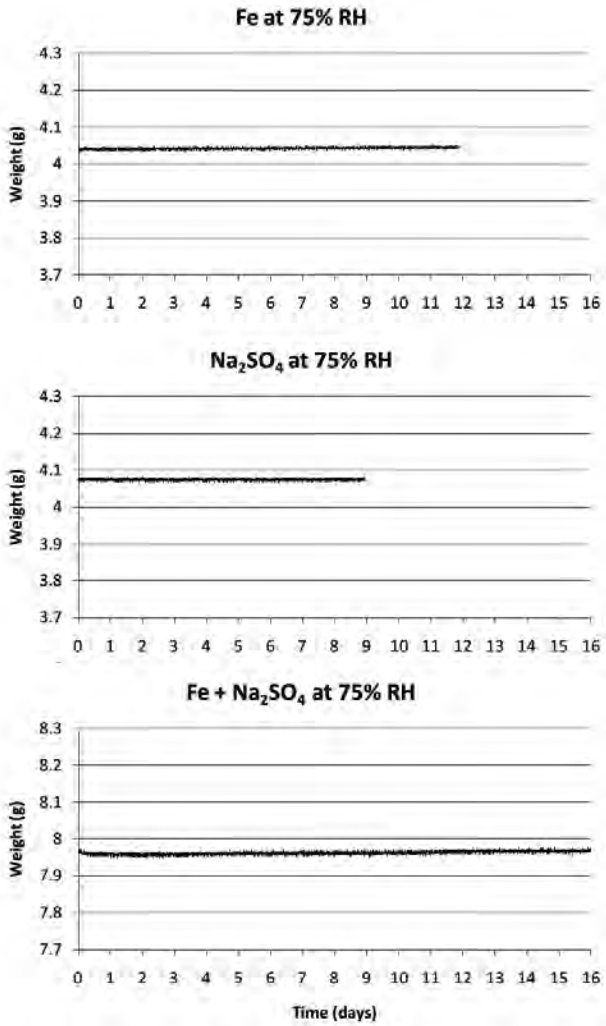

Figure 1. Iron powder and anhydrous Na_2SO_4 at 75% RH at 20°C. From *top:* (a) iron powder, (b) Na_2SO_4, (c) Fe/Na_2SO_4 mixture.

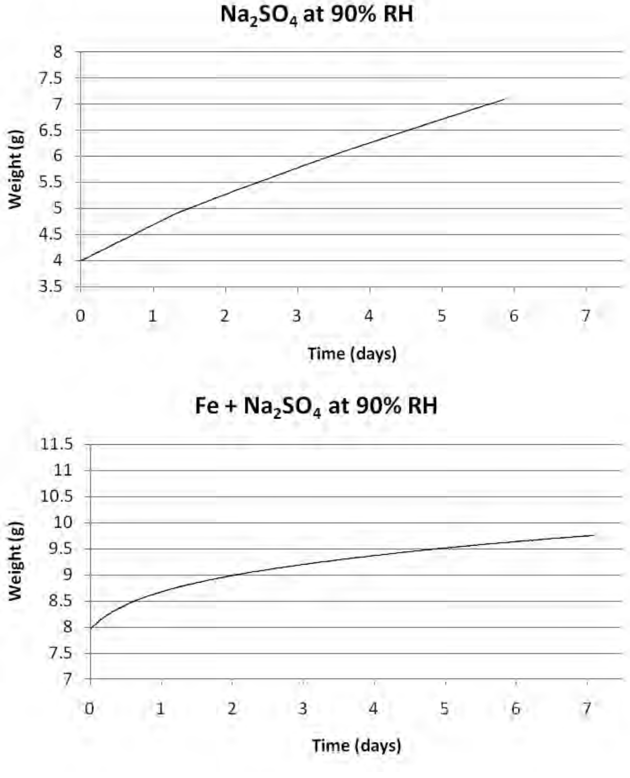

Figure 2. Iron powder and anhydrous Na_2SO_4 at 90% RH at 20°C. From *top*: (a) Na_2SO_4, (b) Fe/Na_2SO_4 mixture.

Exposing $FeSO_4{\cdot}7H_2O$ to 75% RH showed no weight gain over seven days (see Figure 3a). In the same conditions, a $FeSO_4{\cdot}7H_2O/Fe$ mixture gradually gained a very small amount of weight (see Figure 3b), although after eight days a visual inspection could not identify iron corrosion products. Close inspection of the slope reveals a very slight continuous weight gain over a four-day period (see Figure 3c).

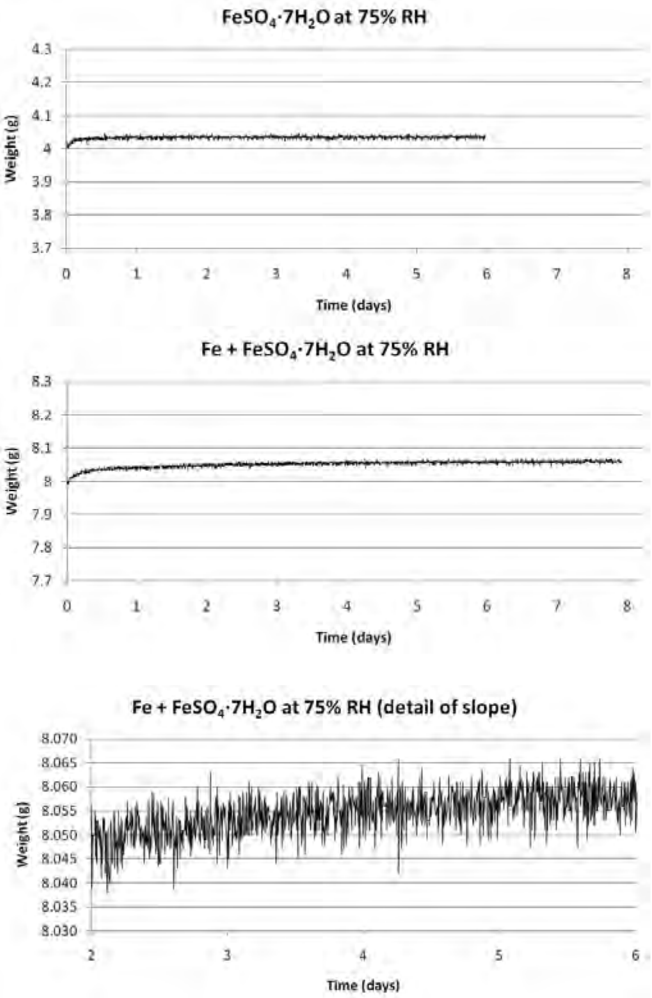

Figure 3. $FeSO_4{\cdot}7H_2O$ and iron powder and at 75% RH at 20°C. From *top*: (a) $FeSO_4{\cdot}7H_2O$, (b) $FeSO_4{\cdot}7H_2O/Fe$ mixture, (c) $FeSO_4{\cdot}7H_2O/Fe$ mixture- detail days 2-6; approximately 0.005g weight gain.

Since exposure of $FeSO_4{\cdot}7H_2O/Fe$ at 75% RH had not caused detectable corrosion of iron, it was determined whether the hydration phase for $FeSO_4{\cdot}4H_2O$ to $FeSO_4{\cdot}7H_2O$ corroded associated iron. A sample of $FeSO_4{\cdot}7H_2O$ was dehydrated to constant weight at 40% RH to form $FeSO_4{\cdot}4H_2O$, this was then mixed with Fe and exposed at 75% RH and 20°C.

$FeSO_4{\cdot}4H_2O$ hydrated much more quickly than the $FeSO_4{\cdot}4H_2O/Fe$ mixture (see Figure 4a and b). The $FeSO_4{\cdot}4H_2O/Fe$ sample comprised 1.118g $FeSO_4.4H_2O$ and 1.1505g of Fe. Consequently, the expected weight gain from hydrating 1.118g (0.005 moles) of $FeSO_4.4H_2O$ to $FeSO_4.7H_2O$ is 0.2668g of H_2O. In 43 days the overall weight gain was 0.4574g; therefore 0.1906g (0.4574g - 0.2668g) is attributable to the formation of new products from corrosion of iron. Figure 4b records most corrosion occurring during the hydration phase of $FeSO_4.4H_2O$, which was completed at approximately 28 days. Examining the period from 28 days to termination at 43 days reveals a regular, but slow, weight gain indicating very slow ongoing corrosion of the iron (see Figure 4c). (In Figure 4b, connection between the balance and the computer was briefly lost at 20 days and from 23-28 days it was intermittent, due to software problems.)

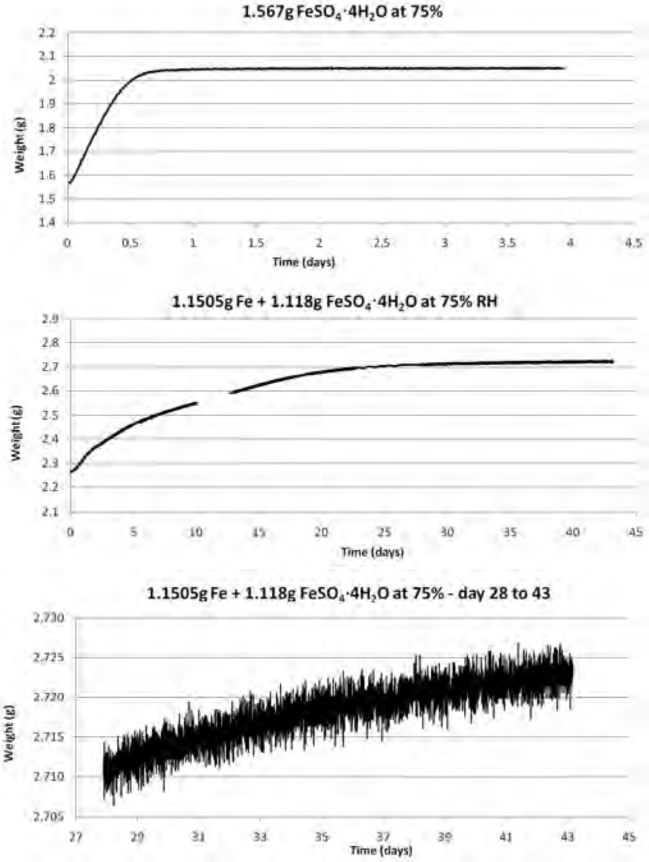

Figure 4. $FeSO_4 \cdot 4H_2O$ and iron powder and at 75% RH at 20°C. From *top*: (a) $FeSO_4 \cdot 4H_2O$ hydration, (b) $FeSO_4 \cdot 4H_2O$/Fe mixture (c) $FeSO_4 \cdot 4H_2O$/Fe mixture- detail days 28-43; approximately 0.012g weight gain.

Upon terminating the experiment the sample was dehydrated at 35% RH until it reached a constant weight (Figure 5). Dehydration was fast and recorded weight loss from conversion of $FeSO_4.7H_2O$ to $FeSO_4.4H_2O$, as well as any dehydration of hydrated iron oxides produced by corrosion of the iron. The weight loss was 0.2868g, which means 0.1706g (0.4574g - 0.2868g) could be attributed to the new corrosion products. This is in good agreement with the 0.1906g weight gain that can be theoretically attributed to corrosion on the 75% RH hydration graph (see Figure 4b). The slight discrepancy of 0.0200g between theoretical (0.1906g) and recorded (0.1706g) corrosion can be attributed to the loss of 0.0200g of water from the new corrosion products during their dehydration at 35% RH.

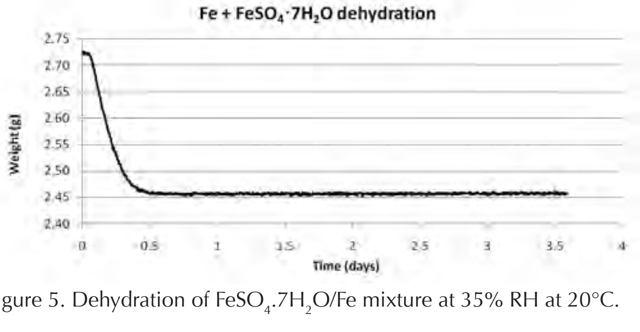

Figure 5. Dehydration of $FeSO_4.7H_2O$/Fe mixture at 35% RH at 20°C.

$FeSO_4 \cdot 4H_2O/FeSO_4 \cdot 7H_2O/NaCl$, produced by solution evaporation from 1M $FeCl_2 \cdot 4H_2O$/1M Na_2SO_4, was mixed with an equal weight of iron powder and exposed at 75% RH. Corrosion was readily visible within hours and weight gain was rapid and continuous (Figure 6). Corrosion was ongoing and greater than for any of the sulphate-containing compounds studied in these experiments.

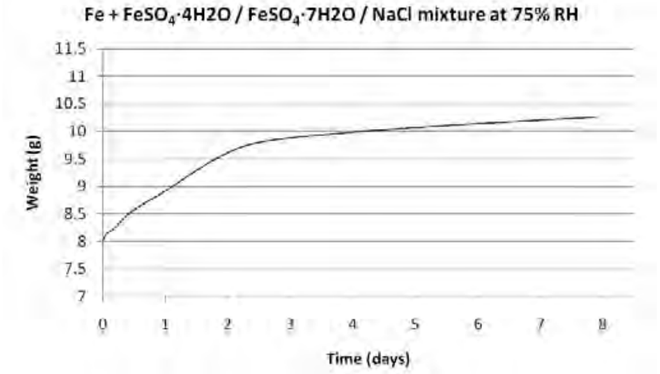

Figure 6. The powder residue from evaporating 200mls of a 1M NaOH/1M Na_2SO_4/0.1M $FeCl_2$ solution mixed with equal weight of Fe and then exposed to 75% RH at 20°C.

Discussion

Incomplete oxidation of Na_2SO_3 upon drying probably results from high SO_3^{2-} concentration and speedy evaporation. Formation of both $FeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 7H_2O$ from the evaporating $FeCl_2/Na_2SO_4$ solution likely resulted from partial dehydration of $FeSO_4 \cdot 7H_2O$ during storage. Many of the compounds formed by evaporation are hygroscopic (see Table 3). NaCl is very hygroscopic and the $FeSO_4 \cdot 4H_2O/FeSO_4 \cdot 7H_2O$/NaCl formed from evaporating $FeCl_2/Na_2SO_4$ caused significantly greater and faster iron corrosion than either Na_2SO_4 or $FeSO_4 \cdot 7H_2O$ or hydration of $FeSO_4 \cdot 4H_2O$ at 75% RH (see Figure 6), although it should be noted that the quantity of chloride in this test was high. Interestingly, evaporation of $NaOH/Na_2SO_3/FeCl_2 \cdot 4H_2O$ at two differing concentrations did not produce any NaOH (Table 2).

Compound	Transition RH	Hydrated form	Deliquescence RH
Na_2SO_4 (thenardite)	76.4%[1]	$Na_2SO_4 \cdot 10H_2O$ (mirabilite)	95.6%[1]
$FeSO_4 \cdot 4H_2O$ (rozenite)	approx. 60%[2]	$FeSO_4 \cdot 7H_2O$ (melanterite)	approx. 95%[3]
NaCl (halite)	N/A	N/A	75.4%[4]

[1]Steiger and Asmussen 2008, [2]Chou et al. 2002, [3]Ehlers and Stiles 1965, [4]Linnow et al. 2007

Table 3. Transition RH and deliquescence RH for the compounds in this study. RH values are given for 20°C.

Although chloride remaining after alkaline sulphite treatment should mostly be at anodes on the metal surface, adsorbed onto α-FeOOH and contained in β-FeOOH, evidence here suggests that small amounts of NaCl may occur as solutions concentrate during drying. No ferrous chloride was detected after evaporation of $FeCl_2/Na_2SO_4$ solution, which is a welcome outcome as $FeCl_2 \cdot 4H_2O$ corrodes iron at very low humidity (Watkinson and Lewis 2005).

Although natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) formed from $FeCl_2/Na_2SO_4$ solution after several weeks, formation of jarosite minerals requires acidic conditions (Baron and Palmer 1996), making them unlikely products of alkaline sulphite treatment. Also, they are stable (Navrotsky et al. 2005) and non-hygroscopic, so do not pose a corrosion risk (Vaniman et al. 2008).

Sodium sulphate offers a limited corrosion threat. It exists mainly as anhydrous Na_2SO_4, (thenardite) and $Na_2SO_4 \cdot 10H_2O$ (mirabilite) (see Table 3). The phase transition RH for $Na_2SO_4/Na_2SO_4 \cdot 10H_2O$ is now reported as 76.4% RH at 20°C rather than 71% (Steiger and Asmussen 2008). Our results agree with this, as anhydrous Na_2SO_4 was stable at 75% RH (Figure 1). While it did produce very minor corrosion of iron over a 17-day period at 75% RH (Figure 1), this may reflect the chamber RH fluctuation of ±1% facilitating a very small amount of corrosion as the phase transition point to $Na_2SO_4 \cdot 10H_2O$ is approached. Although the corrosion risk appears low, longer test periods may reveal continuous slow corrosion that poses a threat during long term storage.

High humidity may cause a corrosion problem with Na_2SO_4, as it deliquesces at 95.6% RH (Steiger and Asmussen 2008). The Na_2SO_4 hydrated quickly at 90% RH (Figure 2a) and corroded iron (Figure 2b). Slow hydration of the Na_2SO_4/Fe mixture is likely due to adhesion of iron powder and Na_2SO_4 reducing diffusion of water to the crystal (Linnow et al. 2006) (Figure 2b). Pragmatically considered, corrosion risks from Na_2SO_4 residues will be limited below 75% RH, and although they increase as 90% RH is approached, the contribution of residual chloride to corrosion will outstrip the threat from Na_2SO_4 hydration (see Figures, 1,2 and 6).

Formation of either Na_2SO_4 or $Na_2SO_4 \cdot 10H_2O$ depends on environmental RH and temperature (Steiger and Asmussen 2008). At RH > 40%, $Na_2SO_4 \cdot 10H_2O$ crystallizes and then dehydrates to Na_2SO_4. At RH <15% only anhydrous Na_2SO_4 forms and between 15%-40% RH both phases occur simultaneously. Above 32.4°C, only anhydrous Na_2SO_4 forms (Rodriguez-Navarro et al. 2000). This suggests that drying objects at low RH will ensure immediate formation of safe Na_2SO_4 and above this the $Na_2SO_4 \cdot 10H_2O$ initially formed will convert to safe Na_2SO_4, unless RH approaches 95%.

Crystallization pressures may cause physical damage in lamellar and porous substrates like corrosion matrices. Na_2SO_4 crystallisation pressures at low RH can be high (Steiger and Asmussen 2008) as formation of $Na_2SO_4 \cdot 10H_2O$ produces large volume increases (Rodriguez-Navarro et al. 2000; Steiger and Asmussen 2008). Solution supersaturation and pore morphology determine which compounds will form and the damage they can produce. Unfortunately, in the absence of quantitative data about corrosion product porosity and geometry in archaeological iron, it is difficult to determine whether drying a Na_2SO_4 solution within it will cause physical damage.

Iron sulphates can occur as Fe^{2+}, Fe^{3+} and Fe^{2+}/Fe^{3+} forms, whose state is controlled by H_2O and O_2 fractions and pH. This study examined reaction of the initial product of iron oxidation in the atmosphere (Fe^{2+}) with alkaline sulphite and chloride, identifying only $FeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 7H_2O$ in evaporation residues (see Table 1). Consequently, the impact of the less common ferrous sulphates and the various ferric sulphates on corrosion were not assessed, although they may offer potential problems (Table 4).

Ferrous sulphate ($FeSO_4$) is not reported naturally in its anhydrous form and, although $FeSO_4 \cdot H_2O$ (szomolnokite) does occur in nature (Hemingway et al. 2002), it is not possible to convert $FeSO_4 \cdot 4H_2O$ into $FeSO_4 \cdot H_2O$ even in completely dry air (Ehlers and Stiles 1965). $FeSO_4 \cdot 5H_2O$ and $FeSO_4 \cdot 6H_2O$ are not thought to be stable (Hemingway et al. 2002). $FeSO_4 \cdot 4H_2O$ (rozenite) and $FeSO_4 \cdot 7H_2O$ (melanterite) readily occur (Hemingway et al. 2002) and their phase transition RH is reported as ranging from 15% to 95% RH (25°C) (Hemingway et al. 2002), with most values around 60% RH (20°C) (Chou et al. 2002). Above 60% RH iron sulphate is said to be hygroscopic and to significantly increase corrosion risk (Jones 1996); it deliquesces around 95% RH (See Table 3).

Compound	Name	Occurrence
$FeSO_4$		rare
$FeSO_4 \cdot H_2O$	szomolnokite	
$FeSO_4 \cdot 4H_2O$	rozenite	common
$FeSO_4 \cdot 5H_2O$	siderotil	rare
$FeSO_4 \cdot 6H_2O$	ferrohexahydrite	rare
$FeSO_4 \cdot 7H_2O$	melanterite	common
$Fe_2(SO_4)_3$		
$Fe_2(SO_4)_3.9H_2O$	Enneahydrate nat. coquimbite	

Table 4. Iron sulphates.

Ferric sulphates have not been considered because they were not detected in tests reported here. Ferric sulphate ($Fe_2(SO_4)_3$) offers a corrosion threat as it is water soluble and hygroscopic. The thermodynamic properties of various ferric sulphates at differing RH values have been reported (Wang et al. 2010), and the phase transition boundary between ($Fe_2(SO_4)_3 \cdot 5H_2O$ and $Fe_2(SO_4)_3 \cdot 7H_2O$) has been examined (Wang et al. 2010). An amorphous ferric sulphate containing 4.5 to 11 structural water molecules per $Fe_2(SO_4)_3$ has been found to precipitate from Fe-SO_4 bearing aqueous solution in extremely arid conditions. Clearly, differing drying environments, pH and solution conditions may form different products than those observed in this paper. Consequently this study must be seen as an insight into one potential room temperature and RH drying route for alkaline sulphite solutions containing chloride and fairly high concentrations of ferrous ions. Examining differing concentrations of solutions at various temperatures, over a range of time periods, would offer additional insight into the compounds that may form and expand our understanding of the potential for further corrosion of iron.

Tests here showed that over a 12-day period at 75% RH, $FeSO_4 \cdot 7H_2O$ did not significantly corrode iron (see Figure 3b and c), but the hydration phase of a $FeSO_4 \cdot 4H_2O$/Fe mixture corroded the iron significantly, then slowed once hydration was complete (see Figures 4b and c). Hydration of $FeSO_4 \cdot 4H_2O$ to $FeSO_4 \cdot 7H_2O$ may proceed via a dissolution-precipitation pathway rather than a solid state transformation, with the dissolution phase providing enough dissolved ions to form an electrolyte to support corrosion. Consequently, humidity fluctuations around the 60% RH boundary will cause corrosion during transition between the $FeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 7H_2O$ hydrates. However, the presence of any residual chloride ions and compounds (see Figure 6) and their significant corrosive ability at low humidity is of much greater concern (Watkinson and Lewis 2005).

Conclusion

This is the first study to investigate the occurrence and corrosion impact of residues from alkaline sulphite treatment for archaeological iron. The ferrous sulphate and sodium sulphate residues identified in this paper offered minor corrosion risks to iron below 75% RH. In the conditions examined here, sodium sulphate was the most abundant residue, but it did not significantly increase iron corrosion below 75% RH. The only iron sulphates detected were ferrous sulphates, and these did not cause significant corrosion of iron at 75% RH, but during the hydration of $FeSO_4 \cdot 4H_2O$ to $FeSO_4 \cdot 4H_2O$ corrosion of iron did occur. This may be less of a risk than first appears as the powdered iron was intimately mixed with the $FeSO_4 \cdot 4H_2O$, which is a situation that will not occur on objects. It would be wise to avoid regular hydration/dehydration phases for ferrous sulphate, as it is during the hydration phase that it appears to be most aggressive to iron. As might be expected, the biggest corrosion accelerator was chloride. It produced rapid and continuous corrosion of iron at 75% RH. Further study is merited, but based on the laboratory models studied here, chemical residues from alkaline sulphite treatment appear to offer minimal corrosion risks for iron in the short term. The influence of the small amounts of corrosion from residues on the structural integrity of iron objects in the long term is less easy to predict and may be significant. Whether attempts to wash out treatment residues are necessary, or are more damaging than beneficial for the long-term survival of archaeological iron treated by alkaline sulphite, should be investigated.

Materials

BDH GPR Iron powder, reduced by nitrogen,
BDH AnaLar Sodium sulphite, anhydrous,
BDH AnaLar Iron (II) chloride 4-hydrate,
BDH AnaLar Sodium sulphate
BDH AnaLar Sodium hydroxide
all from
VWR International Ltd,
Poole, BH15 1TD, England
http://uk.vwr.com

AnaLar Iron (II) sulphate
Fisher Chemicals, Fisher Scientific UK Ltd,
Bishop Meadow Road
Loughborough, Leicestershire
LE11 5RG, http://www.fisher.co.uk

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Q & A SESSION

Tim Foecke: You are doing x-ray diffraction to determine the different phases that you have; do you have any concerns that you are missing anything that might be amorphous?

Melanie Rimmer: It's possible yes. But because we were using pure solutions and evaporating them at room temperature, we saw very good crystallization – the crystals were very clear to see. So it is possible in theory (that we have missed amorphous phases) but I think in terms of the solutions that we used we got a pretty good idea of what was present there.

Gerhard Eggert: Melanie, I was wondering have you also observed natro-jarosite in addition to your iron sulphates or vitriols? These are basic sulphates as corrosion products and I wonder if they could also form artificially from this solution?

Melanie Rimmer: Yes there were jarosites found in one of the solutions – the ferrous chloride and the sodium sulphate solution, which we left to stand in the lab and we saw the formation of sodium jarosite. However the jarosites only tended to form in acid conditions, the pH of that solution was about pH 2, so in terms of the alkaline treatments, with the sodium hydroxide present, I think formation of jarosite is highly unlikely.

Ian MacLeod: I was just wondering, what was the nature of the iron powder that you used, because if you haven't hydrogenated it beforehand the commercial iron powder that you buy is always covered with layers of iron corrosion products, so you would get a different corrosion rate.

Melanie Rimmer: We used nitrogen-reduced iron powder. We didn't see any formation of corrosion products on the surface.

Paul Mardikian: Is there a practical recommendation for conservators here that we could learn from your experience and rinsing protocols? Is there something you could tell us about this?

Melanie Rimmer: Yes. Most conservators when they treat objects with alkaline sulphite tend to run a rinsing program to try and remove the solution from the object. Now, we do not know how effective those rinsing programs are, we don't know whether the sulphate is being properly extracted. And looking at the data that we have so far, my argument is that those sulphate compounds aren't actually that hazardous. We might think about whether rinsing programs themselves are posing a risk to objects. We are putting the objects in oxygenated water: - are we restarting corrosion immediately after the treatment? In that case we might perhaps consider whether rinsing programs are really worthwhile or whether they're more of a risk than what we want to see and more of a risk than the sulphate compounds themselves.

James Crawford: I was just curious to know how your controls might have performed – so just iron filings on their own at the various relative humidities. Whether or not they indeed corroded and achieved some weight gain?

Melanie Rimmer: We ran one control of pure iron at 75% RH and one at 90% RH and we saw the same for both – there was no increase particularly in the corrosion rate that we could detect with this equipment. Iron on its own without the presence of any electrolyte seems not to corrode quickly at all.

James Crawford: Ok, and the atmosphere that this was under at 95% RH, was it in the open air or was it controlled?

Melanie Rimmer: It was inside our climate chamber so the temperature and relative humidity are controlled. Relative humidity to about ± 1%.

CHLORIDE CALAMITIES: ASSESSMENT OF RESIDUAL CHLORIDE ANALYSIS TO COMPARE IRON DESALINATION METHODS

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Abstract

An analytical protocol was designed for the analysis of chloride ions in treatment solutions as well as in solids after desalination to avoid chloride loss during the digestion process. The alkaline sulphite method originally suggested by North and Pearson (North and Pearson 1975) was tested with varying concentrations of sodium hydroxide and sulphite under nitrogen. The excellent desalination efficiency of sodium hydroxide solutions under de-aerated conditions reported by Al Zahrani (1999) could not be confirmed, but this technique seems to be more efficient than alkaline sulphite. Results suggest the use of oxygen-free sodium hydroxide as a desalination technique should be more suitable for mass treatment of terrestrial iron.

Keywords: Iron desalination, nitrogen, sodium hydroxide solutions, alkaline sulphite method, chloride analysis

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Introduction

The corrosion of archaeological iron objects after excavation is a well known problem in the archaeology and conservation community since the 19th century (Krause 1882; Scott and Eggert 2009). This is particularly true when iron is excavated and left to dry and akaganéite has formed as the main corrosion product (Reguer et al. 2007). It is well known that the chloride containing phase akaganéite is responsible for post excavation damage phenomena (Zucchi et al.1977).

North and Pearson developed the alkaline sulphite method in 1975 (North and Pearson 1975) and it has proven to be effective in desalinating and stabilizing iron objects (Rinuy 1979, Rinuy and Schweizer 1982, Watkinson 1983 and 1996, Al Zahrani 1999). Desalination is achieved in an alkaline medium by exchanging OH^- with Cl^- in the akaganéite (Ellis et al. 1976) via a dissolution and precipitation process (Cornell and Giovanoli 1990). In the case of desalination of terrestrial iron, the sulphite acts as an oxygen scavenger (Gilberg and Seeley 1982, Gilberg 1987). Considering the passivating properties of sodium hydroxide for iron in an aqueous solution, what is the exact role of the sulphite in the desalination process of archaeological iron objects? Does the presence of sulphite make a difference or is sodium hydroxide alone sufficient? De-aerated conditions using nitrogen for desalination with sodium hydroxide have been previously investigated (Al Zahrani 1999, Watkinson and Al Zahrani 2008). Attempts to simplify the alkaline sulphite desalination process have been made using room temperature instead of elevated temperature, or by using less concentrated sulphite and sodium hydroxide solutions (Stawinoga 1996, Schmidt-Ott and Oswald 2006). The current project compares the extraction efficiency of solutions of less concentrated sodium hydroxide, with or without the presence of sulphite, at room temperature under nitrogen. Since the complex system of corrosion products on the surface of an archaeological iron object cannot be readily reproduced, the experiments are conducted on real archaeological iron objects.

To assess desalination efficiency, chloride content in the desalination solutions and residual chloride content in the iron objects was determined. Particular attention was given to the analytical protocol used to determine the residual chloride concentrations in the solids. Therefore, this paper has two focal points: the analysis of the chloride content in treatment solutions and desalinated objects using photometry, and the replication and variation of the de-aeration of sodium hydroxide experiments as reported by Al Zahrani (1999).

Chloride Determination – Problems and Solutions

Background

To date, the focus in conservation literature has been on analytical methods suitable for chloride analysis in desalination solutions and desalinated objects. In contrast, sample preparation has been less important. Ellis et al. (1976) report total chloride loss in the form of volatile hydrogen chloride, caused by excessive acid when desolving akaganéite powder in sulphuric acid

Reference	Preparation	c	T °C	Time	Cl^- Analysis
Al Zahrani 1999: 182	HNO_3	27%	18 °C	3 d	ion-selective Electrode
Drews et al. 2004: 250	HNO_3	25%	hot plate	2 d	Pot. Titration/ IC
Rinuy 1979: 139	H_2SO_4/ HNO_3	2.7%/ n. r.	n. r.	n. r.	Pot. Titration
Rinuy and Schweizer 1982: 163	Mechanical + AS	Each 0.5 mol/l	50°C	n. r.	Pot. Titration (?)
Watkinson 1983: 88	H_2SO_4	20%	n. r.	n. r.	n. r.
Watkinson 1996: 209	HNO_3	n. r.	n. r.	n. r.	ion-selective Electrode
Wang et al. 2008	Water	-	n.r.	3 d	IC
Watkinson and Al Zahrani 2008: 80	HNO_3	5 mol/l	n. r.	n. r.	ion-selective Electrode

Table 1. Overview of published methods in the conservation literature for determination of chloride content in iron objects. (*c* = concentration; *d* = days; *Pot.* = Potentiometric; *IC* = Ion Chromatography; *n. r.* = not reported; *AS* = alkaline sulphite solution).

(H_2SO_4, 20% w/w) and, therefore decided to use sealed ampoules for digestion. In addition, Volkwein and Dorner mention an old-fashioned digestion protocol for chloride-contaminated concrete that involved boiling the samples in a solution of 38% nitric acid for 30 minutes. After boiling, 20% of the initial chloride concentration had vanished (Volkwein and Dorner 1986). In contrast, digestion for 10 minutes in cold nitric acid (27%) followed by three minutes in hot, but not boiling nitric acid of the same concentration, is short enough to not interfere with the chloride concentration (Deutscher Ausschuss für Stahlbeton [DAfStb] 1989). In general, iron nails need longer digestion time, which may allow chloride to evaporate as hydrochloric acid. Since this problem has not been adequately addressed in conservation science, our aim is to clarify this situation. The results of these findings may be of great importance for the conservation community.

Analytical Procedure

Determination Method for Chloride Ions

In the current research project, photometric analysis is used for chloride determination as suggested by Wunderlich (Wunderlich 2000) due to its capability to determine small amounts of chloride with deviations of less than 2.5% (Gottwald and Heinrich 1998). The device used for this procedure is a Spectronic Genesys 10 UV-Vis Split-beam Spectrophotometer (with an accuracy of 0.5% deviation). The chemical reaction for chloride determination used in this project is the quantitative reaction of $Hg(SCN)_2$ with chloride to a chloromercurate(II) complex ion, and the freed thiocyanate ions (SCN^-) react with Fe^{3+} to the red iron thiocyanate complex (for details see Florence and Farrar 1971).

Validation of own Digestion and Determination Method

For validation of the measurements used in this study, iron powder was digested in sulphuric acid (20%) with added sodium chloride solution of known concentration. After the iron powder was dissolved, interfering Fe^{2+} ions were oxidized to Fe^{3+} ions ($2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$) by hydrogen peroxide (30%), according to the equation $H_2O_2 + 2\ e^- + 2\ H^+ \rightarrow 2\ H_2O$. Excessive H_2O_2 was expelled by boiling for 30 minutes. After cooling, the volume of the sample solution is measured. Subsequently, the sample is prepared for photometric analysis as per Florence and Farrar (1971), and directly measured. Three measurements give a mean of 1.10 mg/l chloride (standard deviation of ± 0,042) in contrast to the reference value of 1.0 mg/l chloride. The difference of about 0.1 mg/l can be expressed as an error of 10%, which is acceptable considering the numerous interfering ions in the analytes.

Problems of Other Digestion Strategies

After checking the validity and reliability of our own measurements, the protocols used by other researchers were examined. Table 1 shows some published digestion protocols for determination of residual chloride in excavated terrestrial iron objects (with the exception of Drews et al. 2004, which discusses marine objects).

As shown in Table 1, nitric acid is typically used for this kind of application. In general, chloride ions may partially react with nitric acid to form gaseous nitrosyl chloride. If nitrosyl chloride evaporates, an underestimation of chloride concentration can occur. Therefore, nitric acid is a poor choice to dissolve chloride-contaminated iron, if the potential chloride loss is not avoided by other means. In addition, there is the difficulty of excessive iron ions and excessive mineral acid. Therefore, as is the case with many analytical methods, a pre-treatment of the sample is required. For example, Al Zahrani precipitates iron with sodium hydroxide before analysis. This method may induce a loss of chloride ions because the surface of freshly precipitated iron hydroxide is known to be a powerful absorber of chloride ions (Lahann 1976). Potentiometric titration is also disturbed by excessive iron ions (Rinuy 1979). Water is not considered as an adequate solubilising agent for chloride in corrosion layers or objects as suggested by Wang et al (Wang et al. 2008), since structural chloride ions cannot be removed from akaganéite with water (Ellis et al 1976). Furthermore, ion chromatography usually requires the eluent to be neutralized. In addition excessive iron ions may require a specific sample preparation prior to analysis. It should be noted that photometric determination of chloride ions by the previously mentioned protocol interferes with nitrosyl thiocyanate, which is red in colour like the $Fe(SCN)_3$ complex (Jander and Blasius 1985).

Replication of Other Digestion Strategies

Using our validated analytical method and an iron powder sodium chloride mixture, the digestion protocols of Al Zahrani (1999) and Drews et al (2004) were reproduced to check for potential chloride loss. Both procedures were reproduced using sulphuric instead of nitric acid. After three days at room temperature, the iron powder was solubilized inside the beakers covered with watch glass as per Al Zahrani (1999). After oxidation and heating for 30 minutes, no loss of chloride could be detected. In contrast, heating for two days at 80°C as suggested by Drews et al (2004) causes loss of chloride from the iron powder–sodium chloride mixture. Covering of the beaker influences results: no cover plate allows loss, a watch glass prevents it, but the accuracy of the measurement is probably affected by leakage. Pressure-resistant bottles with special gas tight closure heads (DURAN, Germany) prevent chloride loss, even after 48 hours (see Table 2). Obviously, the standard deviation can be better evaluated if it is considered in relation to the mean by the so-called variation coefficient[1]. As can be seen in Table 2, the bottles with a gas tight closure exhibits the highest reliability (i.e. smallest variation coefficient) and highest validity (least difference between mean and reference value).

Conclusion Concerning Digestion Strategies

The above review and laboratory work show that all data reporting residual chloride remaining in desalinated iron objects using digestion strategies based on length of time and hot dissolution without a cover for the solutions used, clearly should be subject to caution. In addition, interpretation of the results without a detailed report about the digestion (see Table 1) is questionable.

EXPERIMENTAL

In the following section of the paper, the replication and variation of the desalination experiments with de-aerated sodium hydroxide solutions based on Al Zahrani (Al Zahrani 1999) are reported, as well as the analysis of desalination solutions and residual chloride analysis of iron nails.

Desalination Experiments

In contrast with Al Zahrani, sodium hydroxide, pure sodium sulphite and alkaline sulphite solutions were tested in a nitrogen atmosphere to examine the role of sodium sulphite on desalination success (if not needed as an oxygen scavenger). Furthermore, the desalination was not terminated until all extractable chloride ions had washed out. This required four treatment baths of 60 days for each test.

Samples

The iron nails used were excavated in 1979 from the Roman site ‘Köngen’ near Esslingen, Germany. Seven sets of 100 g (± 3 g) iron nails of different sizes (on average around 10 nails) with remaining iron-cores were used. The majority of the nails were stored at -20°C and had completely dried out. For the purposes of this study, they were superficially cleaned of loose soil particles with air-abrasion.

Desalination solutions and procedure

The solutions used and their concentrations are as follows: alkaline sulphite, 0.5 mol/l sodium hydroxide (NaOH) and 0.5 mol/l sodium sulphite (Na_2SO_3) (North and Pearson 1975); diluted alkaline sulphite, 0.1 mol/l NaOH and 0.05 mol/l Na_2SO_3 (Schmidt-Ott and Oswald 2006); and NaOH, 0.1 and 0.5 mol/l. One litre of solution was used for each 100g set of nails to ensure comparability of results. Two tests were undertaken, each with a 100g set of nails, except for the 0.1 mol/l sodium hydroxide solution, where only one 100g set of nails was used. After 60 days, the chloride content of the solutions was determined. At a concentration of 0 to 2 mg/l chloride the desalination was considered to be complete. After treatment, the objects were soaked in warm deionised water until the pH was neutral, followed by drying.

Inert atmosphere

The containers with the nails and the desalination solutions were placed in a Binder VD 115 vacuum drying oven (Germany) purged with N_2 in 99.999 %-mol quality (Air Liquide, Germany). Before running the experiments, the oven was evacuated twice and flushed with nitrogen gas. The experiments were conducted at room temperature (20 °C ± 1 °C).

Pre-treatment of desalination solutions for determination of chloride-content

Since sulphite interferes as reducing agent with the protocol as described, it has to be oxidized, and the sample solution has to be acidic. Therefore, a solution containing 5 mol/l nitric acid and 10% hydrogen peroxide has to be added in the ratio 1:1 to the sample

Covering	Reference Amount in ppm Cl$^-$	Measured Amount in ppm Cl$^-$	Mean in ppm Cl$^-$	Standard Deviation in ppm Cl$^-$	Variation coefficient in %
none	1.0	0.413	0.31	0.17	53.96
	1.0	0.117			
	1.0	0.400			
not gastight (watch glass)	1.0	1.344	1.24	0.20	17.74
	1.0	1.106			
	1.0	0.945			
gastight (special bottle)	1.0	1.153	1.06	0.11	10.08
	1.0	1.082			
	1.0	0.943			

Table 2. Demonstration of chloride loss by hot digestion over 48 hours with a solution temperature of 85°C.

solution (Weker and Trojanowicz 1987, Beaudoin and Bertholon 1994). For complete oxidation, the sample stands at room temperature for 24 hours in a closed bottle. The error associated with this pre-treatment can be up to 10%, which, as previously discussed, is acceptable. The pH of desalination solutions containing only NaOH is adjusted by the reagents and needs no further preparation.

Determination of chloride ion concentration

The determination of the chloride ion concentration of the desalination solutions and in the desalinated objects was carried out with photometric analysis and the protocol described above.

Determination of chloride-content of desalinated iron objects

Prior to analysis to determine chloride content, 71 desalinated nails were entirely cut into small cubes approximately 4 mm-long, with a weight of approximately 0.1g each. This was deemed to be a better way to deal with the variation in chloride distribution in the nails. Acceleration of the solubilization process was facilitated by digesting small pieces of the nails, and, given the quantity of material to be analyzed, this method also used less sulphuric acid. 66 of the 71 nails were large enough for two groups of samples to be cut from each nail. The two groups consisted of randomly selected pieces from each nail. The chloride content from these two groups was analyzed. The remaining 5 nails were too small to allow two groups of samples, therefore these 5 nails were each digested whole to determine their residual chloride content. The mean chloride content was determined in ‰. In contrast to iron powder as specimen, the sample solution had to be centrifuged after oxidation for five minutes to separate it from insoluble matter.

RESULTS OF DESALINATION EXPERIMENTS UNDER A NITROGEN ATMOSPHERE

Chloride-content of desalination solutions

The results in Table 3 indicate that the diluted alkaline sulphite solution (DAS) extracted more chloride than the alkaline sulphite (AS) solution, and that there appears to be no significant difference in extraction between 0.5 and 0.1 molar solutions of sodium hydroxide. Data from this part of the experiment show that pure sodium hydroxide solutions without the addition of sulphite extract slightly more chloride in a nitrogen atmosphere, but the difference in concentration of the sodium hydroxide concentration does not seem to play a significant role.

Chloride-content of desalinated iron objects

To evaluate the desalination, in Table 4, the reported

Solution	Bath 1	Bath 2	Bath 3	Bath 4	Total	Mean	Standard Deviation
AS 1	22.22	2.96	1.48	0.00	26.66	25.92	1.05
AS 2	22.22	1.48	1.48	0.00	25.18		
DAS 1	27.41	2.22	4.44	0.00	34.07	37.03	4.19
DAS 2	34.81	2.96	2.22	0.00	39.99		
OH^- 0.5 1	23.07	3.44	1.59	1.59	29.69	41.18	16.24
OH^- 0.5 2	41.96	6.41	2.70	1.59	52.66		
OH^- 0.1	30.85	4.56	1.96	1.96	39.33		

Table 3. Chloride extracted in ppm by alkaline sulphite and sodium hydroxide solutions, each in two test series (one treatment bath = 60 days). *AS* = Alkaline Sulphite solution according to North/ Pearson (1975), *DAS* = Diluted Alkaline Sulphite according to Schmidt-Ott/ Oswald (2006), *OH^- 0.5* = Sodium hydroxide 0.5 mol/l, *OH^- 0.1* = Sodium hydroxide 0.1 mol/l

Column	1	2	3	4	5
Treatment	Absolute weight of objects	Absolute Cl^- extracted by treatment	Absolute residual weight of Cl^- in objects	Absolute weight of chloride in objects	Relative amount of Cl^- extracted by treatment of total Cl^- in objects
	in kg	in mg	in mg	in mg	in %
AS	0.10058	26.66	19.48	46.14	58
AS	0.10104	25.18	18.60	43.78	58
MEAN	**0.10081**	**25.92**	**19.04**	**44.96**	**58**
DAS	0.10005	34.07	15.40	49.47	69
DAS	0.10124	39.99	32.12	72.11	55
MEAN	**0.10065**	**37.03**	**23.76**	**60.79**	**62**
OH^- 0.5	0.10053	29.69	14.80	44.49	67
OH^- 0.5	0.10190	52.66	22.00	74.66	71
MEAN	**0.10122**	**41.18**	**18.40**	**59.57**	**69**
OH^- 0.1	**0.10310**	**39.33**	**30.34**	**69.67**	**56**

Table 4. Extracted chloride in absolute and relative amounts to assess desalination success. *AS* = Alkaline Sulphite solution according to North/ Pearson (1975), *DAS* = Diluted Alkaline Sulphite according to Schmidt-Ott/ Oswald (2006), *OH^- 0.5* = Sodium hydroxide 0.5 mol/l, *OH^- 0.1* = Sodium hydroxide 0.1 mol/l

weight of extracted chloride by treatment (column 2) and the residual chloride (column 3) are added to get the total amount of chloride in the object (column 4). Extraction efficiency is calculated in terms of relating the chloride amount extracted by treatment to the total amount of chloride in the object expressed in % (column 5). The chloride content of each 100g batch is calculated by relating the individual chloride contents to the masses of the corresponding objects. For example, the residual chloride content of an object weighing 5g will not influence the mean residual chloride content as much as the content of an object weighing 30g.

Table 4 provides the extraction pattern as a function of total chloride in the iron. A sodium hydroxide solution of 0.5 mol/l extracts the most chloride by treatment (column 2), and exhibits the least amount of residual chloride (column 3). In contrast, sodium hydroxide 0.1 mol/l shows an extraction amount similar to the other solutions during desalination (column 2), but the weight of remaining chloride is the highest for all objects tested (column 4). Further, the alkaline sulphite solutions show similar extraction behaviour, but the level of extracted chloride is slightly less compared to the other desalination solutions.

With regard to the quality of the data, the average variation coefficient of the 66 means resulting from two residual chloride measurements per nail described above (with an average standard deviation of 0.054 ‰) is 21.63%[1]. This means that the measurements show a very good reliability and reproducible results, though archaeological finds were used as specimens and a special sample preparation strategy was used. In general, the chloride contamination of the iron finds from the Roman site ‘Köngen’ seems to be relatively low. Nevertheless, this comparatively low chloride level is still causing post excavation active corrosion.

Discussion

Since post excavation corrosion appears to be caused by the residual chloride, the amount of residual chloride after desalination should be the main criterion for evaluating the treatment. The least amount of residual chloride in the Köngen objects was found in those desalinated under nitrogen with 0.5 mol/l sodium hydroxide, alkaline sulphite, and diluted alkaline sulphite, while the most chloride was found in objects desalinated with 0.1 mol/l sodium hydroxide. However, the efficiency of the methods does not vary that much. For alkaline sulphite, our data for Köngen (58% extraction of total chloride) are lower than the ca. 70% of Rinuy and Schweizer (Rinuy and Schweizer 1982), the ca. 87% of Watkinson (Watkinson 1996) and the 96% of Al Zahrani (Al Zahrani 1999). The desalination efficiency of 0.5 mol/l sodium hydroxide (69% extraction of total chloride) under nitrogen is confirmed, but not the 99.5% extraction efficiency cited by Al Zahrani. Considering the absolute residual chloride of 0.5 mol/l sodium hydroxide (18.4 mg), alkaline sulphite (19 mg) and diluted alkaline sulphite (23.8 mg), sulphite concentration does not seem to affect the desalination as expected (see Watkinson and Al Zahrani 2008).

Evaluating the data reported here, it should be kept in mind that significant differences between desalination strategies are always difficult to compare due to the inherent heterogeneity of archaeological iron samples. Firstly, the chloride distribution inside objects from the same site can vary significantly. Secondly, the structure of the corrosion products in each object plays a major role in the diffusion processes. An accurate analysis of desalination solutions is difficult to achieve due to interference with sulphite, iron, mineral acid and other ions.

Conclusion

The data reported here show that the digestion strategy can affect the results of residual chloride analysis, and should be measured carefully to avoid loss into the air during hot acid digestion. If not accurately measured, the result is biased in terms of overestimation of the desalination by treatment method. In the aqueous desalination treatments described by the authors, chloride-free objects were impossible to achieve.

Since the sulphite component does not need to perform its deoxygenation function under a nitrogen atmosphere, and it neither interfered nor facilitated the desalination, an option is to desalinate with high concentrated sodium hydroxide solutions. However, the desalination solutions with a reduced NaOH concentration also show similar results, and should be noted as further alternatives. Several advantages are to be mentioned: using nitrogen helps to save costs by reducing or omitting chemical agents and saving time in weighing and disposing — these benefits meet the requirements for mass treatment of archaeological iron objects.

This work will be continued since sizeable amounts of data allow a thorough evaluation of desalination treatments. In the near future, more experiments will be conducted regarding the concentration of sodium hydroxide, as well as the role of sulphite in desalination experiments under aerated and de-aerated environments, for example, those under vacuum.

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Endnotes

[1] The variation coefficient is a relative measure which expresses the standard deviation as a percentage of the mean. It is calculated as per (standard deviation*100/ mean) in %. The smaller the variation coefficient, the better the data.

Materials

All chemicals used were of high purity, analytical grade (pro analysi), the water used was deionised. All chemicals were purchased at:

Carl Roth GmbH + Co. KG
Schoemperlenstraße 1-5, 76231 Karlsruhe, Germany
Telephone: 0049-721-56060
http://www.carl-roth.de

Mercury thiocyanate
VWR International GmbH
(Hilpertstraße 20a, 64295 Darmstadt
Telephone: 0049-6151-39720
http://www.chemie.de/firmen/e/12501/vwr_international_gmbh.html

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Q & A SESSION

Jettie Lanschot: It is not so much a question, but more a comment: Many years ago I made a lot of corrosion potential measurements on archaeological iron in sodium hydroxide with different concentrations of sodium hydroxide. It is clear that the more negative potential you get, the higher is the pH so I think the diffusion of chlorides is also potential-dependent so knowing the concentration of the sodium hydroxide is essential. So if you are continuing with your work it would be interesting if you also did some potential measurements on the different concentrations of sodium hydroxide.

Britta Schmutzler: Yes, thank you for this comment.

David Watkinson: I might be slightly revisiting some of the things that we discussed in Stuttgart a few months ago but there are a couple of things I wanted to raise: one of them was the efficiency that you got out of the treatment – you are starting with incredibly low levels of chloride, I mean 60 ppm chloride overall after a digestion is almost considered chloride-free by people. We've treated – Melanie in her project treated 150 objects and the quantities of chloride in those varied from around about 5000-7000 ppm down to maybe 200 ppm to begin with and we were getting excellent results for objects in terms of stability when we were testing them at high humidities, with 200 ppm in the metal. The efficiencies you are showing then, you've got very small figures to determine the efficiencies so it is a difficult experimental setup. For instance with a 5000 ppm object you can get down to 50 ppm and that's 90% efficiency. And you were finding you were getting 40% and 50% and 60% and I just wondered there, what you were actually saying about the efficiencies that had been recorded by other people? Because it is all relative to quantities of chloride and forms of chloride and whether you have β-FeOOH, or whether you've got free chloride. And I just wondered whether you could comment on that?

Britta Schmutzler: This was a lot of questions in one, so…

David Watkinson: The question at the end of the day then, having set the scene relative to the quantities of chloride in the objects, would be are you saying that you can't achieve 90% or 95% extraction efficiency? I wasn't quite clear on what you were saying, or what you were questioning about the treatment.

Britta Schmutzler: The question is if I think I can achieve 90 – 100% desalination, is that right?

David Watkinson: Yes, that's right. It seemed to be you were saying that those figures that had been published that are achieving those high levels of efficiency maybe aren't achieving those levels, is that right?

Britta Schmutzler: Sorry I don't understand the question…

David Watkinson: Gerhard, should we do a duet?

Gerhard Eggert: David she clearly stated that the jury is still out, we don't know… she is absolutely clear in that we are very low in chloride and there are a lot of other nails treated to be analyzed, so we have other figures. What I say is that she has shown with her work that all the published write-ups of chloride analysis using digestion methods if you don't know what they really did, the results are questionable. We can't rely on this if we don't know how they did it, because most of the chloride is simply evaporated into the air and not into the analyte, so you can't find it. She can show that from a chemical point of view, you can tell that if there is a lot of chloride present, the loss couldn't possibly be lower, but she showed that even with being small, you normally would think that nothing would go out at such a diluted solution, but her tests show that even then the effect is quite high. So I think she should continue to desalinate the more contaminated solutions and then we will possibly get an idea of what is better. But in the end she says, there is value in this Al Zahrani approach using the de-aerated solutions.

David Watkinson: Can I just agree that certainly a protocol for digestion is important, covered beakers, covered containers and also reproducibility. It is expected that you would adsorb chloride ions on to ferrous hydroxide, you should run blanks and check if that's the case to check on reproducibility; I agree, that's important. Can I just ask one other question relative to this issue: how did you digest the samples that you treated?

Britta Schmutzler: The old discussion, yes. It is hard to explain but I desalinated the nails, I cut them after desalination completely into small cubes, and from these batches of cubes, on an individual level, I took two samples, dissolved them and at the end I calculated the mean relating to the object.

David Watkinson: So it was a test, rather than a complete digestion of the whole object. So you extrapolated that to the whole object.

Britta Schmutzler: Yes. The selection of the cubes was at random, so it was a double-controlled random-study – take any cubes from the nail and calculate the mean, so this was my way.

Nestor Gonzalez: When you ran the photometry, what was the limit of detection of the system?

Britta Schmutzler: The limit of the detection? It goes down to 1 ppm or smaller.

Jannecke Nienhuis: You stated at one point that you used plastic containers. Was that PVC or something because then it might affect your results.

Britta Schmutzler: No they were PP – polypropylene

DDN Singh: Could you please suggest the reason why de-oxygenated alkaline solutions gave you better results compared to the normal de-oxygenated ones?

Britta Schmutzler: I worked with archaeological finds so it is difficult to explain the difference between my specimens. If I had used standardized specimens, I could maybe have related it to the treatment but at this stage it may be the variation of chloride contamination in the finds from the site, so I am sorry but I can't explain it.

Lyndsie Selwyn: We will save that for the panel discussion

DDN Singh: Yes I understand, but I would like to have some suggestion for if it is oxygen that is playing this role, then why not add hydrazine hydrate in sodium hydroxide solution? It will play a better role compared to the nitrogen there. Hydrazine hydrate is very commonly used in thermal power plants.

Lyndsie Selwyn: Yes, let's keep this for the panel discussion after the coffee break.

DDN Singh: Ok, I can give you the formula and show you how to do this.

Britta Schmutzler: Ok thank you.

KEEP COOL? DEEP-FREEZE STORAGE OF ARCHAEOLOGICAL IRON

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Abstract

Post excavation corrosion of archaeological iron can cause severe damage to iron artifacts, particularly due to the formation of akaganéite. In this study, powder test samples of a 1:1 mixture of iron and iron(II) chloride tetrahydrate were stored at -23°C (± 3°C) and at room temperature, 21°C (± 3°C), to test whether storage at low temperature could inhibit corrosion. The oxidation of a synthetic iron and iron(II) chloride tetrahydrate mixture to form akaganéite, β-FeO(OH), mimics the reactions that take place during post excavation corrosion of archaeological iron. The formation of akaganéite was observed by Fourier transform infrared (FTIR) spectroscopy on the test samples over a period of two and a half years. Compared to the test samples that were stored at room temperature, the conversion of the initial compounds appears to be delayed at -23°C (± 3°C), but slow conversion is clearly visible. This study demonstrates that storage of archaeological iron artifacts at -23 °C (± 3°C) does not appear to completely inhibit post excavation corrosion.

Keywords: archaeological iron, storage, corrosion, akaganéite, FTIR spectroscopy, deep-freeze storage

Introduction

The post excavation corrosion of archaeological iron artifacts can be described as an autocatalytic cycle by the following reaction equations:

(equation 1)
$2\ FeCl_2 + 3\ H_2O + ½\ O_2 \rightarrow 2\ FeO(OH) + 4\ HCl$

(equation 2)
$2\ Fe + 4\ HCl + O_2 \rightarrow 2\ FeCl_2 + 2\ H_2O$

Charge-balancing chloride ions from the surrounding soil are attracted by dissolved ferrous ions near the metallic iron core. This reaction results in the formation of an acidic solution of ferrous chloride in pores and cracks within the corrosion layer near anodic areas. Excavation leads to desiccation of the object and facilitates the access of oxygen to the metal enabling further oxidation to ferric ions and precipitation as the chloride containing phase akaganéite, β-FeO(OH). The increase in volume and vertical crystal growth associated with the formation of akaganéite at the metal/corrosion interface can cause spalling of the corrosion crust, which may contain valuable information, such as the original surface of an object, decoration or tool marks. The hydrochloric acid formed in equation 1 promotes further dissolution of ferrous ions and sustains the corrosion cycle as long as oxygen, water and iron are available. (Turgoose 1982, Selwyn et al. 1999, Scott and Eggert 2009)

The corrosion process described can generate the formation of noticeable amounts of akaganéite within days after excavation in uncontrolled storage conditions. In order to inhibit post excavation corrosion, both active and passive conservation strategies can be implemented. Various studies have shown that the extraction of chloride ions from the corrosion layers of iron artifacts significantly improves the stability of these objects; as demonstrated, for example, by Keene and Orton (1985). No desalination treatment for the extraction of chloride ions from corrosion layers is known to be 100% efficient. However, treatment in oxygen-free solutions of sodium hydroxide, often employed as the well-established alkaline-sulphite desalination method, show particularly good chloride extraction efficiency (North and Pearson 1975, Rinuy 1979, Selwyn and Logan 1993, Watkinson 1996, Al Zahrani 1999). As the formation of akaganéite proceeds, lower extraction efficiencies and longer treatment times have been reported (Gilberg and Seeley 1982). As a consequence, it is necessary to either start desalination immediately after excavation, or prevent post excavation corrosion using suitable storage systems.

Watkinson and Lewis (2004) have shown that storage below 12% relative humidity (RH) is effective in preventing post excavation corrosion. This level can be reached by packing objects with a desiccant or moisture and oxygen absorbers as tested by Guggenheimer and Thickett (2008). During storage, special packing materials with low permeability for water vapour and/or oxygen such as ESCAL must be used. The major problem with these storage systems is the need to regularly monitor the artifacts and storage conditions and replace packing materials.

Deep-freeze storage at temperatures around -20°C has been applied for decades in several museums and conservation laboratories to store excavated iron artifacts. An example includes approximately 16 tons of excavated iron stored in a deep-freeze chamber of the Landesdenkmalamt Baden-Württemberg in Esslingen, Germany. Several authors have hypothesized that storage of archaeological iron at deep-freeze temperatures would achieve stability. However, systematic studies to confirm these statements have never been conducted (Born 1982, Scharff and Blumer 1994, Costain 2000, Greiff and Bach 2000).

The Arrhenius equation describes the dependence of the reaction rate constant on temperature and is the background for the simplified rule that the reaction rate is doubled by an increase in temperature of 10°C (Atkins 1993). Thus, slowing down of post excavation corrosion processes could be expected at deep-freeze temperatures. Nevertheless, the corrosion of iron meteorites (Buchwald and Clarke 1989)[1] and iron building components of expedition huts in Antarctica (Hughes et al. 2002), follow the same mechanisms as post excavation corrosion, raising doubts about the long-term stability of archaeological iron in deep-freeze storage.

Objectives

In the present study, the reaction of post excavation corrosion was simulated at different temperatures to answer the following questions:

Can deep-freeze conditions (around -20°C) inhibit post excavation corrosion of archaeological iron finds? Is deep-freeze storage of iron artifacts acceptable as a short or long-term conservation storage option?

Experimental

Experimental procedure

Thirty test samples were prepared by mixing equal weights of synthetic iron powder and iron(II) chloride tetrahydrate. The samples were stored in a defrost-free Liebherr Elektronik freezer at -23°C (± 3°C). One test sample was stored at room temperature of 21°C (± 3°C) [2]. Glass containers were used to house the test samples during the experiment. To exclude dust while allowing air circulation, the containers were sealed with pieces of cotton wool only[3].

Instrumentation

To observe the transformation of the test samples, FTIR spectroscopic measurements were carried out using a Bruker Vertex 70 IR-spectrometer. Measurements included 16 scans in a wavenumber range from 4000 cm^{-1} to 400 cm^{-1} with a 4 cm^{-1} resolution. All measured spectra were modified with a baseline correction using the standard setting of Brukers optics user software, before further evaluation.

Calibration

The IR-spectrum of akaganéite shows a specific absorption band at 852 cm^{-1}, which is not overlaid by bands caused by the initial test sample compounds (see Figure 1) (Cornell and Schwertmann 1996, Thickett 2003)[4]. The intensity of this peak can be used for a quantitative evaluation of the akaganéite content in a sample (Zeeh 2005).

Akaganéite was synthesised by the thermal hydrolysis of a 0.1 M ferric chloride solution at 70°C for 48 hours following Cornell and Schwertmann (1996). A calibration line was created by measuring pellets with known amounts of synthetic akaganéite and potassium bromide following Thickett's protocol (Thickett 2003). Spectra of these measurements showed a significant band between 939.5 cm^{-1} and 789.5 cm^{-1} with a peak at 856.6 cm^{-1}. A slight overlapping of this band with another akaganéite band at lower wavenumbers can be observed (see Figure 2). Two calibration test series were produced, each starting with a pellet with a known akaganéite and potassium bromide content. After the first FTIR measurement, the pellet was split into two parts; one part was weighed, powdered again, mixed with a known amount of potassium bromide and pressed again for the next FTIR measurement. Each test series was conducted until the measured spectra showed no significant peak at 856.6 cm^{-1} (see Figure 2).

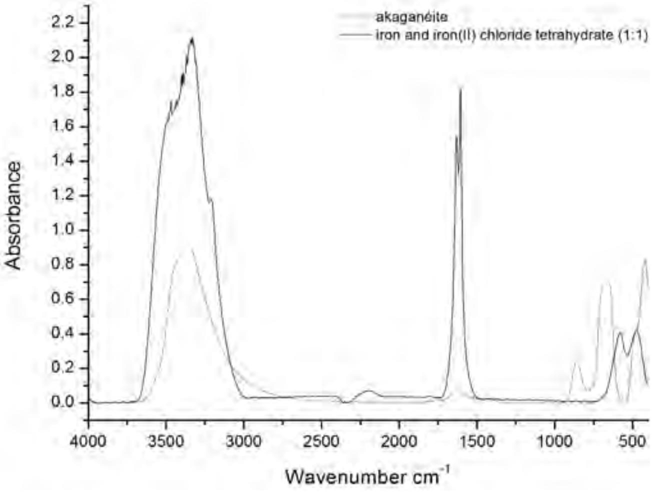

Figure 1. FTIR spectra of akaganéite and the initial powder mixture (ferrous chloride tetrahydrate and iron, 1:1)

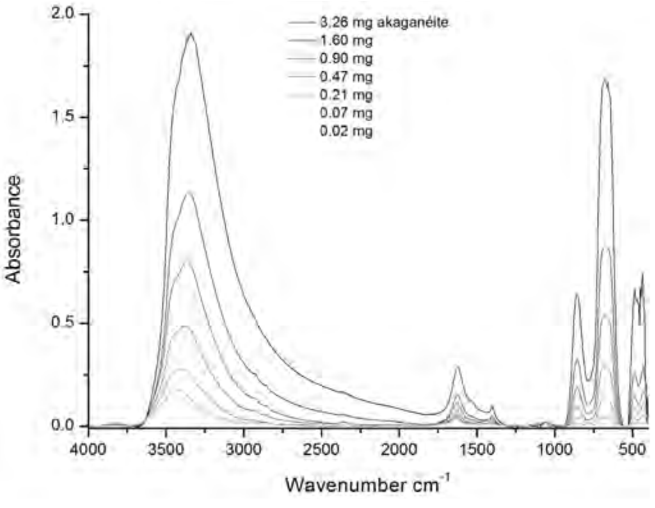

Figure 2. Spectra from one series of FTIR spectroscopic measurements used for the creation of a calibration line.

Calibration measurements with 0.07 mg and 0.12 mg of akaganéite in the pellet still showed a weak, but identifiable band in the significant area. The peak height at 856.6 cm^{-1} was calculated by creating a straight line, at the intersection between the curve of the spectrum at 939.5 cm^{-1} and 789.5 cm^{-1}. The height of this line at 856.6 cm^{-1} was subtracted from the total absorption value at 856.6 cm^{-1}, thereby eliminating the background under the akaganéite peak (see figure 3). The calculated peak height at 856.6 cm^{-1} was plotted against the weight of akaganéite in each pellet and a linear least-squares fit was used to create a calibration line (see figure 4)[5].

Evaluation of test samples

Test samples stored in deep-freeze conditions were assessed with FTIR spectroscopy after 7, 25, 46,131, 210, 417, 754 and 901 days. Test samples stored at room temperature were assessed in the same manner after 7, 25, 46,131, 210 and 901 days. For analysis, one test sample from the freezer was removed at each date, weighed, ground with potassium bromide, pressed as three or four pellets, the pellets were weighed and analyzed. An amount of about 20 mg from the test sample stored at room temperature was removed at each date with a spatula and processed in the same manner [6]. The weight of akaganéite in each pellet was determined using the calculated peak height at 856.6 cm^{-1} and the equation of the calibration line. The percentage of akaganeite in the test sample was then calculated using its weight in the KBr pellet. Each pellet produced for this test contained between 1.54 and 8.00 mg test sample. Results of the FTIR analysis for all of the test samples is presented in Table I.

Results

The average content of akaganéite calculated in the test samples after a given period of time in storage is shown in Figure 5. The test sample stored at room temperature showed a significant akaganéite content of 6.18 % after seven days, which further increased during storage. The variation in the result after 131 days was not clear. After seven days, the powder had developed a rusty, orange brown colour, which seemed to intensify further after 25 days. No additional changes were observed during subsequent analysis.

In the test samples stored at deep-freeze temperatures, akaganéite was not detected before 754 days. However, when compared to the initial spectrum, slight changes could be observed in the spectrum of one measurement after seven days, and in all following spectra obtained

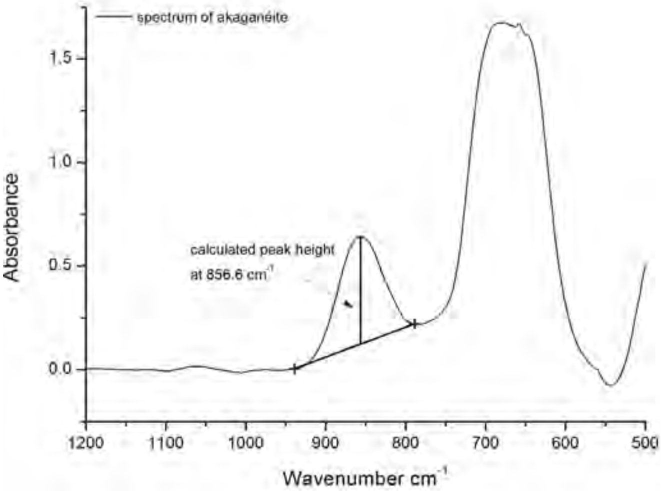

Figure 3. Method of calculating the peak height at 856.6 cm^{-1} for the evaluation of calibration and test sample measurements.

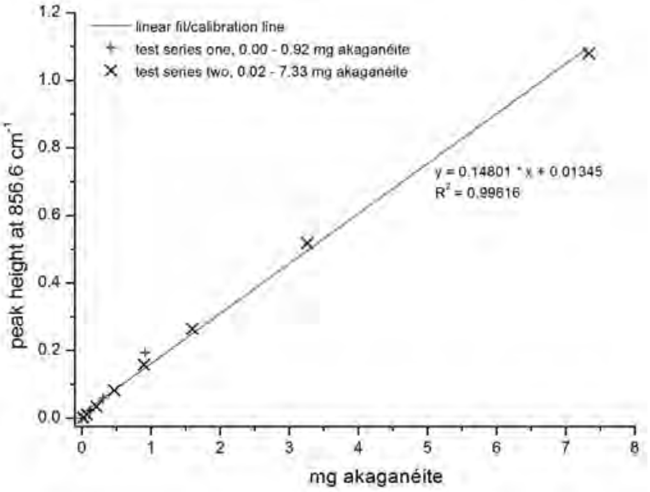

Figure 4. Calibration line.

sample #	date of measurement	storage temperature (°C)	weight of test sample in pellet in mg	calculated peak height at 856.6 cm^{-1}	calculated weight of akaganéite in pellet in mg	calculated wt% of akaganéite in test sample	mean value
1	22.06.2007 (0 days)	-	5.08	0.00531	-0.05497	-1.08%	-1.34%
2		-	4.55	0.00265	-0.07299	-1.60%	
3	29.06.2007 (7 days)	21	3.33	0.03259	0.12935	3.88%	6.18%
4			2.65	0.03861	0.16998	6.42%	
5			3.06	0.05079	0.25228	8.24%	
6	29.06.2007 (7 days)	-23	3.53	0.00311	-0.06985	-1.98%	-4.55%
7			4.19	-0.04947	-0.42507	-10.15%	
8			4.78	0.00260	-0.07330	-1.53%	
9	17.07.2007 (25 days)	21	3.78	0.09170	0.52870	13.99%	13.99%
10	17.07.2007 (25 days)	-23	3.53	-0.00200	-0.10438	-2.99%	-2.99%
11	07.08.2007 (46 days)	21	3.50	0.17421	1.08616	31.03%	30.46%
12			3.30	0.15783	0.97546	29.56%	
13			4.43	0.21530	1.36375	30.78%	
14	07.08.2007 (46 days)	-23	4.19	-0.02587	-0.26564	-5.35%	-4.61%
15			4.78	-0.02121	-0.23416	-4.02%	
16			5.73	-0.02438	-0.25556	-4.46%	
17	31.10.2007 (131 days)	21	1.54	0.17692	1.10448	71.72%	66.84%
18			2.00	0.20399	1.28737	64.37%	
19			1.97	0.20937	1.32371	67.19%	
20			1.98	0.20125	1.26884	64.08%	
21	31.10.2007 (131 days)	-23	4.06	0.00331	-0.06850	-1.69%	-2.04%
22			2.89	0.00264	-0.07305	-2.53%	
23			3.05	0.00310	-0.06994	-2.29%	
24			3.76	0.00419	-0.06254	-1.66%	
25	18.01.2008 (210 days)	21	2.37	0.16954	1.05461	44.50%	44.64%
26			2.36	0.16864	1.04853	44.43%	
27			2.61	0.18581	1.16452	44.62%	
28			2.98	0.21208	1.34200	45.03%	
29	18.01.2008 (210 days)	-23	4.25	0.00258	-0.07345	-1.73%	-1.53%
30			3.91	0.00419	-0.06254	-1.60%	
31			4.03	0.00401	-0.06379	-1.58%	
32			4.76	0.00483	-0.05824	-1.22%	
33	12.08.2008 (417 days)	-23	5.35	-0.00949	-0.15500	-2.90%	-2.20%
34			3.98	0.00243	-0.07448	-1.87%	
35			4.50	-0.00333	-0.11340	-2.52%	
36			5.05	0.00217	-0.07619	-1.51%	
37	14.07.2009 (754 days)	-23	4.61	0.02274	0.06279	1.36%	2.33%
38			6.54	0.03542	0.14843	2.27%	
39			5.23	0.03577	0.15081	2.88%	
40			8.00	0.04672	0.22480	2.81%	
41	08.12.2009 (901 days)	21	4.42	0.32006	2.07158	46.87%	47.68%
42			3.73	0.28557	1.83850	49.29%	
43			3.88	0.29951	1.93267	49.81%	
44			3.12	0.22010	1.39617	44.75%	
45	08.12.2009 (901 days)	-23	4.12	0.03407	0.13932	3.38%	3.28%
46			5.57	0.03933	0.17485	3.14%	
47			5.79	0.03916	0.17370	3.00%	
48			5.89	0.04469	0.21108	3.58%	

Table I: Results for test sample measurements and their evaluation

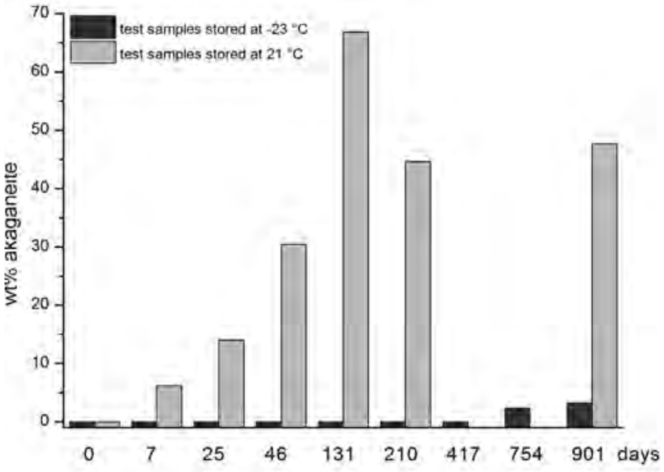

Figure 5. Graph of average akaganéite content (wt%) versus time (days) for powdered test samples exposed at -23°C (*dark grey*) and 21°C (*light grey*).

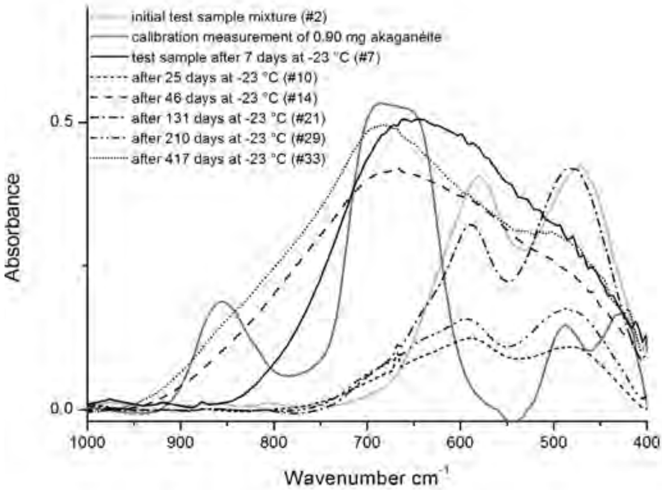

Figure 6. Details of the FTIR spectra of test samples after different periods of storage at -23°C (refer to Table 1).

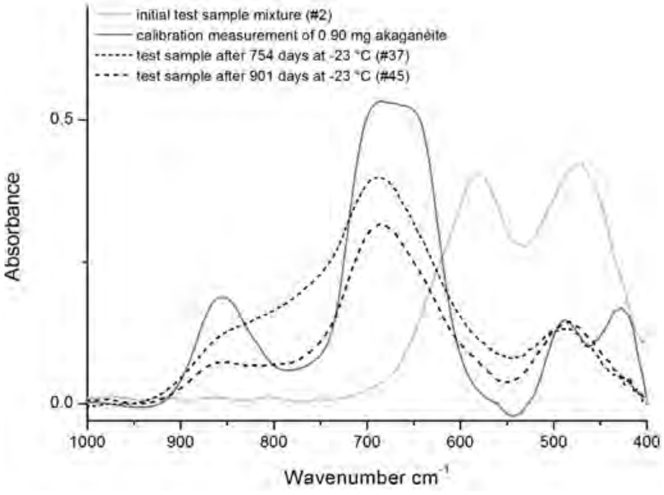

Figure 7. Details of the FTIR spectra of test samples after 754 and 901 days of storage at -23°C (refer to Table 1).

from test samples stored at -23°C, as shown in Figure 6. These spectra show a partial or complete fusion of the two initial bands at lower wavenumbers and a broadening of the absorption area between 950 cm^{-1} and 400 cm^{-1}. After 754 and 901 days, the typical akaganéite bands with peaks at 856.6 cm^{-1} and 680 cm^{-1} became clearly distinguishable in the spectra and akaganéite was clearly identified (see Figure 7). Earlier changes noted in the FTIR spectra are possibly due to an intermediate compound that could not be characterized.

No visible changes in the test samples stored in deep-freeze conditions were observed after seven days, but a slight color change to a more brownish shade was observable after 16 days. This change in colour seemed to gradually increase at each measurement after 25, 46, 131 and 210 days, but was still marginal, and seemed to be less reddish in colour compared to samples stored at room temperature. After 417 days the brown colour had clearly intensified. Until then, test samples stored in the deep-freeze appeared to be more moist than the reference sample, stored at room temperature. After 754 days, orange brown droplets — presumably an acidic solution containing iron chloride — had formed at the inner sides of the test sample containers stored in the deep-freeze. After 901 days the solution had dried and left an orange precipitate. Aside from this, the test sample powder showed a darker brown colour with a slight orange tint, and metallic iron particles could still clearly be observed in these particular test samples.

Conclusion

In reference to corrosion mechanisms occurring on archaeological iron, the experimental results of this study show that significant amounts of akaganéite can form within days in laboratory conditions of 21°C (± 3°C). These reactions would cause visible changes to a real artifact. On test samples stored in deep-freeze temperatures of -23°C (± 3°C), slight changes in colour and the IR spectra also indicate ongoing chemical reactions after only a few days. However, corrosion reactions are significantly delayed in deep-freeze storage conditions, as the formation of akaganéite was only detected after 754 days. Deep-freeze storage for archaeological iron may represent a short-term alternative to minimize post excavation corrosion between excavation and active treatment. However, this technique cannot be recommended as a long-term storage solution due to the increasing formation of akaganéite, as demonstrated in this study. Systematic observation of possible post excavation corrosion phenomena on real iron artifacts stored in deep-freeze conditions would be valuable to confirm the results of this study.

The method applied for the quantitative evaluation of FTIR spectroscopic measurements showed only limited applicability. Therefore, an exact comparison of reaction rates at different storage temperatures was not possible. The human eye proved to be a more sensitive detector of slight corrosion changes than FTIR spectroscopy, therefore systematic colour comparison of test samples using a colorimeter could also prove useful for further studies.

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Endnotes

[1] The average temperature in Antarctica is estimated at -30°C, but it has been observed that the temperature of meteorite surfaces may rise above the melting point of water for short periods. It is not possible to tell if the described corrosion phenomena are only due to this period of time above the melting point.

[2] The same amounts of test sample were stored in the freezer and at room temperature. For the storage in the freezer, several containers were used to avoid the removal of all test samples during sampling, which would have disrupted the storage schedule. A limited number of other chemicals (in closed containers) were stored in the freezer during the experiment. The freezer door was never opened for longer than 30 seconds.

[3] Access of air was allowed at both storage conditions, as only the influence of different temperatures on the corrosion reaction was assessed in this study. RH was not monitored during the experiment.

[4] All observable absorption bands in the spectra of the initial compounds can be ascribed to iron(II) chloride tetrahydrate, as metallic iron is not IR-active. Bands in the spectrum of iron(II) chloride tetrahydrate are observable in the area around 1600 cm^{-1} and above 3000 cm^{-1} and can be due to O-H-vibrations. Iron(III)-chloride, which can occur as an intermediate compound, also produces absorption bands in the range above 1400 cm^{-1}. Both compounds show specific bands only in the area of very low wavenumbers below 700 cm^{-1}. The akaganéite-specific band at 852 cm^{-1} can be ascribed to interactions of water molecules with the hollandite structure. Further bands in the IR spectrum of akaganéite are observable in the area of lower wavenumbers at 670 cm^{-1} and between 300 cm^{-1} and 500 cm^{-1}, which are caused by Fe-O-vibrations. Absorptions at wavenumbers around 3450 cm^{-1} are caused by OH^- and H_2O-streching vibrations. Less intense bands at around 1615 cm^{-1} and 1400 cm^{-1} are caused by OH^- und H_2O-bending vibrations (Raman et al 1991).

[5] Akaganéite as well as iron(II) chloride tetrahydrate are hygroscopic. Minor influences of differing hydration at variable RH on weighing, and hence calibration, cannot be excluded. However, the intensity of bands, which are caused by water in the calibration and test sample spectra, seem to depend on the intensity of other bands, which are caused by the hygroscopic compounds. Hence there seem to be no significant differences in hydration levels during the experiment.

[6] Measurements after 25 days were kindly undertaken by a colleague in Tübingen. Only one measurement of a test sample from each storage environment was conducted at this time.

Materials

Iron(II) chloride tetrahydrate, reagent plus 99 %
Sigma-Aldrich Chemie GmbH
Munich, Germany
Phone: +49 89 6513 0
Fax: +49 89 6513 1169

Iron(III) chloride hexahydrate, puriss. p. a. and potassium bromide, IR-grade
Fluka Chemie AG
Industriestrasse 25
9470 Buchs, Switzerland
Tel: +41 (0)81 755 25 11
Fax: +41 (0)81 756 54 49

Iron powder
Merck KgaA
Frankfurter Strasse 250
64293 Darmstadt, Germany
Tel: +49 6151 72-0
Fax: +49 6151 72 2000

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Q & A SESSION

David Thickett: A comment on the Infra-Red: I'm not 100% sure but that intermediate phase you were seeing looks like an amorphous iron corrosion product that was identified but not fully characterized by Raman in 1992 and I could pass that reference on to you if you thought that would be worth comparing.

Paul Mardikian: Did you measure the relative humidity at cold temperatures?

Charlotte Kuhn: We didn't measure it over the whole storage period but we did it one time and it was about 40% RH then in the freezer. The relative humidity will also depend on the freezing system you use, and if you store your objects in sealed containers or…

Jannecke Nienhuis: While doing your visual examination did you take your samples out of the freezer? And how does that influence your results?

Charlotte Kuhn: Yes, each time we conducted a measurement we took out only one sample from the freezer. There were several samples stored in the freezer so we always took one out, took the measurement and looked at them.

Jannecke Nienhuis: Ok, and you compared the ones that were still in the freezer and the ones that you took out with each other? Did you see any difference in the results?

Charlotte Kuhn: Yes, we compared the ones we took out from the freezer to the picture we had from the initial test sample.

Jannecke Nienhuis: Ok thank you.

Gerhard Eggert: I was very surprised when we saw that even after a few days we could see something. And it turned out that your eye is much more sensitive than the Infra-Red spectrometer, so really could see a color difference. And so there is a possibility of using visual optical light control to see if your objects change, so there might be some value in that. So this is a very interesting point that you can see the changes with your own eyes, they are so sensitive to the color changes – more sensitive than your analytical instrument.

THE USE OF SUBCRITICAL FLUIDS FOR THE STABILIZATION OF CONCRETED IRON ARTIFACTS

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Abstract

The objectives of this study were to determine whether marine or terrestrial archaeological iron artifacts can be effectively stabilized using a subcritical fluid prior to cleaning, and to evaluate the effects of this technique on the artifact's concretion or mineralized layers. The artifacts treated were two wrought iron nut and bolt assemblies from the American Civil War-era submarine, H.L. Hunley (1864) and four Medieval iron nails from a terrestrial site at Formigine castle in Modena, Italy. Four of the artifacts were stabilized using a subcritical, 0.5 wt.% NaOH solution at 180°C and a pressure of 50 bar. No stabilization required more than 10 days. The effect of the subcritical stabilization on the artifacts was evaluated by visual and instrumental assessment, including digital radiography, electron microscopy and micro Raman spectroscopy. Based on the assessments pre- and post-treatment, it was concluded that the artifacts had been stabilized and that, when present, the concretion or the mineralized layers remained intact. Results from this study suggest that it is possible to stabilize an artifact prior to deconcretion or cleaning using subcritical treatment.

Keywords: subcritical, chloride, iron, iron corrosion, concretion, conservation, micro Raman

Introduction

A required step in the successful stabilization of iron archaeological artifacts is the elimination of chloride (and other salts) that came in contact with the artifact during burial. This step is especially critical in the case of materials recovered from saline environments. Failure to reduce the chloride concentration in the concretion or corrosion products to minimum levels may translate into the loss of information contained on the original surface of the artifact and eventually the artifact itself (North and Pearson 1978, Turgoose 1982, Pearson 1987, Drews et al. 2004, Dillman et al. 2007).

The search for an effective, safe and relatively fast technique to remove chloride has driven research on the utilization of subcritical fluids for the stabilization of archaeological iron (Drews et al. 2004, de Vivies et al. 2007, Gonzalez et al. 2007). To date more than 120 experiments (Drews et al. 2004, Drews et al. 2005a, Drews et al. 2005b, Mardikian et al. 2006b, de Vivies et al. 2007, Gonzalez et al. 2007, Drews et al. 2010, Mardikian et al. 2010) have been performed to evaluate the effects of subcritical treatment on a variety of archaeological wrought and cast-iron samples from terrestrial and maritime sites. This process employs alkaline solutions at temperatures above 100°C, typically between 130°C and 230°C and pressures above 30 bar (Drews et al. 2010). The encouraging results obtained to date have been attributed to the changes in the transport properties of the treatment solution. As indicated by the data in Table 1, viscosity, surface tension and density all decrease in pure water or a dilute water solution such as the 0.5 wt.% NaOH used in this investigation. An increase in the diffusion constants for Cl^- and OH^- of about 9% also occurs, relative to the diffusion constants at 25°C and 1 bar when the temperature and pressure are increased to 180°C and 50 bar, respectively (Bird et al. 1998). Recently, it has been shown that the transformation of certain iron corrosion products into more stable phases occurs as well (i.e. akaganéite and lepidocrocite into hematite) (de Vivies et al. 2007).

One of the most promising characteristics of this alternative treatment is the short treatment times required compared to traditional techniques (i.e. chemical, electrochemical or gaseous), with an average treatment time of less than 15 days, as reported here. Another attractive characteristic of this technique is its potential ability to permeate corrosion layers, including those that are part of the original surface of the artifact, as well as extraneous layers — often referred to as a ‘crust’ on terrestrial artifacts or a ‘concretion’ on marine iron objects. This led to the hypothesis that certain iron artifacts could be pre-treated or even stabilized prior to removal of these layers. These layers can be several centimeters thick and are typically composed of iron corrosion products mixed with sand and clay on terrestrial objects and a mixture of iron corrosion products and calcium carbonate on marine objects.

Property	Viscosity, cP	Surface tension$^{(1)}$, N/m	Density, g/cm^3
25ºC, 1bar	0.889	0.072	0.997
180ºC, 50bar	0.151	0.042	0.889
Change, %	83%	42%	11%

(1) Saturation values.

Table 1. Transport properties for pure water at room temperature and subcritical conditions (Wagner and Pruss 2002).

This study had two main objectives: the first was to determine whether archaeological iron artifacts, those from a marine environment with a concretion, or those from a terrestrial environment fully covered with mineralized layers, could be effectively stabilized using subcritical fluids. Terrestrial artifacts can be too fragile to be cleaned prior to consolidation, a step that is likely to interfere with the extraction of the salts. The ability for any given treatment to effectively stabilize the residual metal core while the object is still embedded in its concretion is therefore of interest. The second objective of this investigation was to evaluate the effects of the subcritical treatment on the concretion or mineralized layers on the artifacts, especially the cohesion of the original surfaces and their adhesion to the core metal. The artifacts that were used in this study are two untreated wrought iron nut and bolt assemblies recovered during the excavation of the American Civil War-era submarine *H.L. Hunley* (1864), and four untreated Medieval iron artifacts from a terrestrial site at Formigine castle in Modena, Italy. A variety of techniques were used to evaluate the results of the subcritical treatment, including: visual assessment, optical microscopy, scanning electron microscopy, digital radiography and micro Raman spectroscopy for the characterization of the changes in the corrosion products before and after treatment. The effect of the treatment on the cohesion of the concretion or mineralized layers was evaluated qualitatively by comparing the ease of deconcretion prior to and after treatment. It was hoped that the outcome of this study might suggest new treatment paths for conservators who deal with unstable iron artifacts.

Experimental Procedure

Specimens and treatments

Since excavation, the two heavily concreted wrought iron bolt and nut assemblies were stored in a closed container in tap water at room temperature for three years until they were treated in this study. The four wrought iron nails had a significant metal core and they were entirely covered with a corrosion crust. The nails were received dry, two of them exhibited signs of active corrosion during storage in the laboratory and akaganéite was identified in their corrosion products. The six specimens in this study, their pre-treatment weight, and a treatment summary are presented in Table 2.

HL-3378: This fully concreted object was treated under

Specimen ID	description	Provenience	Type of burial environment	Mass before treatment, g $^{(1)}$	Treatment summary
HL-3378	Nut and bolt assembly fully concreted	H.L.*Hunley*	Marine	198.32	Subcritical treatment for six days, mechanically deconcreted, subcritical treatment for two additional days.
HL-3379	Nut and bolt assembly fully concreted	H.L.*Hunley*	Marine	85.38	Mechanically deconcreted (partially) prior to subcritical treatment, subcritical treatment for 5 days, remaining concretion removed.
WL-475	Nail – part of the mineralized layer spalled off during storage	Formigine castle, Modena, Italy	Terrestrial	16.75	Untreated
WL-476	Nail – part of the mineralized layer spalled off during storage	Formigine castle, Modena, Italy	Terrestrial	18.53	Untreated
WL-479	Nail completely encased in mineralized layer	Formigine castle, Modena, Italy	Terrestrial	58.45	Subcritical treatment for 10 days.
WS-575	Nail completely encased in mineralized layer	Formigine castle, Modena, Italy	Terrestrial	87.36	Subcritical treatment (3 days), treatment was stopped before its completion.

(1) Prior to any intervention being performed on the specimen (i.e. cleaning or desalinization)

Table 2. Summary of specimens used for the present study.

subcritical conditions for six days, rinsed with dionized water (DIW) immediately following treatment, dried in silica gel, mechanically deconcreted with hand tools and rotary micro tools. It was then treated again under subcritical conditions for an additional 2.2 days, rinsed with DIW immediately following treatment, dried in silica gel and the fragile thread was consolidated with an acrylic resin (5%-10% w/v Paraloid® B72).

HL-3379: This object was partially deconcreted while wet with a scalpel and rotary micro tools, treated under subcritical conditions for 5.1 days, dried in silica gel, mechanically deconcreted with hand tools and rotary micro tools and the fragile thread was consolidated with an acrylic resin (5%-10% w/v Paraloid® B72). Following conservation, both HL-3378 and HL-3379 were stored in normal laboratory environmental conditions (20-26ºC, and 40-70% relatively humidity). No coating was applied.

WS-575: This object was immersed in a 0.5 wt.% sodium hydroxide (NaOH) solution at room temperature for 24 hours (upon arrival) to permeate the corrosion layers as a pretreatment prior to subcritical treatment. The nail was treated under subcritical conditions for three days, stored in a closed container with 700 mL of 0.5 wt.% NaOH for 27 months, rinsed with DIW, dried in silica gel and cleaned using a scalpel and rotary micro tools.

WL-479: This object was stored dry under normal laboratory conditions for 18 months. It was then immersed in 0.5 wt.% NaOH solution at room temperature for 24 hours, treated under subcritical conditions for 9.9 days, rinsed with DIW and dried in silica gel. Seven months after treatment the artifact was cleaned using a scalpel and rotaty micro tools. No consolidant was applied during the cleaning process of WL-479 or WS-575 in order to avoid interference with the subsequent surface analysis.

WL-475 and WL-476: These two objects were stored under normal laboratory conditions for 26 months. After approximately 20 months, signs of active corrosion became obvious during storage, causing the mineralized layers to spall and expose the core metal.

During the subcritical treatment, the artifacts were encased in a 304 stainless steel mesh, placed in the 316 stainless steel 600 mL reactor's cell, pressurized using a single-piston HPLC pump and heated by a fluidized bath. The pressure inside the reactor was controlled with a back-pressure regulator, and the solutions employed as eluent were made up of 0.5 wt.% NaOH (ph 13.0) in 18MΩ DIW (see Figure 1a). The treatment conditions employed in this study were 180ºC and 50 bar (Figure 1b). The average fluid flow rate through the cell was in the range of 50-100 mL/h.

Chloride analysis

During subcritical treatment, 5 mL aliquots from the eluent at the exit of the reactor (Ei samples) and from the collection container (Ci samples) were taken. The Ei samples reflect the Cl^- composition inside the cell at the time they are taken, while the Ci samples give an accumulative value of the total Cl^- extracted from the specimen under treatment. Previous to the Cl^- determination, the pH of the samples was adjusted with HNO_3 to a final pH of 7.

The Cl^- concentrations were measured using ion chromatography[1] and the data was analyzed using Dionex Chromeleon® software. The instrument was calibrated using a 30.0 ppm of Cl^- standard, with a limit of detection of less than 0.1 ppm. Each data point reported represents a single measurement.

Determination of Cl-

The presence of elemental chlorine, assumed to be present as Cl^- in the specimens, was studied by using an ultra large chamber variable pressure scanning electron

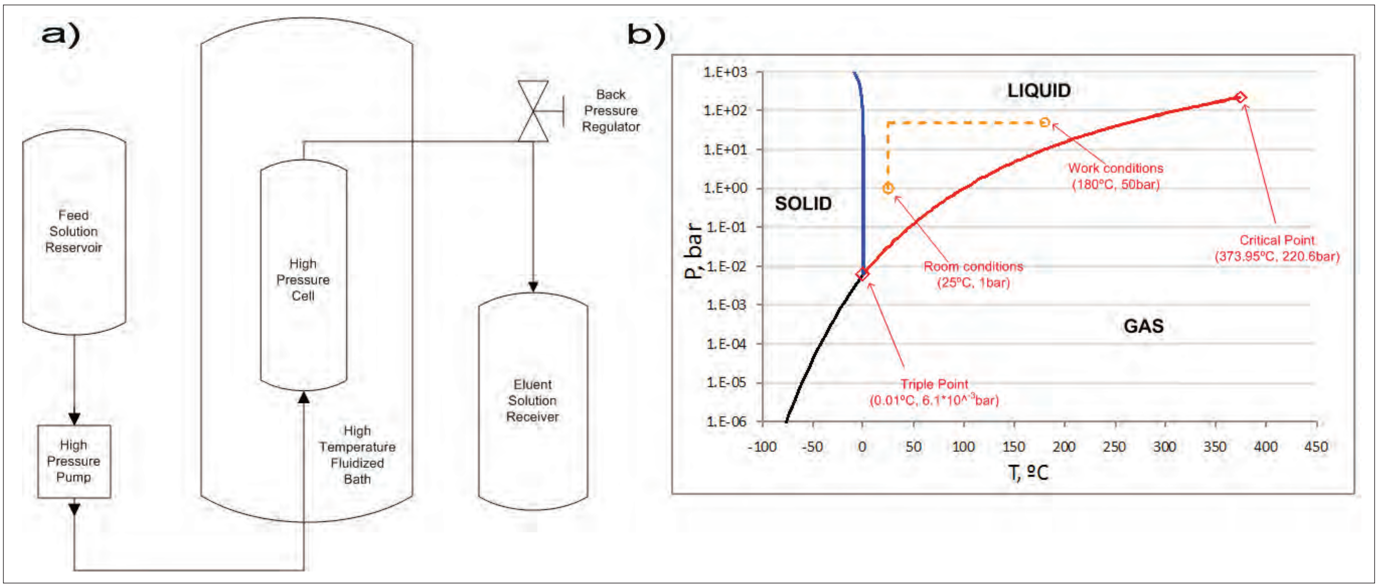

Figure 1. a) schematic diagram of the subcritical reactor b) Phase diagram of water showing room (25ºC, 1 bar) and working conditions (180ºC, 50 bar) during subcritical treatment.

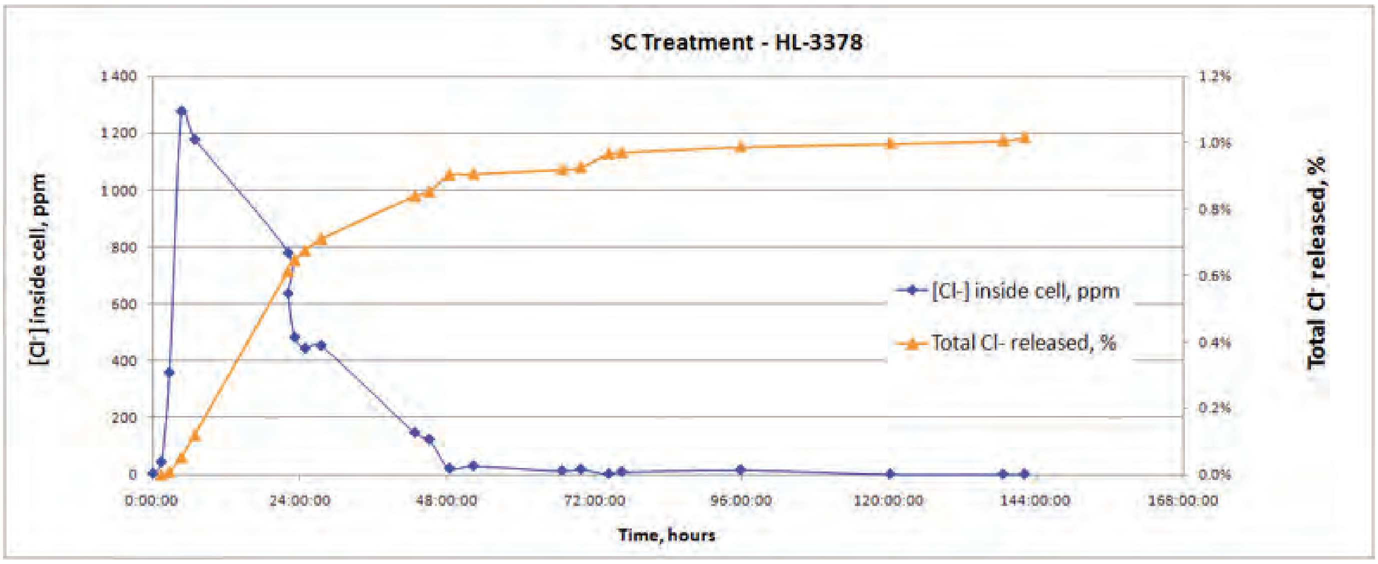

Figure 2. Cl^- concentration inside the reactor's cell (measured at the exit of the reactor, Ei samples) and the total wt.% Cl^- released (Ci samples) vs. time for the treatment of HL-3378.

microscopy (VP-SEM)[2] at 20kV acceleration voltage and a pressure of 70 Pascal. Elemental analysis was performed using energy dispersive X-ray spectroscopy (EDS) with a silicon drift detector[3]. The instrumental limit of detection for chlorine is 0.1 wt.%. For the analysis the entire specimen or specimen fragment of interest was placed inside the SEM.

Identification of corrosion products

Characterization of the corrosion products was undertaken using a dispersive micro-Raman system[4]. Spectra were produced using a 532 nm diode laser. The laser power was filtered to 0.2 mW. Spectra were acquired using a 50x bright field long working distance objective, a detector aperture of 50x1000 μm, an integration time of 30 seconds with three co-additions at 3-5 cm^{-1} spectral resolution, over a spectral range 70-1555 cm^{-1}. Data collection and processing was performed using Opus Version 6.5 software[5].

For EDS analysis, the entire specimen or fragment of interest was mounted on a xyz stage for analysis. The areas selected for the analyses where chosen based on their color and appearance, giving special attention to oddities. For each area of interest, the analyses were repeated at least three times. Identification of the corrosion products was made by comparing the spectra obtained to those from standards as well as from literature references (Oh et al. 1998, Oh et al. 2000, Neff et al. 2004, Neff et al. 2006, Réguer et al. 2007).

Digital radiography assessment

The effects of the subcritical treatment on the concretion or mineralized layer on the artifacts, especially the cohesion of the original surfaces and their adhesion to the core metal, as well as the formation of cracks was studied using X-ray digital imaging[6]. The images were obtained using a 300 KV X-ray source[7], the parameters used for these particular artifacts were: 150 KV, 3 mAand one minute exposure time.

RESULTS AND DISCUSSION

Marine Artifacts: Bolt and Nut Assemblies

Based on the Cl^- concentration in the exit stream, subcritical treatment of the bolt and nut assembly HL-3378 was considered complete after the initial run of six days. The Cl^- concentration inside the reactor and the total Cl^- released versus time are shown in Figure 2. During this first subcritical run the total Cl^- removed from HL-3378 was 1.0 wt.% relative to the original mass of the specimen (artifact and concretion). It was observed that 95% of the total Cl^- release occurred within the first 72 hours of treatment.

Visual assessment after treatment suggested that the concretion layer had stayed in place during the subcritical treatment without any visible damage like the formation of visible cracks or separation from the core metal. This was also confirmed by the X-ray images (see Figure 3b).

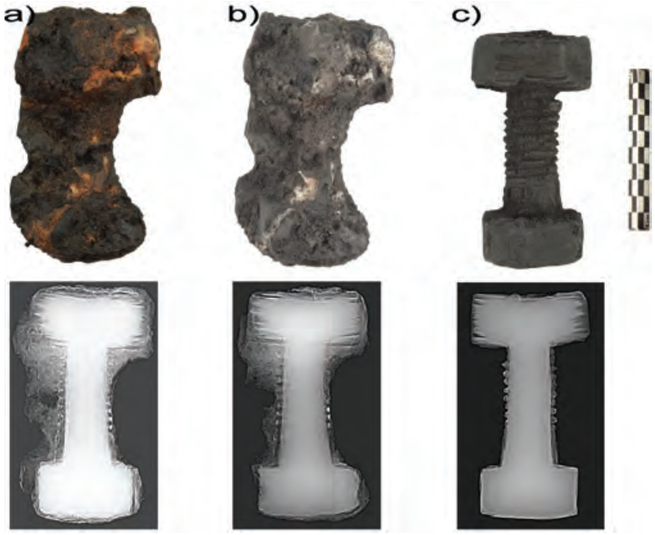

Figure 3. Photographs and X-ray images of HL-3378. (a) Fully concreted before subcritical treatment. (b) After the first 6 days of treatment. (c) After deconcretion and before second subcritical run (shown with 5 cm scale bar, 0.5 cm divisions for scale).

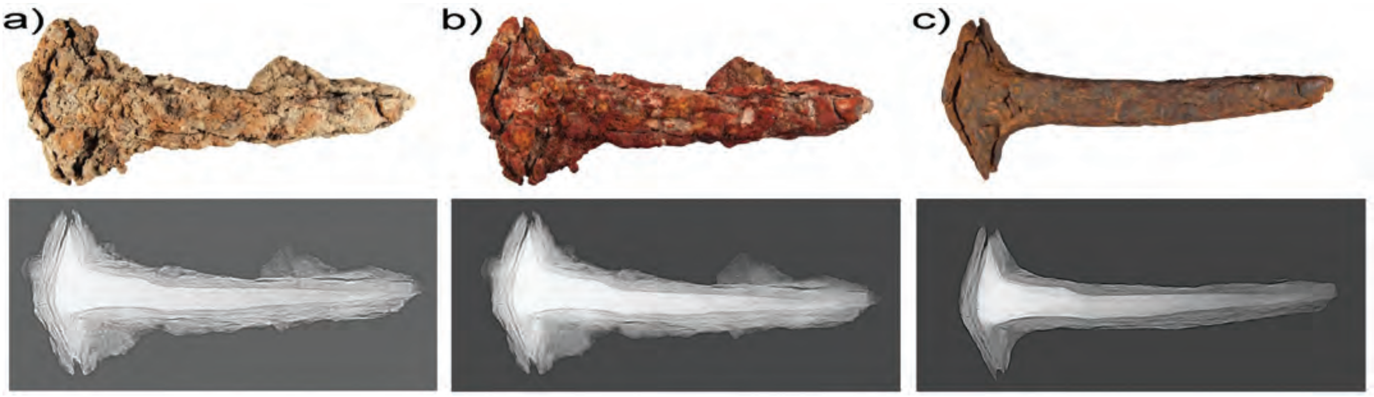

Figure 4. Photographs and X-ray images of WS-575: (a) before subcritical treatment (b) after treatment (c) after deconcretion.

Following deconcretion, which exposed the original surface of the artifact, a second subcritical treatment was undertaken on this object to determine if any significant Cl^- was left after the initial run. During this second treatment, the total Cl^- released was less than 0.01% indicating that the concreted artifact had been successfully stabilized by the initial treatment.

Due to the difficulty in finding the original surface of the mineralized thread during deconcretion of HL-3379 while the artifact was still wet, a decision was made to desalinate it first, and then resume the deconcretion when the object was dry. During subcritical treatment, a total of 0.08 wt.% of chloride was removed relative to the mass of the pre-treatment specimen (70.99 g). In comparison with HL-3378, the relatively low amount of Cl^- extracted from HL-3379 could be explained by the fact that a significant amount of Cl^- was removed when the object was deconcreted prior to subcritical treatment.

Both HL-3378 and HL-3379 appeared black after treatment. Micro Raman spectroscopic analysis of several areas on both surfaces indicated that the black coloration was due to the presence of magnetite (Fe_3O_4). This black coloration has been observed on many of the iron artifacts excavated from the *H.L. Hunley* before treatment while wet, and after subcritical stabilization. During the drying process a few red spots appeared on the artifact. Analysis of the spots by micro Raman identified only the presence of hematite (a-Fe_2O_3). The surfaces of both artifacts were also examined by SEM-EDS. Using color photographs as a guide it was possible to identify the areas on the surface with the red spots and no Cl^- was found. In fact, EDS chemical analysis did not detect the presence of Cl^- anywhere on the surface of either artifact after treatment.

To date, two years after their conservation, no signs of active corrosion have been observed on either artifact. Comparatively, untreated rivets from the *H.L. Hunley* have degraded extremely quickly (within a few weeks) and displayed signs of active corrosion such as weeping, cracking and spalling when left exposed to the normal laboratory environment (Mardikian et al. 2006)

Terrestrial artifacts: nails

WS-575 was the first terrestrial artifact entirely enclosed in a corrosion crust to be subjected to the subcritical treatment (see Figure 4). At the time of this experiment, the effect of subcritical treatment on the physical integrity of these types of corrosion layers was unknown. Therefore, the subcritical treatment was stopped after three days in order to assess its effect on the corrosion crust as well as the artifact itself. Although a significant change in color occurred, and despite the original concern with regard to the physical integrity of the original surface of the object, no evidence of delamination, spalling or crack formation was observed after treatment (see Figure 4b). During treatment, 0.06 wt.% of Cl^- was removed with a concentration of Cl^- inside the reactor of 14 ppm at the time the run was stopped. Because the treatment was stopped before the chloride removal had been completed (Ei>1.0 ppm Cl^-), WS-575 was subsequently stored in NaOH prior to the analysis of the corrosion products. The Cl- released during this time was 0.13 wt.%, with a final Cl^- concentration in the storage solution of 0.8 ppm.

Based on the results obtained with WS-575, the second nail, WL-479, was treated to completion. The Cl^- concentration inside the reactor's cell and the total wt.% Cl^- released versus time for the treatment of WL-479 are shown in Figure 5. The total Cl- removed from this nail was 0.32 wt.% relative to the mass of the artifact.

As shown by data presented in Figure 5, the graph of Cl^- concentration inside the cell of the reactor versus time for WL-479 exhibited two distinct peaks, one within the first 10 hours of treatment and the second at around 100 hours. This behavior had never been observed in any prior subcritical experiments. Moreover, this was the first time a terrestrial artifact fully covered with a corrosion crust was subjected to a subcritical treatment that was carried out to completion. Typical behavior observed during subcritical treatment is represented by the results from the treatment of HL-3378 shown in Figure 3, a single peak occurring during the first 12 hours of treatment.

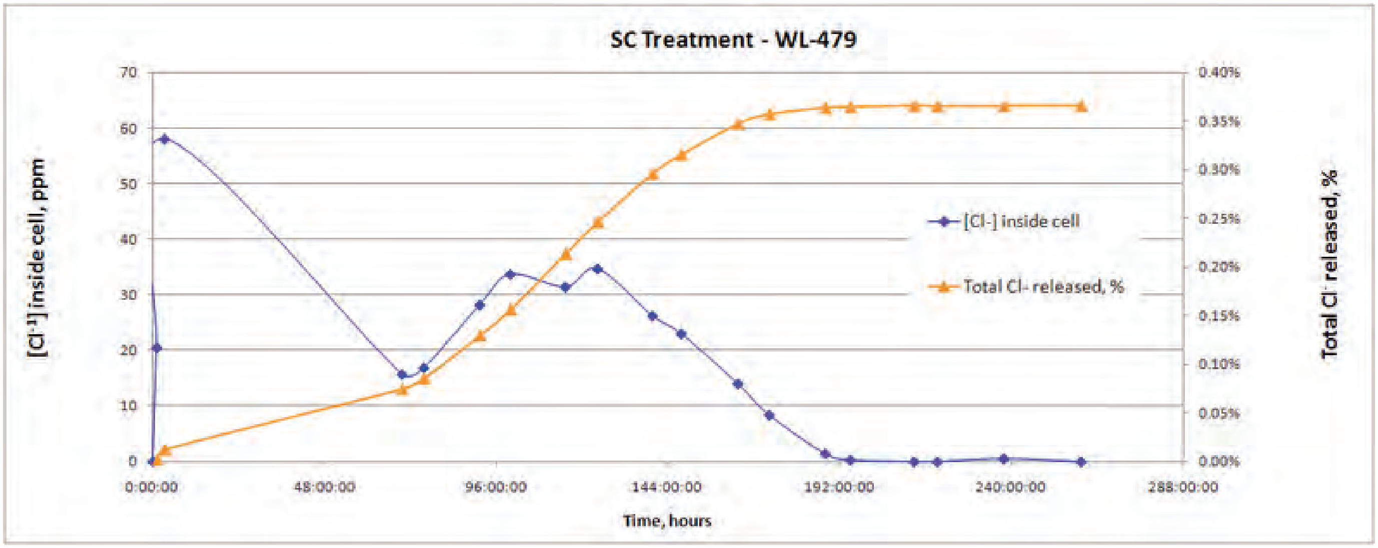

Figure 5. Cl$^-$ concentration inside the reactor's cell (measured at the exit of the reactor, Ei samples) and the total wt.% Cl$^-$ released (Ci samples) vs. time for the treatment of WL-479.

This two-peak release pattern could be explained using the abrupt model proposed by Selwyn and McKinnon (Selwyn 2001), where most of the chlorides are considered to be concentrated at the iron surface. After the initial release of the readily washed out Cl$^-$ located in the exterior crust, a second peak may have been caused by the delayed release of the Cl$^-$ that has to diffuse out from the inner corrosion products. This delay may be increased if the Cl$^-$ release involves the transformation of corrosion products. Further research will be needed to determine whether this result is characteristic of this type of artifact or whether this was a singular event.

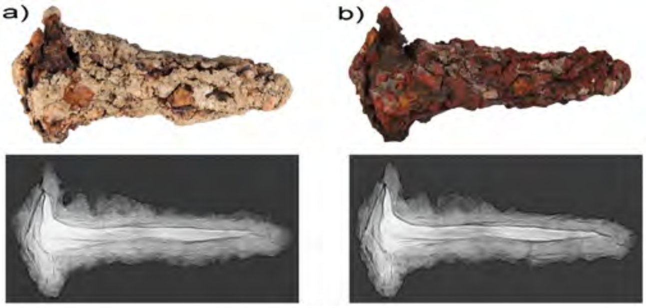

Figure 6. Photographs and X-ray images of WL-479: (a) before subcritical treatment (b) after treatment.

Micro Raman analysis was performed on the exterior of the mineralized layer of WL-479 and WS-575 before and after subcritical treatment (see Table 3). In these same areas no Cl$^-$ was detected by SEM-EDS, indicating that if any Cl$^-$ was present; its concentration was under the 0.1 wt.% (1000 ppm) instrumental limit of detection. After treatment, both specimens were sectioned (see Figure 7) and analyzed using SEM-EDS to look for chlorine, and micro Raman to determine the composition of the corrosion products. No Cl$^-$ was detected by SEM-EDS. See Table 3 for a summary of the corrosion products detected.

During storage, the two untreated nails, WL-475 and WL-476, displayed obvious signs of active corrosion. In fact, spalling of the mineralized layer occurred, exposing the core metal of these artifacts (see Figure 8). The core metal and the corrosion products from the outer layers were characterized by micro Raman and SEM-EDS (see Figure 6).

The characteristic akaganéite and goethite crystal structures are evident in Figure 6. This is consistent with the SEM-EDS analysis for these areas. A total of 43 EDS spectra were collected on WL-475 and 21 on WL-476. In the areas with a strong akaganéite Raman signal, average concentrations of Cl$^-$ of up to 7.5 wt.% were found on WS-475 and 6.4 wt.% on WL-476, whereas in adjacent areas where a strong goethite Raman spectra had been observed, average concentrations of Cl of up to 0.1 wt.% were found.

In the two nails treated with subcritical, WL-479 and WS-575, no Cl$^-$ was detected after treatment in the corrosion layer adjacent to the residual metal. Thus,

Specimen	Before Treatment		After Treatment	
	Exterior surfaces	Interior surfaces	Exterior surfaces	Interior surfaces
WL-475	Goethite, Lepidocrocite, Magnetite	Akaganeite, goethite, magnetite	n/a	n/a
WL-476	Goethite, Lepidocrocite, Magnetite	Akaganeite, goethite, magnetite	n/a	n/a
WL-479	Goethite, Lepidocrocite, Hematite	n/a	Hematite, Goethite, Magnetite	Hematite, Goethite, Magnetite
WS-575	Goethite, Lepidocrocite, Hematite	n/a	Hematite, Goethite, Magnetite	Hematite, Goethite, Magnetite

Table 3. Summary of the corrosion products detected.

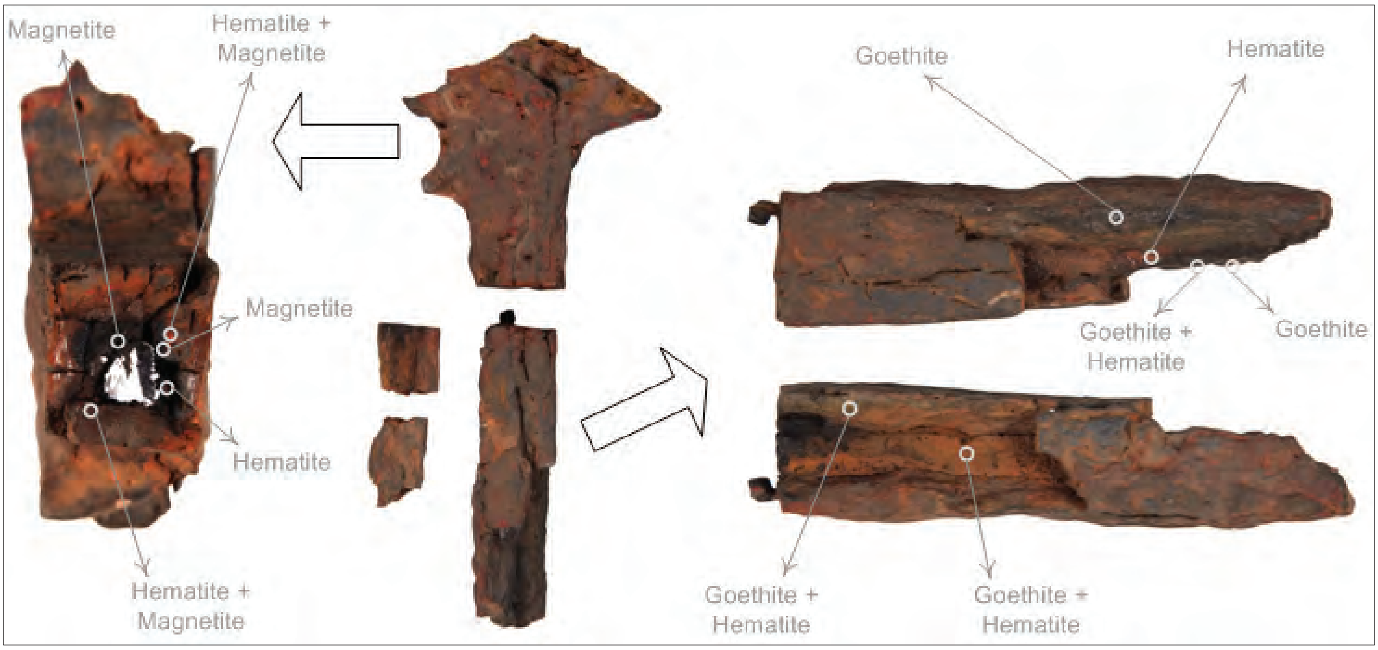

Figure 7. WL-479: Cut fragments and areas around the core metal where corrosion products were analyzed by micro Raman.

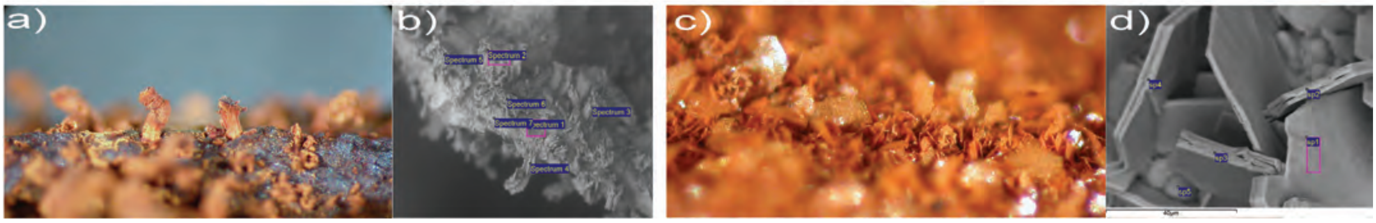

Figure 8. Akaganéite crystals on the metal core of WL-475 viewed under (a) optical stereoscope and (b) with SEM. Akaganéite crystals and goethite crystals were observed on the metal core of WL-476 in adjacent regions. Goethite crystals from WL-476 viewed under (c) optical stereoscope and (d) with SEM.

considering that Cl^- was removed from the artifacts and a significant amount of it would have been expected in this area (Selwyn 2001), it can be concluded that the subcritical treatment was able to remove significant amounts of Cl^- from the innermost areas of the artifacts through the corrosion crust.

In a previous study on the transformation of the corrosion products on dried metal shavings from rivets from the *H. L. Hunley* submarine prior to subcritical treatment (de Vivies et al. 2007), magnetite, goethite, lepidocrocite and akaganéite were identified. After treatment, only magnetite, goethite and hematite were found. Analyses of the corrosion products in the inner surfaces of WL-479 and WS-575 only identified hematite, goethite and magnetite. This suggests that if lepidocrocite and akaganéite had been present before treatment (they were present in WL-475 and WL-476 that are similar objects excavated from the same site) they would have been transformed during subcritical treatment. In addition, lepidocrocite was detected on the nail's inner crust surface before but not after treatment.

With regards to the physical appearance of the mineralized layers on the treated nails, changes in color after treatment were obvious, from light ochre tones before treatment to red coloration after treatment. These changes could be attributed to the transformation of some iron corrosion products into hematite (de Vivies et al. 2007). Careful observation of the X-ray images before and after treatment has not revealed the formation of new cracks or delamination during treatment.

An interesting observation that was made during the SEM-EDS analysis of the sectioned pieces of the treated nails was that sodium was found everywhere in the nails treated under subcritical conditions, whereas none was found in the non-treated nails. Since Na is present in the treatment solution as NaOH, this would suggest that the penetration of the solution has reached the inner most areas of the artifact.

Summary and Conclusions

The objectives of this study were to determine whether archaeological iron artifacts — concreted marine or terrestrial completely covered with mineralized crusts — can be effectively stabilized using subcritical fluids and to evaluate the physical effects of this particular technique on the artifact. The artifacts in this study were stabilized using a subcritical, 0.5 wt.% NaOH solution at 180°C and a pressure of 50 bar. No stabilization required more than 10 days.

After treatment and mechanical cleaning, no Cl^- was found on the surface of the two nut and bolt assemblies (HL-3378 and HL-3379) from the *H. L. Hunley*. In addition, after two years of storage under normal laboratory environmental conditions and without any protective coating, no signs of active corrosion have been observed. Cl^- was not detected by SEM-EDS analyses of the terrestrial artifacts (WL-479, WS-575) either on the inner surfaces or in the crust. The absence of Cl^- and the presence of sodium that was observed in the case of the treated terrestrial artifacts and the absence of sodium in the non-treated nails (WL-475 and WL-476), suggest that the alkaline water solutions used under subcritical conditions do completely penetrate through the concretion layers and remove chloride away from the innermost surfaces.

Based on the results of pre and post-treatment, visual, microscopic and digital radiography evaluation of the four artifacts in this study, it was concluded that the concretion layer and the mineralized layer stayed in place during the subcritical treatment, without the formation of visible cracks or separation of the concretion or the crust from the core metal. Micro Raman analysis of the iron corrosion products show that if less stable phases such as lepidocrocite and akaganéite were present in the object prior to treatment, they were transformed by subcritical treatment to more stable phases such as goethite, hematite or magnetite. Changes in color from light ochre tones to red tones are in agreement with these findings.

Based on the results of this study, it can be concluded that it is possible to stabilize an iron artifact using subcritical treatment prior to removing its concretion or crust with little risk to its structural integrity. This may offer a viable alternative to traditional treatments and open up the way to new possibilities particularly in terms of long term storage and mass treatment of archaeological iron artifacts (Mardikian et al. 2010).

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Endnotes

[1] Ion chromatograph ICS-90 ion chromatography system with an AS40 automated sampler, Dionex, Sunnyvale, CA, USA.

[2] Scanning electron microscope: S-3700N, Hitachi, Tarrytown, NY, USA.

[3] Energy dispersive X-ray spectroscopy: NCAx-act LN2-free Analytical Silicon Drift Detector, Oxford Instruments, Concord, MA, USA.

[4] Micro-Raman system: Senterra, Bruker Optics, Billerica, MA, USA.

[5] Opus Version 6.5: Bruker Optics, Billerica, MA, USA.

[6] X-ray digital imaging: Dynamix CR system with Dynaview Workstation software (VF-C1), FUJIFILM NDT Systems Inc., Hanover Park, IL, USA.
X-ray source: Eresco MF1, Seifert & Co., Ahrensburg, Germany.

Materials

Stainless steel mesh #100
Small Parts Inc.
Miramar, FL, USA
http://www.smallparts.com/

Single-piston pump
Lab Alliance Series III pump
349 North Science Park RD
State College, PA 16803, USA
http://www.laballiance.com/

Fluidized bath
Techne Fluidized Bath SBL-2D
Techne Inc
3 Terri Lane, Suite 10
Burlington, NJ 08016, USA
http://www.techneusa.com/

Back Pressure Regulator
Tescom 26-1700 Series
Emerson Process Management
TESCOM
12616 Industrial Blvd
Elk River MN 55330, USA
http://www2.emersonprocess.com/en-US/brands/tescom/Pages/Tescom.aspx

Sodium hydroxide (NaOH), Pellet, ACS
Mallinckrodt Baker Inc.
222 Red School Lane
Phillipsburg NJ 08865, USA
http://www.mallbaker.com/Default.asp

Nitric acid (HNO3), Certified A.C.S. Plus
Fisher Scientific
2000 Park Lane Drive
Pittsburgh, PA 15275, USA
http://www.fishersci.com/wps/portal/HOME

Cl^- standard: Multi Ion Anion IC Standard (Dionex)
Alfa Aesar
26 Parkridge Rd
Ward Hill, MA 01835, USA
http://www.alfa.com/

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Q & A SESSION

Rick Dorrance: Nestor what are the factors that are preventing the construction of a larger, a much larger reactor chamber that can treat much larger objects?

Lyndsie Selwyn: … like the *Hunley*?

Nestor Gonzalez: Resources.

Rick Dorrance: Be more specific

Nestor Gonzalez: If you are going to treat something that big, you need money. Money for the studies, because technology changes and money to build and of course time and we don't have all of that. You will see our 40 L chamber today at the lab. That was actually $155,000 for the 40 L capacity. If you want to build something cannon size, you need some money to study how to change the technology, the engineering part, and then you have to build it. If you want to put the *Hunley*…!!!!.

Tom Chase: The threads on those two bolts are particularly interesting. One of the radiographs shows the threads as little separate white lines. There is something happening on those threads that is making them radiograph particularly nicely. And I'm not sure what it is but the interesting thing is, on the x-radiograph to the left of the same object, you've lost some of those lines. Would you like to expand on what the difference between the treatments was?

Nestor Gonzalez: Correct. Remember that I said we took the x-ray, treated the artifact and then deconcreted the artifact when dry. In this case the deconcretion was pretty easy. Remember that in one photograph the concretion was chipped, that was good. We tried to also do the deconcretion while wet, before treatment and this was where I said the conservators decided to stop the deconcretion, as we were damaging the artifact. This is the consequence.

Tom Chase: That's very interesting. When you're actually treating artifacts, there seem to be a number of things with sometimes solution treatments that increase the cleavage at the interface. The layers are trying to cleave and I wanted to know more about why those threads look like that on that radiograph but that is a separate question.

Stéphane Lemoine: The white line that the artifacts show reminds me of a tin-plated object of the Middle Ages. Was this object tin-plated before?

Nestor Gonzalez: This is just iron. Only iron.

Rolf Schlake: A comment and a question both: There is under consideration a large chamber for doing subcritical water, that will be about 2 ft in diameter and 10 ft long. This will be a mobile system that will be put on a flatbed that could be moved around and leased to the individual establishments that will require this kind of treatment. Now my question on that is as well: Since you are in the range of supercritical CO_2 and the idea of providing coatings, as well as some of the polishing coatings, has there been any consideration of using supercritical CO_2 to coat the individual pieces of metal if they so require?

Nestor Gonzalez: The work I presented today is just a part of the research we are doing at our lab. There are two other components of this, one is coatings and the other component is supercritical CO_2. Our team presented in WOAM a few months ago the use of supercritical CO_2 for the conservation of waterlogged cork. And yes we have been discussing this. The things you can apply with supercritical CO_2 are just unlimited. The question is: are they practical?

Treatment Of Archaeological Iron

Chair: Lyndsie Selwyn
Panelists: Melanie Rimmer, Britta Schmutzler, Charlotte Kuhn, Nestor Gonzalez

David Thickett: The first point you made about knowing whether your site has iron in it…it's just to say that I have been doing some work with oxygen depletion. If you take something that is relatively dry, enclose it, and measure the oxygen concentration for about two weeks, if you see oxygen reduction then you've probably got an unstable object. If you don't see oxygen reduction after two weeks probably if the corrosion layers aren't too thick you've got a stable object. We've used this a lot for display. There's a problem if you've got wet material because you can get hydrogen evolution instead of lepidocrocite reduction, but certainly for dry material it seems to work very well, it is a very good way of picking out what's your unstable iron and what's your stable iron, which means you can concentrate resources.

David Watkinson: I'd just like to pick up on what David was saying and that to say that that's obviously a good way of detecting an individual object. I think the difficulty comes if you look at sites. There's an idea that maybe the objects have similar concentrations of chloride and certainly we have looked, David is shaking his head, but I think it is a preconception in some areas and we've looked at sites, and for instance, one site that we had from a Medieval site in Cardiff where some objects had 9000 ppm chloride in them, and from the same site you were getting object with 300 ppm, and by digesting the objects we were able to find all the chloride concentrations. When you plot them on a graph there is no pattern, it's totally unpredictable. You might be able to relate that to features on the site, whether they're human occupation or dumps and look at that, but I guess the idea that you could get an idea of what a site has is not really there, but obviously you can look at one object. Thanks.

David Thickett: When I was at the British Museum we looked at low temperature plasma and at about 180°C we were seeing changes to the microstructure on things like bladed objects and I was wondering if you had looked at any microstructures for your metals? Or other objects that might have steel-type structures?

Nestor Gonzalez: We have not, however the temperature we are working at [180°C] is very low.

David Thickett: We've seen it with low temperature plasma at 180°C - we have seen microstructural changes.

Nestor Gonzalez: We haven't looked into that, we do not expect anything but we haven't looked into that.

Gerhard Eggert: Definitely temperature is an issue with a lot of conservation methods. I did not look deeply into it but we could have martensite on objects that have been quenched in water after smithing and we know that even at the lowest temperatures, there could be some changes in the microscopic structure with the sub-grains, that could start even at 50°C. So if you take this, you would argue again not to do anything to warm up your iron. At the British Museum they've measured the Vickers hardness and they found some changes in the hardness, which is to be expected. There was a paper in Chile [by Dusan Perlik, published in Metal 2001] from the Czech Republic who showed that the plasma treatment [up to 200°C] had no measurable effect on the microstructure [on steel] but affected the micro hardness. Therefore it is critical to document the conservation treatments to avoid misinterpretation. At the end I think that if this is for a good cause, you might possibly want to heat your object.

Paul Mardikian: When you put those comments into the wider perspective of the history of iron conservation for the last 30 years going from the hydrogen furnace [at 1000°C] to the modified Australian version operating at 400°C to plasma and now to subcritical [below 200°C], we steadily went down in temperature. In a recent conversation with David Scott in Germany, he indicated that he would be happy to look at the microstructure of some of the rivets of the *Hunley* before and after treatment with subcritical. So this is something that is planned and that we certainly have to look into. On the other hand I want to say, and Nestor is here to confirm, that we really looked at the lowest possible temperature, the mildest pH and the lowest concentration of caustic we could use, for the treatment of our samples and we found that 180°C offered the best compromise. This is fine-tuning. It may not work like Nestor said for every artifact and in some cases you may not want to affect some of the characteristics of your metal but you need to look at the big picture of what you are achieving with this technique and how much stability you gain in the process.

Nestor Gonzalez: I would like to add a couple of things. What Paul says is very important, our team is very small and this research has a lot of different areas and angles of attack but we don't have unlimited resources for this, however we are always open to other groups and people to come on board to work with us. In the past we have treated samples and artifacts for other groups. If you want to send us a sample, we will treat it for you, stabilize it and then you can analyze it. Keep in mind that this technique is currently limited to the stabilization of iron. Also you always need a conservator in the process. It is not just a matter of putting a piece of archaeological iron in the reactor. You need to know what you are doing, and when you are done with the stabilization you need to give the artifact to a conservator who will know how to deconcrete it, this is not a miracle and this is very important to keep in mind.

Peter Northover: The general question of stability of microstructure, which we've come on to - you have to remember it is temperature *and* time. Considering metallographic mounting processes, if you are hot mounting you are going up to 180°C under pressure but you are up to temperature and down again in 9 minutes that is not, even at transmission electron microscope resolutions, going to have a huge impact on the structure, and certainly won't have any visible effect on the optical metallography. With treatments going on for hours or days at 100°C, 180°C that will produce, certainly in iron and probably in some non-ferrous metals and alloys, changes in the dislocation structures you can see at the transmission electron microscope level but not many people go that far looking at archaeological materials. Come down to low temperature, it is well know the effect of discontinuous precipitation of copper in silver over archaeological time. Say in sterling silver it probably has an incubation period of about 200 years before you see something in the optical microscope. But again, if you're treating things with silver at a moderately elevated temperature you probably will have effects. The same effects happen in arsenical copper. The low temperature metallurgy is something we do have to think about, generally the times involved are much longer than most conservation treatments. There is more low temperature metallurgy going on than we allowed ourselves to believe in the past. It is something we should look at more.

Gerhard Eggert: If we are talking about alkaline sulfite treatment, the classical way was to heat the solution at 70°C for half a year and very possibly it could have a greater effect than doing subcritical for a short time. So the classical methods could stress the metals or could have effects and we do not know that much about that. This is why it is important to document the treatments. For a fair comparison between methods we have to keep time in mind and some desalination methods take quite a long time and of course the subcritical is so exciting because it takes less time.

Nestor Gonzalez: Gerhard, in addition to the thermal effects, you need to consider like you said the time effects and in addition to that the chemical effects because the solution we use is a 0.5% sodium hydroxide. If you are using a 2% sodium hydroxide plus other chemicals what are the effects? So it is really a balance.

Panagiota Manti: It is often the case where we have tin coatings on iron and clearly at these temperatures we would start having diffusion of the tinning layers into the substrate, so it is quite likely that at these temperatures, without considering any dissolution of tin in the solution, eventually the tin would be diffused in the metal at a rate depending on temperature, time and the interdiffusion coefficient of the metals involved, leading to the loss of a significant part of your tin coatings. So, it is something one needs to take into account prior to treatment; investigative cleaning is quite necessary.

Nestor Gonzalez: Remember that what we treat is plain iron, no alloys, without coatings, and mostly American Civil War iron.

Panagiota Manti: So we can't use this technique for Medieval artifacts then?

Nestor Gonzalez: For composite artifacts we need to do the research. For iron-based materials we know it works. For a bronze object I do not know, for something coated, I do not know.

Paul Mardikian: I think we always thought about applying this technique to other metals but like Nestor said it requires a lot of time and funding to do that. We want to extend that to copper alloys, maybe aluminum. We could also try that with just water without having a caustic solution or another corrosion inhibitor. The possibilities are huge and the sky is the limit here. It is just up to us to put that research together.

Ian MacLeod: This is an observation on Britta's paper. John Carpenter who is the only man I know that has successfully treated every cannon he has been given but owing to some occupational health and safety issues- namely asbestos - in our laboratory, we were not able to access officially artifacts for 9 years and just storing a load of cannon in caustic solutions and just periodically changing them turned out to be one of the most efficient methods storing them in 20 grams/liter -half molar caustic - was actually, in terms of getting the amount of chloride out of the artifacts, just as good as alkaline sulfite, except it took 9 years. But who cares it keeps you employed for a long time.

Paul Mardikian: Well Ian you are referring to marine artifacts that have not dried out here but when we are dealing with terrestrial artifacts or marine artifacts that have dried out, we see that the solubility of the chloride ions contained in the corrosion products is much lower and that the removal of the bound or occluded chloride ions requires another more potent technique. This is maybe where we need to clarify or determine what each treatment is doing to the corrosion products particularly to the ones that contain akaganéite. We have demonstrated and published that free or occluded chloride ions can be removed all at once using subcritical. This is a big hope that we have that this technique can successfully stabilize terrestrial artifacts where those particular corrosion products have formed. Like Ian said, when you work on marine iron [that has not dried out] and put it in a solution of sodium hydroxide and cover it to prevent the formation of carbonates, the chloride diffusion works beautifully. We found that if we keep the artifacts in storage in a 1% sodium hydroxide and leave them for several years in there and then treat them with subcritical there is only a very little amount of chloride left in the object at this point. So soaking marine iron in sodium hydroxide works very well even if it is true that it may not be as fast as other techniques but it does work well. Just need to remember that it does not work as well on terrestrial artifacts or marine artifacts that have dried out, we know that for sure.

Lyndsie Selwyn: Now I was wondering if Melanie would talk about her 150 objects she's treated for her research?

Melanie Rimmer: Yes, David mentioned earlier that as part of my PhD research I treated 150 objects in a variety of desalination solutions, primarily alkaline sulfite and deoxygenated sodium hydroxide, and we were seeing quite good extraction rates of chloride in terms of percentage efficiency. We're looking for most objects between 60 and 99% efficiency. But what we were also interested in was the residual chloride content in terms of absolute content, and off the top of my head we had about 85% of our objects had their chloride content reduced to less than 1000 ppm, and when we tested those objects at high humidity and high temperature, the majority of them seemed to be stable – they didn't gain any weight over the period of time that we tested. So, we think that from a chloride removal point of view, even if you can't remove all of the chloride in an object, a desalination treatment can remove the majority of the free chloride that causes the worst of the corrosion problem. Of course over long time periods you might see some chloride release from the akaganéite that's left, but in terms of an immediate effect in terms of controlling corrosion, we think desalination can contribute quite significantly in terms of slowing down corrosion rates quite substantially.

Lyndsie Selwyn: Your 150 objects, were they freshly excavated, were they allowed to dry, were they terrestrial?

Melanie Rimmer: They were terrestrial artifacts that had been allowed to dry out, the majority of them were excavated more than 20 years ago, so these are the kinds of artifacts that museums holds in large numbers that have been in storage for a long time and are causing problems. One of the things we would like to look at is the difference between freshly excavated and dried objects because my suspicion is that freshly excavated objects are much easier to desalinate than dried objects.

David Watkinson: Could I just speak at what Melanie said about the residues of chlorides in objects and quite rightly you picked up Lyndsie about whether the objects had been put in the atmosphere beforehand. Looking at the amount of chloride left it's the context of what that chloride is because if its been in the atmosphere a while, you could be looking at objects with substantial amounts of chloride, but if that object has been through an alkaline treatment, you could be left with β-FeOOH or akaganéite, which is substantially stable, in terms of it doesn't have its mobile surface chloride in place, and some of the tunnel chlorides disappear, so, objects could have fair amounts of chloride and yet not be reacting in the environment. And, so in a way that comes back to what you measure about efficiency of treatments and although I was always interested in how effective a treatment was at removing chloride; there's obviously a question about the amount of chloride left, because as I said before, 90% of 10,000 is different to 90% of 1000, and the form of that chloride that's left and how it reacts in the environment. It would be good to see lots of work going on in that area, we're certainly carrying out some more work in that area, but if other people were…it's a good area to work in.

Peter Northover: A question for Charlotte and probably Gerhard as well. If you are freezing and the RH is 40%, what issues are there with ice add with people going in and out of the freezer to collect and change samples? And what happens in the routine storage if you are bringing an object in that's essentially damp from the ground? So, how much is ice an issue in these processes?

Charlotte Kuhn: Well, as I said the research we did focused only on synthetic test samples, so we can't say anything about…

Peter Northover: So, there was no ice forming on the samples?

Charlotte Kuhn: No, not on the samples. The freezer we used didn't have a defrost device, but there was some ice formed in the freezer but not directly on the samples, so we couldn't observe any influence of ice on the samples, but it might have an influence regarding real artifacts.

Peter Northover: Because you know, water expands as it freezes, so that in the general protocols for cold storage of objects…

Charlotte Kuhn: Yes, it is also mentioned in the literature that you should freeze your objects very quickly to avoid huge ice-crystals to form, but they might also form in the long-term if you leave the objects there.

Nestor Gonzalez: I would like to add something. If my psychrometry is not too wrong, I would say that 40% humidity at minus 20°C and 40% humidity at 20°C doesn't mean the same amount of absolute humidity. There is a big difference there.

Lyndsie Selwyn: Paul, can I call on you to talk about the treatment that you plan to do for the *Hunley*? Can you explain the *Hunley* and its treatment goals?

Paul Mardikian: You will see the submarine tonight, so you will see that amazing piece of technology. The submarine was raised in 2000, and was excavated for a number of years, the human remains were removed, the forensic study was done, even the facial reconstruction, the genealogy of the people was studied. And then the hull was documented and then the artifacts were of course treated and there have been a number of steps that we have taken in order to understand how the hull was corroded. We put a treatment plan together that was submitted to the Navy and peer reviewed. In a nutshell I would say that the idea was that it was very difficult to stabilize an artifact that is composed of thousands of different pieces using traditional techniques. I mean hundreds of rivets, plates assembled together, and to do that we would probably need to separate the pieces and treat them separately and then put them back together, which is a very big problem for an artifact that was constructed during the Civil War that has this historical fabric. Therefore, there was a need for finding a more holistic way to do that and the possibilities right now are pretty limited. The possibilities are that you would want to treat the artifact and increase the stability of the artifact meaning you want to decrease the amount of chloride from the overall structure without interfering with that structure. You've got cast iron, you've got wrought iron, the interfaces are complex on the *Hunley* and we have analyzed that structure so that we know in one area we can have a horrible amount of chloride and in some areas you are almost chloride free, so it is very heterogeneous. The submarine is leaning the same way it was during the recovery, because for the archaeologists it was impossible to excavate the interior of the submarine, remove the 10 tons of sediment, remove all of the bodies, can you imagine the bodies, the fabric, the bones, it is very complex. This is a huge composite artifact, and therefore the angle of the submarine had to be preserved. There will be a talk during this week about the rotation of the submarine and how complex it is to just put that submarine upright, the way it was supposed to be seen, and the way it was constructed. Once the submarine is upright, the plan is to deconcrete the surface of the hull, put the submarine in caustic for a number of years and increase the stability of the hull by reducing the chloride level. We know that even if we leave the submarine for 20 years in solution, and Ian can testify that for the *Xantho*, after a number of years in treatment, all of the pieces that were put together were not fully stabilized. The possibilities if using subcritical on something like the *Hunley* would at this point be completely crazy, so we don't want to do that. The agreement we have with the Navy is that we are going to put that submarine in caustic, we are going to monitor the chloride release, we are going to put the submarine in an environment that is going to optimize the chloride diffusion. We are not going to heat the solution but we are going to cover the tank, we are going to monitor the potential, we are going to check the ph. We've got a plan that is pretty clear, but we know that we will never get to the zero level [of chlorides], never ever under those conditions, therefore we have to provide the *Hunley* with an environment after treatment that should be optimal. So, we have talked with David Watkinson, we have talked with David Thickett about this environment - what would be the optimal environment that would not be crazy. You can think about an inert gas, extremely dry conditions, we have not decided yet but more or less the problem is going to be to construct a showcase that will be able to show that submarine and not limit the public for viewing. So you need to think creatively here and I think the bottom line is going to be the relative humidity we have in that showcase. We have to come up with a way that is not going to be horrendous, is not going to be something completely crazy, where you would have the lowest relative humidity, and possibly I would say way under 10%. So the challenge for us is to come up with a showcase that will hold that. We can do with the *Hunley* what we cannot do with a monument or giant boats; reducing relative humidity is possibly the only way right now. We might also use an inert gas, I am not sure at this point. This is in itself a very interesting study to do. You have to balance the fabric of the artifact – it's a risk assessment basically, and you also need to look at the cost and of course have everyone to agree on a plan, which is not always easy.

CONSERVATION OF MARINE ARCHAEOLOGICAL OBJECTS

Session Chair: Paul Mardikian

CORROSION AND CONSERVATION MANAGEMENT OF THE HMAS *AE2* SUBMARINE (1915) IN THE SEA OF MARMARA TURKEY

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Abstract

The wrecksite of the Australian World War I submarine HMAS AE2 in the Sea of Marmara, Turkey, had a salinity of 26‰ (parts per thousand) for the first 13 metres, which increased to 41.3‰ at 21 metres. At this point, the salinity remained constant to the seabed at 72 metres where the dissolved oxygen was 3.1 parts per million (ppm). The vessel is protected by a very dense anaerobic concretion and lies half buried in a silt mound. Cross-sections of concretion samples revealed the original surface, associated paint films and a series of burial-exposure episodes that reflected periodic changes in the silt levels associated with major storm events. Core samples of sediment have established the impact of the vessel on the site. Corrosion simulation experiments have established the direct linkage between chloride levels underneath the concretion layer and the pH of the entrapped solution. This data has lead to the development of in-situ conservation models that will be applied in 2012.

Keywords: *AE2* submarine, Turkey, First World War, *in-situ* conservation, sediment cores, corrosion, simulation

Introduction

The Australian submarine *AE2* was built in 1912 by Vickers Armstrong at Barrow-in-Furness England, launched in 1913 and arrived in Australia on May 24 1914 under the command of Lieutenant Commander Henry Stoker. After service in New Guinea when sister ship *AE1* was lost with all hands, the boat travelled from Australia to the Turkish island of Tenedos in the Aegean Sea. After penetrating the heavily mined Dardanelles, a narrow strait in northwestern Turkey connecting the Aegean Sea to the Sea of Marmara, the *AE2* successfully reached the Sea of Marmara on the 25 April, providing a boost for the Australian and New Zealand Army Corps (ANZAC) Gallipoli Campaign. The submarine created havoc for five days before it was penetrated by gunfire from the Turkish torpedo boat *Sultanhisar* when it broached after mechanical problems. Stoker ordered his crew to abandon ship and then scuttled the vessel. The vessel now lies in 73 metres of water in a silt mound at the bottom of the Sea of Marmara at position 47º32′ N, 27º 17′E.

The wrecksite was discovered by Selçuk Kolay, director of the Rami Koçh museum in Istanbul, in 1995, and the identity was confirmed by a combined Turkish-Australian team in 1998. Owing to its cultural significance to both Turkey and Australia, and the relatively small size of the vessel at 55 metres long, there was an intense debate about the prospects of either full recovery and conservation at a land based facility, or moving the vessel to depths of 20-25 metres where normal scuba supply diving would enable full maritime archaeological inspection, documentation and *in-situ* conservation.

Previous experience with *in-situ* conservation of historic iron artefacts has demonstrated that the monitoring and treatment of anchors, cannon and the *Xantho* engine was practical as long as the sites were accessible by scuba (MacLeod 1986, 1996). Since the submarine lies in deep water, all diving involves use of mixed gases (helium, oxygen and nitrogen) and this necessitates short bottom times and two hours of decompression from each half-hour dive. An additional complication to any proposed recovery or movement to shallower waters is the presence of one unexploded torpedo in the stern of the boat. Both the explosive charge and the mercury fulminate detonator become increasingly sensitive to shock over time. Until the interior of the submarine can be analysed for any traces of high explosive, which would indicate the warhead is wet — and therefore, safe, it has to be regarded as being very sensitive to shock and vibrations. The 2007 expedition was the outcome of the need to provide both governments with preservation options of this iconic wreck.

Physical Oceanography of the wreck site in the Sea of Marmara

On Sept. 10, 2007, the water column above the wreck was measured for salinity, dissolved oxygen (YSI probe) and temperature at 0.5 metre intervals, using a TPS 90DC meter that logged the data, to a maximum depth of 73 metres. The first 13 metres had a mean salinity of 26.1±0.1 ‰, which reflects evaporative concentration of the 18‰ water inflowing from the Black Sea. Over the next 8 metres the salinity rapidly increased to 41.3±0.8 ‰, typical of the hypersaline Aegean Sea, which enters the Sea of Marmara via the Dardanelles. Such marked changes in salinity are known as haloclines and show that there is little mixing of the two bodies of seawater. At the halocline there was a corresponding thermocline (change in temperature) where the temperature fell from 26° to 18°C, and a second thermocline at 40 metres saw the temperature fall from 18°C to 16°C (see Figures 1 & 2). A drop camera inserted through the partly opened hatch inside the conning tower recorded an apparent halocline, but limited cable length prevented quantification. As the submarine was scuttled, initial flooding with surface waters was followed by the hypersaline waters to create the halocline inside the vessel.

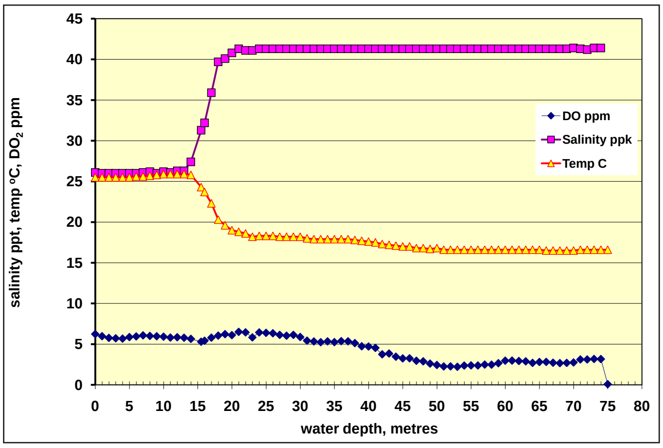

Figure 1. Plot of salinity, temperature and dissolved oxygen, *AE2* site, Sea of Marmara, Turkey September 2007.

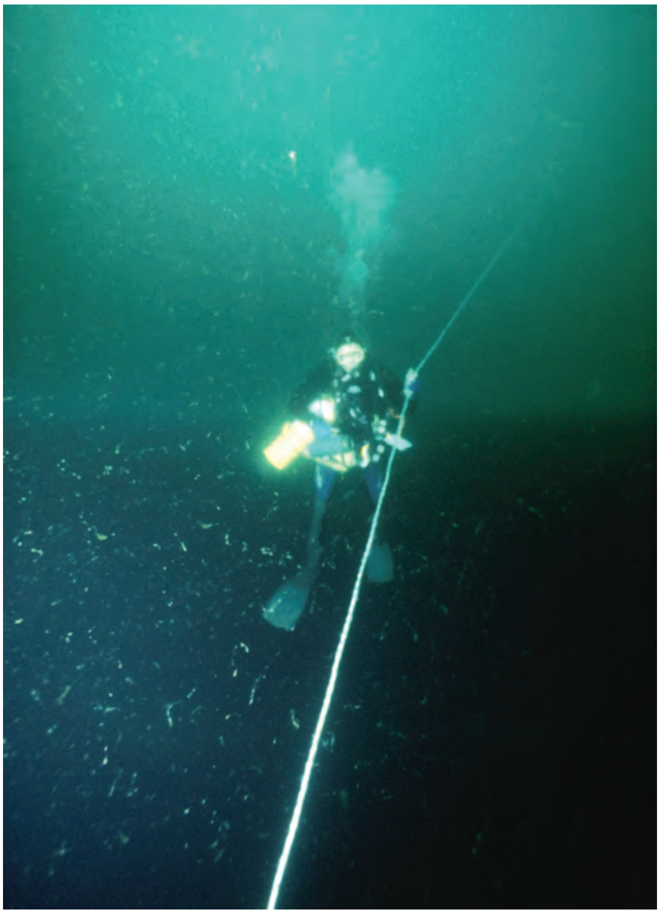

Figure 2. Photo of diver at the halocline showing sharp layer with different optical properties. Photo by MarkSpencer.com.au

The small variations in the dissolved oxygen measurements seen in Figure 1 are due to the vertical movement of the dive support vessel causing hysteresis in the response of the electrode. The surface waters are well oxygenated at between 7 and 5.5 ppm with a gradual fall from 5 to 3 ppm as the depth increases from 35 to 50 metres. At the upper works of the submarine the dissolved oxygen was recorded at 2.8±0.2 ppm which represents 36% saturation of the seawater for a salinity of 41.3‰ at 16°C (Riley and Skirrow 1975). With the oxygen probe in the silt a value of 0.07 ppm was recorded.

Corrosion of the submarine in the Sea of Marmara

The submarine lies on the bottom of the Sea of Marmara with the hull half buried in a silt mound. Images of the wreck at www.submarineinstitute.com show that a combination of corrosion and trawler net damage has perforated the thin plate sections at the bow and on the casing (the structure that covers a range of fittings to streamline the water flow) behind the conning tower, leaving frames exposed (see Figure 3 and 4).

The drop camera showed that the non-ferrous metal fixtures on the interior of the conning tower were covered in a thin layer of concretion from the galvanic protection afforded by the surrounding iron objects (MacLeod 1982). The interior of the conning tower was made of bronze to ensure that the magnetic compass

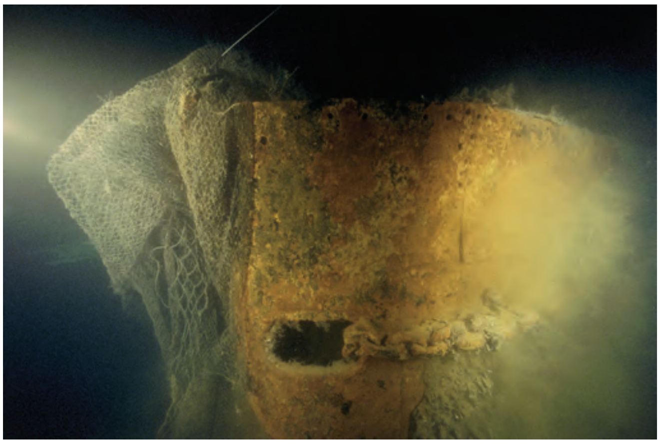

Figure 3. Bow of *AE2* showing anchor chain and fouled fishing nets. Photo by MarkSpencer.com.au

Figure 4. Metal loss on the combing aft of the conning tower showing flash rusting after recent deconcretion: Photo by MarkSpencer.com.au

would not be affected by the proximity of ferrous metals. The hatch cover, ladder, control valves and steering gear were made of brass or bronze. Owing to the confined nature of the seawater inside the vessel it is likely that the massive banks of batteries will be involved in long-range or proximity corrosion that will have affected the electric motors and the diesel engines used for recharging the battery banks (North 1989). Proximity corrosion refers to long-distance galvanic coupling found on historic shipwreck sites and on submerged off-shore modern structures, such as production platforms. When dissimilar metals are covered with a concretion layer they lose their electrical isolation and the more reactive metals corrode while the more noble alloys are protected.

In-situ Corrosion assessment

Owing to a combination of bad weather forcing repositioning of the dive support vessel, strong underwater currents, zero visibility and a serious diving incident, there was only one set of *in-situ* corrosion measurements recorded. Details of the methodology and equipment used have been previously reported. However, special 'O' ring seals for electrode wires and a polycarbonate baffle plate between the pH and volt meters provided extra strength to withstand the pressure at 100 metres (MacLeod 2006, 2007). The surface pH was measured after drilling through rock-hard anaerobic concretion with a masonry tipped drill bit. The measurements were made ≈ 6 metres aft of the leading edge of the casing behind the conning tower. The $^{AE2}E_{corr}$ value was -0.619 volts vs. $Ag/AgCl_{sea}$ (-0.391 volts vs. the normal hydrogen electrode (NHE)), which is the same voltage as the turret and armour plating sections of the USS *Monitor* (1862), which had a mean value of -0.600 ± 0.016 volts vs. Ag/AgCl. The depth of the wreck sites is the same (Arnold 1991). The pH of the submarine was 7.27, which is the same as the mean pH of 7.11 ± 0.54 for the WWI "J5" submarine in Bass Strait, off the coast of Victoria, Australia. The E_{corr} of *AE2* was more negative than the mean corrosion potential $^{J5}E_{corr}$ was -0.382±0.005 vs. NHE, which is expected since the *AE2* is twice as deep as the Victorian wreck.

Concretion on the AE2 and site history

The accidental impact of a 2-tonne concrete anchor with the *AE2* on Sept. 14 deconcreted a section of the hull that enabled direct measurement of metal thickness and recovery of some samples. A remotely operated vehicle (ROV) inspection in May 2010 by Ballard has shown that the bare metal is now covered by a new concretion layer (Neill 2010). A detailed examination of the samples with scanning electron microscopy (SEM) and with a binocular microscope showed a typical anaerobic concretion with a very dense milieu of sharp shell debris and black iron corrosion products. The iron corrosion consisted of magnetite (Fe_3O_4 determined by petrographic analysis) and a number of iron sulphides that included ferrous sulfide (FeS), based on atomic ratios. In addition to these compounds, a number of other species containing iron, sulphur, chloride and oxygen were present (Ozenbas 2008). Samples of the priming coat of red lead oxide, Pb_3O_4, were found at the original metal surface that was covered by a primary layer ≈1.6 mm thick, a secondary layer 8.8 mm thick, and an outer layer 3.9 mm thick. Sections of concretion showed pitting corrosion beneath the original surface to a depth of 3 mm. Since colonisation of the conning tower and the upper sections of the combing are very different to lower parts of the wreck, this is a strong indicator that the sediment levels have not always been the same as those found when the site was inspected in 2007. The concretion model indicates an initial four to five years of relatively intense corrosion as paint layers are penetrated and a steady corrosion rate is established (MacLeod et al. 2004). The primary corrosion layer in the concretion appears to correspond to the first 13±2 years of immersion i.e. from 1915 to 1928. Changing conditions due to massive storms disturbing the site resulted in the second and third corrosion layers.

Assessment of the corrosion rate on AE2

The mean hand-held readings from the Cygnus® ultrasonic metal thickness gauge gave 4.6±0.9 mm for the deconcreted section of the ballast tank for which the original specification stated that it was 6.35 mm thick. The apparent loss of 1.55 mm of metal over the 92.4 years of immersion gave a corrosion rate equivalent to 0.017 ± 0.003 mm/year. Comparative data from the *Monitor* showed that the interior of the turret, which was in an anaerobic microenvironment like the *AE2*, had a corrosion rate of 0.016 mm/year (MacLeod et al. 2008). The corrosion rate for iron shipwrecks in open-ocean waters can be calculated using an empirical equation relating the log of the corrosion rate, measured in mm/year as d_g or depth of graphitisation of cast iron objects on the wreck, to water depth d in metres (MacLeod 2006); viz.,

$$^{\text{Open-ocean}} \log d_g = -0.630 - 0.0156\, d,$$

Using a water depth of 71 metres, the above relationship predicts a corrosion rate of 0.0183 mm/year for *AE2*, which is the same as the observed rate of 0.017 ± 0.003 mm/year. The silty microenvironment of the submarine would naturally result in an overall lower corrosion rate than that for wrecks lying proud of the seabed in well oxygenated conditions.

Sediment cores

It was important to determine the nature of the sediments in the immediate vicinity and at a distance of 20 metres from the *AE2* in order to determine the nature of the interaction of the submarine with its marine environment, and gauge what possible effect relocation might have. Measurements of the dissolved oxygen, pH and redox potentials, using rhodium wire, were made by inserting micro-electrodes through pre-drilled 3 mm diameter holes in the polycarbonate core holders. The holes were sealed with PVC tape until access was required to take measurements. The mean redox potential of the sediment core adjacent to the vessel was +0.119 ± 0.044 volts vs. NHE, which was statistically indistinguishable from the off-site core, +0.157 ± 0.038 volts (see Figure 5). The $^{AE2}E_h$ fell by 180 mV from 0.260 vs. NHE in the first 5 cm of sediment while the off-site sample took 30 cm to fall to the same minimum value of 0.082 ± 0.003. The more rapid fall in the redox potential for the *AE2* core indicates that the microenvironment near the submarine rapidly becomes anaerobic as a direct result of the corrosion process consuming oxygen trapped in the silt. This supposition is additionally supported by the observation that, as the core depth increased, the core close to the boat remained relatively constant at 0.107 ± 0.014 volts, while the off-site redox potential had a mean value of 0.142 ± 0.020 or some 35 mV more oxidising than that by the submarine. This indicates that the submarine has an impact on the microenvironment to a distance of less than 20 metres.

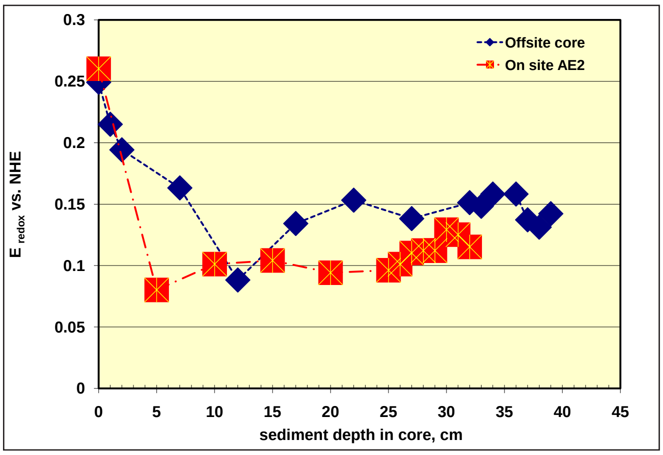

Figure 5. Redox potentials of sediment cores adjacent to and 20 metres from the submarine.

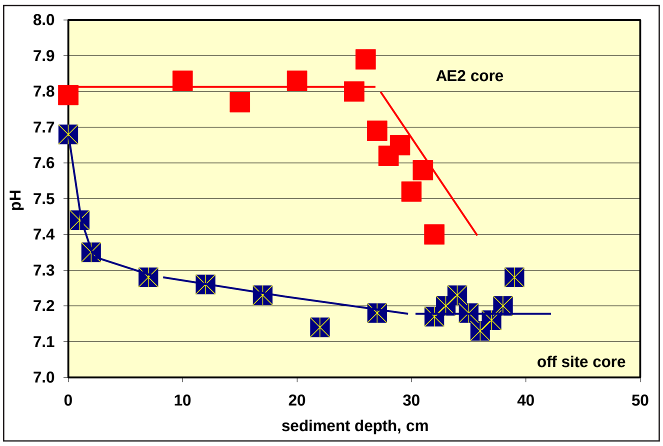

Figure 6. Plot of pH values of the *AE2* site and off site cores as a function of sediment depth.

Analysis of the redox and the pH data of the *AE2* core indicated that the reduction of dissolved oxygen present in the sediment is the dominant electrochemical process, viz,

$$\frac{1}{2} O_2 + 2H^+ + 2\ e^- \rightarrow H_2O$$

The regression analysis of the E_h and pH data conformed to the equation $E_h = 0.759 - 0.084\text{pH}$ vs. NHE, which had an R^2 of 0.9090. The intercept value of 0.759± 0.069 volts is the same as the standard reduction potential of 0.680 volts for the above oxygen reduction reaction, However, the slope for the pH at 84 ± 9 mV is higher than the theoretical 59 millivolts. The off-site core data does not follow any systematic trend. The $^{AE2}\text{pH}_{core}$ values shows a steady alkaline microenvironment for the initial 25 cm at pH 7.80±0.02 before rapidly falling over the last 7 cm at a rate of -0.05 pH per cm distance down the core (see Figure 6). The change in $^{AE2}\text{pH}_{core}$ may reflect a limiting impact of the vessel on the sediment since the pH values for both cores coincide at 7.3±0.1 after a core depth of ≈ 30 cm of sediment. The $^{off\text{-}site}\text{pH}_{core}$ rapidly fell from its initial value of 7.7 to 7.1±0.1 in the first 25 cm of sediment.

The dissolved oxygen measurements in the *AE2* core recorded 7 zero values with a mean of 0.018 ± 0.023 ppm, i.e. essentially zero while the off-site core mean was 0.067 ±0.068 ppm with five zero values. In the off-site core, it was noted that the oxygen concentration increased from zero to 0.2 ppm in the last 7 cm of core that may be a reflection of reduced microbiological activity in this zone leading to less consumption of the small amount of dissolved oxygen in the sediments.

Modelling corrosion processes on AE2

A piece of *AE2* concretion was attached with Dow Corning Silastic®, leaving a 1 mm gap, to a section of corroded wrought iron recovered from an 1890's paddle steamer boiler. The plate was pre-drilled to accommodate measurement of chloride and pH in the interstitial solutions and insulated copper wires were silver soldered to it before the electrode was cast in epoxy resin with a geometric surface area of 40 cm^2. After filling the cell with seawater from Bathers Bay, Fremantle, 35.7‰ plugs were inserted into the measuring holes and the unit was placed in a 4 litre plastic container for 11 months. Australian quarantine protocols prohibited importing sea water from the Sea of Marmara, so local seawater was used in the corrosion experiment. This configuration simulated the microenvironment of hull plates from the *AE2* except for the seawater being at 22 ± 2ºC. There was a systematic increase in the acidity and the chlorinity of the solutions trapped underneath the concretion with increasing immersion time. The pH fell from 7.94 to a value of 4.33 while the chloride concentration increased from 16,300 ppm to 34,600 ppm. In order to show the direct link between increased chloride and acid levels, the acidity function pOH, where 14= pH + pOH, is plotted against the square root of time in Figure 7.

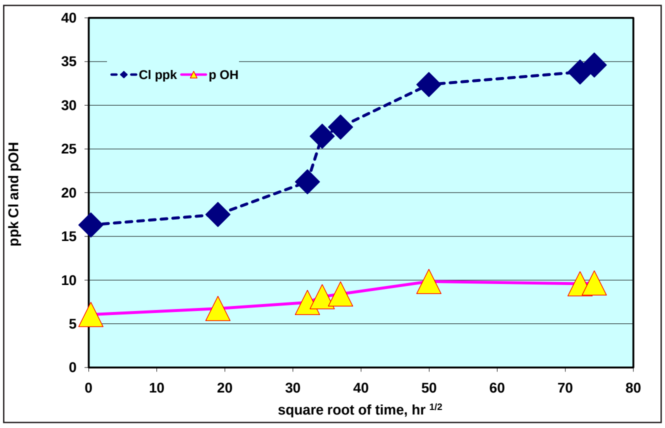

Figure 7. Plot of the chlorinity and acidity, or pOH, as a function of the square root of time for the *AE2* corrosion cell experiment.

Inspection of the chloride and pH/pOH data show that the shape is a classic sigmoidal or 'S' shaped curve that characterises chemical reactions in which there is a limited supply of active components. The data indicates that the chloride and pH equilibrium was reached after 10 months, supporting the belief of shipwreck conservators that the *in-situ* E_{corr} and pH data reflect the dynamic equilibrium between the corrosion of the metal and that of the hydrolysis reactions to produce the acidity. In the first three months where relatively rapid corrosion occurs, the ratio *Cl/pOH* was 2.73±0.12, but after the turning point the value was 3.47±0.15. This supports the thesis that reduced acidity is due to formation of secondary corrosion products and reaction with the concretion. The changing values of chloride and pH best fitted square root of time plots, which support the diffusion controlled nature of the corrosion process. The simple *AE2* concretion corrosion cell showed that the chloride ion concentration increased by a factor of 2.12 times after 11 months in an unstirred laboratory bench experiment. In comparison, the high energy associated with the corrosion of a sealed *Zuytdorp* (1712) cannon bore resulted in an increase in the chloride ion concentration by a factor of 2.90 times after being exposed to heavy surf for 270 years (MacLeod 1996).

During the active corrosion phase, the ${}^{cell}E_{corr}$ values fell linearly with the logarithm of the time by 130 mV, according to the equation. $E_{corr} = - 0.552 - 0.0256 \log t$, with an R^2 of 0.9892, which is a good indication of a chemically controlled reaction. During the next eight months, the E_{corr} gradually increased -0.593 volts vs. Ag/AgCl or -0.393 vs. NHE, which is the same value as the E_{corr} of the *AE2* in the Sea of Marmara. This indicates that the 2007 microenvironment of *AE2* may have only taken a few years to establish.

Additional information about the corrosion process in the cell was obtained through a series of current-voltage scans using a traditional three-electrode system with a Gamry Reference 600 potentiostat. Data from the Tafel plots (±200 mV from the E_{corr} value) were analysed using the Gamry eChemAnalyst software and extrapolated to zero scan rate to estimate the equilibrium values. The large voltage scan was taken to provide comparative data from previous experiments with concreted iron artefacts. It is noted that contemporary practice would involve scans of ± 50 mV around the E_{corr} value. The Tafel slope relates to the number of millivolts needed to achieve a 10-fold increase in corrosion current over the section of the current voltage curve where there is a linear relationship between the applied voltage and the logarithm of the current. The scans were done in 36‰ and 44‰ salinity solutions and the results are summarised in Table 1, which shows that the E_{corr} is essentially independent. This is due to the fact that the corrosion microenvironment for the metal has not fundamentally changed with the increase in salinity.

Seawater solution	E_{corr} vs. Ag/AgCl	i_{corr} mm/year	β_{anodic} mV	$\beta_{cathodic}$ mV	Theoretical slope, mV
36‰	-0.596	0.396	521	324	380
44‰	-0.598	0.300	413	270	340

Table 1. Corrosion parameters from Tafel plots on the *AE2* corrosion cell.

The calculated Tafel anodic and cathodic slopes and the corrosion current had smaller values for the higher salinity solution where the amount of dissolved oxygen is 6% lower. Previous work on concreted marine bronze fittings from the wreck of the *Rapid* (1811) has shown that electrochemically deduced corrosion rates are an order of magnitude higher than those observed on historic artefacts (Taylor and MacLeod 1985). Therefore, the calculated rate of 0.30 mm/year is reduced to a value of 0.03 mm for the higher salinity environment. Measurements of surface roughness of the corroded boiler section used in the *AE2* corrosion cell showed that the surface areas typically are 14 times the geometric area. When the 'real surface area' is used in the calculations, the simulation rate in the 44‰ solution is the same as that calculated from direct measurement of metal thickness at 0.022 mm/year (Heldtberg et al. 2004).

Previous work has shown that for aerobically concreted marine objects, the Tafel slope can be predicted from values of the dissolved oxygen concentration in the seawater (MacLeod 1995). The data in Table 1 show that the calculated and observed values of $\beta_{cathodic}$ or cathodic Tafel slopes are very close to each other and are smaller than the values for the oxidation of the iron. This similarity indicates that the overall corrosion is still controlled by the cathodic processes, which include the major contribution of reduction of oxygen on the external surface of the concretion as well as reduction of iron corrosion products within the concretion matrix.

Conclusion

The data gathered from *in-situ* corrosion measurements on the hull of the submarine *AE2* and the core profiles close to and 20 metres from the vessel show that the dense marine concretion and the great depth of the wreck site is providing a relatively benign storage environment for the vessel. The rate at which the dissolved oxygen profile fell in the two core samples indicated that the submarine corrosion is consuming oxygen from the surrounding silty sediments. Analysis of the pH and E_{corr} data from the cores shows that the sample near the submarine is controlled by the reduction of oxygen in the sediments. Whereas, this is not the case for the core some 20 metres distant from the submarine. It can be concluded that the submarine has a real but limited impact on the silt and sediments.

Data from the corrosion simulation experiment show that it takes approximately one year for a concreted lump of iron to establish the long-term microenvironment that is routinely assessed when making *in-situ* measurements on historic shipwrecks. Not only does this data of direct measurement of chloride ion activity and the pH of the interstitial solution confirm the nature of the corrosion mechanism for marine iron, but also provides opportunities to test the efficacy of changing the environment as a means of moderating the rate of decay of historic iron shipwrecks. Now that it has been established that 'real life' values of chloride and pH can be obtained using appropriate corrosion cells, it is possible to look at the impact of cathodic current, from anodes or from direct current power supplies, on marine iron and measure how long it will take to remove the accumulation of chlorides from the metal microenvironment. Comparison of data from real metal thickness and that deduced from electrochemical scans indicate it is possible to obtain reliable indicators of the impact of changes in the external environment on the corrosion of historic iron objects. Conservators can now establish appropriate model systems to test before attempting to prove the effectiveness of the same in the field.

Since shallower waters provide increased flux of dissolved oxygen to the corroding concreted hull through wave action and currents, it is recommended that moving the vessel to 'safer' operational depths, without the protection of sacrificial anodes, would be prejudicial to the longevity of the submarine. Relocation of *AE2* to a shallower site would increase the corrosion rate and shorten the life of the vessel. Planning and diplomatic clearances are in progress for a detailed internal examination of the submarine that will include full high definition videography and sampling of the oxygen, temperature and salinity levels in May 2012. At that time it is planned to attach a series of zinc anodes to the wreck and to provide equipment to enable remote monitoring of the 'treatment'. Water samples from the stern will be obtained and analysed for traces of explosives to establish the nature of the risk from the presence of the unexploded torpedo.

Acknowledgements

Special thanks are given to Vicki Richards who prepared the field equipment, the AE2 Commemorative Foundation provided logistical and financial support for the Turkish operations, Roger Neill and Peter Graham from the Defence Science and Technology Organisation gave vital assistance in the field. The reviewers feed back on the manuscript has been of immense value.

Materials

TPI WD30 with 80 metres cable to connect YSI dissolved oxygen meter and TPS salinity meter, TPS Brisbane, Queensland, Australia

Rhodium and platinum wire electrodes were home made from pure metal wire silver soldered to insulated copper electrical cable. The rhodium wire was sealed in a Vycor glass seal and the Pt wire was cast with a two-pack epoxy casting resin. Silver chloride double junction electrode with gel filled reference solution by Ionode and the flow through version for meter boxes by Dimet®

Microelectrodes INC combination type sensor MI-800-P with bevelled needle fitting, coupled to an IQ instruments pH meter (Model: IQ 150) (http://www.microelectrodes.com/)

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Q & A SESSION

Jean-Bernard Memet: Ian, you didn't mention the corrosion induced by micro-organisms and particularly sulphate-reducing bacteria. Do you think the decrease of your pH until 4 can be linked to that phenomenon?

Ian MacLeod: Yes, I do believe that. We had a bit of very old untreated iron that had been previously anaerobically corroded, and that's why we chose it to put the concretion on top of that and very quickly the voltage dropped, and you would get consumption of all the oxygen that had been trapped in between that layer of concretion. And very quickly you go into an anaerobic environment and as soon as you've got that your SRB's become active and the acidity goes up. But it's really nice data, being able to get in the lower part of the curve, you've got one ratio of chloride to pH, and in the upper part of the curve, you've got a different ratio. And so it's the classic issue, in the beginning when the voltage was falling, you've got one chemical reaction, which is the initialization of the corrosion cell, the formation of $FeCl_2$ and then in the latter part when you've got more chloride and it is stabilizing you've got a conversion to other corrosion products and you've settled down into a steady state situation.

Jean-Bernard Memet: Second question, can you tell us something about the corrosion speed at this depth. The theoretical corrosion speed of steel is about 0.1 mm per year but I know in archaeological studies it is slower so can you comment on this?

Ian MacLeod: Yes, the work I've done on open-ocean wrecks and on wrecks in Chuuk lagoon shows that the log of the corrosion rate in seawater falls linearly with water depth, so what was interesting was, the theoretical corrosion rate that I predicted from my equation was 0.032 mm per year. The actual depth measured by the divers, from the ultrasonic metal thicknesses was 0.031. So I was quite pleased and it is the same as Dave Krop's depth, of corrosion of the USS *Monitor* turret at the same water depth 72 m. His is off Cape Hatteras, mine is off Cape Karaburun, but same depth, same material, same corrosion rate.

Paul Mardikian: I know, when someone finds a shipwreck there is always the will to raise the shipwreck – people have dreams and fantasies about shipwrecks. Have you been confronted with the problem of having to assist in raising the boat or keeping the boat in situ? And what role did your expertise play in that situation?

Ian MacLeod: Fortunately the fact of the unexploded torpedo being onboard limited in some people's minds the scope of options, which [in this case] was not to move it. But there were those who said: 'we'll bear that risk and we want to raise it' and I did calculations and worked out that it would take roughly $38 million even with a few years of pretreatment to conserve the submarine. And the $38 M price-tag made most people either pale or blanch. And also there were other ideas that we should move it into shallower water, and with the corrosion simulation on the cell I was able to show that that would really make the corrosion rate much worse. So by doing the experiments and arguing through the logic I was able to stop the desire of people to lift it.

Paul Mardikian: Is there any risk with attaching anodes or using an impressed current on a submarine that has loaded weapons?

Ian MacLeod: Yes. What we'll be doing in 2012 if we have permission is taking the remote observation vehicle down right into the stern of the submarine and then we'll have communications to suck in through big syringes samples of seawater, analyze those through GCMS, and if we see traces of TNT or any metabolites we'll know that the warhead is wet and it will be safe to vibrate it.

APPROACHES TO THE PRESERVATION OF SUNKEN HISTORIC AIRCRAFT

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Abstract

Despite more than 30 years experimentation and research, comprehensive and widely accepted treatment and management plans for sunken aircraft have yet to be standardized. This is primarily due to the complexities of corroding aluminum alloys and duplex metals, coupled with the fundamental philosophy of many aviation museums and enthusiasts who favor completely rebuilt structures to the preservation of original, historic materials. This paper outlines the preservation challenges, ethical concerns, and research potential of recovering sunken aircraft, raises questions regarding the future of this particular discipline within the field of preservation, and offers possible solutions to some of the management and preservation problems.

Keywords: aviation archaeology, aluminum-alloy conservation, historic preservation, historic aircraft, corrosion studies, submerged aircraft

Introduction

During the last three decades, philosophical differences in approach and methodology pertaining to the preservation and management of historic aircraft have shaped an increasingly contentious situation. On one side of the dispute are those who consider the material integrity and authenticity of the structure to be the paramount concern. The opposing viewpoint is entrenched in the desire to have an aesthetically pleasing visual exhibit or functioning artifact.

With the decreasing availability of derelict aircraft or semi intact wreckage on land, there has been a growing interest in utilizing submerged wrecks for exhibition and reuse. Long-term management of these cultural objects, however, has not always been kept at the forefront of these efforts. Submerged aircraft do qualify as a potential archaeological resource and the current capacity to handle the long-term preservation of aircraft recovered from a marine environment serves to further compound management issues. Two of these issues are the focus of this paper, and include 1) the complexities of conservation associated with an underwater site; and 2) historic preservation practices for sunken aircraft.

Object conservation developed from the craft-based practice of restoration, which sought to preserve the outward appearance of valuable artifacts. The mid-20th century shift to a scientific methodology reflected the academic development of archaeology and the analysis of artifacts (Newey 2000). Despite this paradigm, there remains a tendency by many museums and aircraft enthusiasts to completely rebuild significant aircraft structures rather than preserve the majority of recovered planes. As a result, many in the viewing public expect to see a finished airplane that frequently looks better than the original working craft. The dichotomy of these approaches highlights the potential loss of historical information, and the repercussions of historic aircraft restoration.

These issues are brought to light in order to examine ways in which the treatment of historically significant or rare sunken aircraft wreck sites can be improved to meet the standards imposed and universally accepted for other archaeological sites. We hope this will prompt a dialogue that will raise awareness and guide the future path for submerged aircraft study, preservation, and exhibit.

Restoration versus Reconstruction

Michael Blaugher, in his *Guide to Over 900 Aircraft Museums, USA & Canada* (2004), lists 1,192 aircraft museums and single aircraft displays in the United States. In Texas alone, there are 33 museums and one aircraft carrier, focused on the interpretation of historic aircraft. The large number of dedicated museums exemplifies the considerable link that American's have with this portion of their collective heritage, and public interest continues to increase. Unfortunately, the frequent rush to collect and exhibit examples of different aircraft types has left many of the artifacts with little remaining original material. For many people involved in the 'restoration' of aircraft, the guiding philosophy has been to replace parts or features with new material or components stripped from other aircraft. This action results in an artifact of limited historic or archaeological value, as in the case of a Douglas SBD-3 *Dauntless* recovered from Lake Michigan (see Figures 1 and 2). Salvaged 48 years after its sinking, the structure, hardware, equipment, and furniture underwent an extensive reconstruction; so much that original material cannot be distinguished. On many similar reconstructed aircraft, the provenance record keeping and general documentation of new versus original parts is frequently found to be substandard, if existing at all.

Figures 1, 2. A restored Douglas SBD-3 Dauntless which crashed into Lake Michigan during carrier qualification training in October, 1943. Photographs by P. Fix.

Restoration, as defined by the *Secretary of the Interior's Standards and Guidelines*, is 'the act or process of accurately depicting the form, features, and character of a property as it appeared at a particular period of time by means of the removal of features from other periods in its history and reconstruction of missing features from the restoration period (36 CRF Part 800)'.

Restoration allows for the reconstruction of missing features, not the wanton replacement of integral items and structure. Thus, many older aircraft already on exhibit in museums are mere replicas of the original object.

Many aviation enthusiasts and aviation museum staff do not consider archaeology a relevant issue with regard to submerged historic aircraft (War birds Information Exchange). This mindset must be challenged. While the archaeological site may be narrowed to the region around or in the object itself, much could still be learned from close archaeological investigation. One example would be the role of environmental factors in materials deterioration. Without documentation of the surrounding water or sediment chemistry, microbiological habitation, and localized hydrology, there is no way to compare *in situ* preservation among aircraft. This understanding could be imperative to determine the best environment for long-term preservation.

Past Conservation Efforts and Research

Since historic aircraft were constructed from a range of materials and processes, preservation of these composite artifacts present difficulties not encountered elsewhere. Aircraft materials may include wood, metal, textile, glass, and an assortment of adhesives. For example, the metal that comprised the Douglas Aircraft Company TBD-1 Devastator structure, furniture and hardware were cast and wrought, heat treated and cold worked, annealed and quenched. In addition, there were numerous different alloyed metals, and many in close contact. Examples of metal components used on the Devastator include Alcad aluminum, different aluminum alloys, brass, bowdenite, iron, zinc, lead, nickel, bronze phosphor, tinned copper, and annealed steel (Douglas Aircraft Company 1937). To logically approach the long-term conservation of such composite objects, the characteristics of each material component should be well understood, together with the correct methods of working and storing them.

Apart from some noteworthy scientific scholarship (MacLeod 1983, Degrigny 1990; Adams 1992, Adams and Hallam 1993), in comparison to other areas of archaeological investigation, recovery, and conservation, preservation techniques for aircraft are in general underdeveloped. Perhaps the earliest published attempt at stabilizing a corroding aluminum alloy aircraft component is the treatment undertaken by Ian MacLeod and the Western Australian Museum on a sea-plane float. The float came from a Junkers W33 aircraft abandoned at Cape Bernier in 1932, and it was eventually used as a sailing vessel by the crew to reach safety (MacLeod 1983). An ammonia leaching method was used to treat this artifact through chloride removal. After the exterior of the float was mechanically cleaned it was placed in a tank of deionized water, in which the chlorides were monitored weekly, along with reduction potential of the solution and the corrosion potential of the metal. After three weeks, ammonium sulphate and ammonia were added to the solution and the object was periodically removed, cleaned, and re-immersed in fresh baths until it was finally allowed to air dry. The textile between riveted components of the float was treated separately, and the entire ammonia leaching treatment took a total of 14 months. MacLeod reported that after four months of ambient-air storage, no signs of recurring corrosion were observed (MacLeod 1983).

In 1992, a French group undertook the stabilization of a BMW 801D-2 radial aero engine (from a Focke Wulf 190A-8), which had been recovered from the Loire River (fresh water), near Orleans, France in 1990. The goal of the project was to remove encrustations from the engine and leach out the chlorides that had impregnated the metals, which consisted mostly of aluminum alloys and iron alloys. The method employed by the conservators differed from previous simple immersion techniques, in that it utilized electrical potentials. The treatment included mechanical cleaning, washing the material in chemical baths of buffered sodium citrate, followed by submergence in sodium metasilicate while undergoing electrolysis. Following a final mechanical cleaning, the engine was treated with a diniatrol 4010 varnish to protect it from the elements. The entire treatment took one month and proved successful (Adams 1992, Degrigny 1995).

Noted by conservation scientist Christopher Adams, surface coating or inhibitor treatments would not stop the long-term corrosion of the metals as ‘all the necessary chemical species that are involved in the corrosion reaction are still present under the coating’ (Adams 1992). His observations are particularly foreboding considering the excessive use by many museums in treating original aircraft or aircraft parts solely with corrosion inhibitors.

In 2002, a corrosion study was begun by the Western Australian Museum on five sunken Japanese naval aircraft that were lost during a bombing campaign at Chuuk Lagoon, Micronesia. Adding to a series of earlier corrosion studies on similar archaeological sites, the museum experimented with several of the sunken craft.

The studies conducted on the aircraft in Chuuk Lagoon produced valuable results. It was found, for example, that on the Judy dive bomber, increased pH at depth is consistent with a reduction in the rate of corrosion. Analysis of the Zeke fighter planes demonstrated that there was a variation in the rate of corrosion at an individual site (for example, between starboard wing skin and landing gear), subject to the constant flux of fully oxygenated seawater, which was measured at each site. In addition, there were marked variations in the corrosion potential on different sections of the same aircraft part (for example, on the port wing of the Zeke fighter), likely due to the different alloys used in its construction (MacLeod 2006). Though this method of *in situ* preservation is still in its early stages, this study has clearly shown that there are non-destructive methods of assessing condition and analyzing the rate of decay of submerged historic aircraft, which should be more fully explored in the laboratory and developed to extend the life of these craft.

These and a string of other studies show that our knowledge of metal corrosion rates and long-term conservation methods can, and should be, improved. Undoubtedly, more research needs to be conducted regarding the survival potential of submerged metal alloys and preservation of original aircraft fabric. One thing is known, however: recovery of submerged aircraft without a comprehensive plan can lead to disastrous results, as in the case of these parts from a Grumman F6F-5 Hellcat recovered from Martha’s Vinyard, Mass., left to deteriorate while new components were being fabricated (see Figures 3 and 4). If reconstruction is the goal, this decision is less significant as much of the original material will be replaced. This, however, introduces a host of ethical concerns as described above. Once the historic materials are permanently removed, the information about original construction methods, historically accurate coloring, and authenticity as a whole are lost without a way to retrieve them.

Figures 3, 4. Parts of a Grumman F6F-5 Helldiver recovered from the water off Marthas Vinyard, MA, lay on racks slowly disintegrating while new pieces are fabricated. Photographs by P. Fix.

Historic Preservation Policy for Sunken Craft

Often when a sunken historic U.S. Navy aircraft is discovered, one of the first steps beyond basic research and identification is to determine its eligibility for listing on the National Register of Historic Places (NRHP). Listing on the NRHP is an important step in a nationwide preservation process, which can involve several participants (private individuals, state and federal historic preservation offices, local governments, and American Indian tribes), and ends with the Keeper of the National Register. The sets of criteria necessary for listing on the NRHP are consistent with the Secretary of the Interior's *Standards and Guidelines for Archeology and Historic Preservation*, which are uniform and national standards for preservation activities (National Park Service 1997).

Whether the aircraft is determined to be an historic structure or an archaeological site, historic preservation law implies that the historical integrity of the site has remained intact. According to National Park Service preservation terminology:

> Preservation is defined as the act or process of applying measures necessary to sustain the existing form, integrity, and materials of a historic property. Work, including preliminary measures to protect and stabilize the property, generally focuses upon the ongoing maintenance and repair of historic materials and features rather than extensive replacement and new construction (Secretary of the Interior website, accessed 20 January 2010).

Substantial removal and replacement of original components effectively transforms the original into an object with little authenticity. The only surviving German Albatros D-VA, from WWI, was reconstructed by the National Air and Space Museum (NASM) in the late 1970s and early 1980s. A decision was made to completely disassemble the aircraft and replace many of the original pieces — rotting wood, fuselage skin, and textile coverings — to create an aesthetically pleasing museum piece. The engine was removed, chemically treated, and repainted. Modern adhesives, cotton textile and varnishes were applied. In its current state, the Albatros D-VA has a varnish that does not yellow in a similar fashion as the original varnish. As a result, the plane has a bright and unrealistic hue, vastly different from the 'few nitrate dope coats hastily applied during war time' (Mautner 1995). This aircraft now hangs in the NASM War Gallery, and appears to be a glossy replica rather than a veteran of World War I.

Since then, NASM has taken measures to more effectively preserve the integrity of the aircraft in its collection. Beginning in the 1980s, NASM shifted away from major restorations to focus on preserving original parts and finishes. A conservator was hired and preservation efforts began on various aircraft in NASM's collection. The Aichi M6A1 Seiran, the sole remaining example of this type, was preserved successfully with minimal intrusion and stands as a worthy example of a possible future goal for the rest of the collection (Mautner 1995) (see Figure 5).


Figure 5. Aichi M6A1 Seiran on display in the Udvar-Hazy Center of the Smithsonian's National Air and Space Museum. Photograph by Szuyuan Huang, 2007.

Possible Preservation and Management Approaches

Not all sunken historic craft should be recovered and conserved. Due to the high cost of conservation and the need to learn more about the treatment of aluminum alloys, *in situ* preservation is a practice widely accepted by the conservation community until better conservation techniques can be developed and a cost effective plan can be devised for historically significant examples.

If an adequate plan for stabilization of an aircraft cannot be generated, or funding is in question, one approach toward responsible management and long-term preservation of a submerged aircraft is to involve both federal and state government as well as the general public in protecting the site. A 2010 discovery of an SB2C Helldiver by a dive shop owner in Hawaii has spurred just this sort of cooperation (see Figure 6). The initial approach taken by the U.S. Navy, which is responsible for the protection and long-term preservation of the Helldiver under the *Sunken Military Craft Act* (2004), is to monitor the site and engage the dive shop owner in this endeavor. The site will be mapped and recorded in detail by archaeologists, then regularly monitored by the dive shop owner to protect against site disturbance. The dive shop benefits from this cooperation by gaining official recognition from the Navy, ensuring the long-term preservation of the site for recreational diving purposes, and by becoming part of a nationwide preservation effort for historic craft.


Figure 6. A well-preserved Helldiver discovered *in situ* on the Hawaiian sea floor. Photograph by Sean Dyer, 2010.

Another way forward is to involve the preservation community and form working groups to assess the condition and preservation needs of particular craft. This working group should include members of all stakeholder organizations such as aviation museum staff, responsible preservation groups, academic groups, archaeological conservators, state and federal historic preservation officers, the Advisory Council on Historic Preservation (ACHP), aviation enthusiasts, and veterans. Among other strategies, this group might develop a classification system, similar to one created by NASM in the late 1970s, which would prioritize the preservation needs of historic aircraft. Such a system might rate these craft by their historical importance, technological complexity, rarity, or lack of these attributes (similar to the NRHP criteria). This could be coupled with another classification system that ranked the condition of the aircraft and the urgency of conservation intervention. The proposed group should be designed so that it could reach a consensus on how such historic aircraft should be treated.

Along the same lines, organizations wishing to recover and/or preserve sunken historic aircraft should seek the guidance of a professional conservator before state or federal authorities issue a permit. An example of such consultation is the Conservation Plan for an Avro Arrow Model through Recovery Phase, Surface Assessment, Cleaning, and Transport prepared by the Canadian Conservation Institute for the Aerospace Heritage Foundation of Canada. This detailed report outlined all relevant considerations, from potential deterioration to field documentation and conservation efforts for the recovery of historic model aircraft lost in Lake Ontario in the mid-1950s (Binnie 2001).

It is also important to involve the ACHP more in the determination of a site's historical/archaeological significance, and emphasize the Secretary of Interior's standards for the treatment of archaeological sites and historic structures. More emphasis might be placed on accurate recording of the site prior to disturbance, artifact recovery and conservation, detailed report writing and timely dissemination, and long-term preservation of historic and rare aircraft.

Conclusion

As briefly outlined above, there are a number of unresolved issues regarding the best approaches toward preservation of sunken historic aircraft. Notions of restoration born of antiquated attitudes toward maintaining aesthetically pleasing replicas of original craft need to be challenged as the number of historic aircraft rapidly diminishes. Information will continue to be lost until a reasonable national standard of preservation can be accepted and enforced.

A few possible solutions were mentioned in this article, but the first step should be to form groups of interested stakeholders so that discussion on how best to proceed can begin. Reaching these goals will require considerable effort and education to gain the support of both the lay public and museum professionals that are ensconced in the notion that only a visually appealing artifact has value. This, however, is a campaign that must be initiated before more significant materials and structures are lost.

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Q & A SESSION

Jonathan Leader: As you know South Carolina has been blessed with any number of aircraft wrecks. I was looking forward to this paper and I have enjoyed it and thank you very much for doing it, I think you did an excellent job at pointing out some of the problems. There is a problem however, that I think needs to be addressed and that is the ACHP, when you’re talking about the criterion, you’re talking about buildings, the archaeology came in late – it came in under these subsets which have not been fully put into place and their advancement towards and any regulation towards aircraft is problematic. The large quantity of aircraft that was produced during this time and at other times rather precludes the issue of national significance. There are other issues involved such as the battlefield or specific use, or personality like Amelia Earhart. And the normal thing that has been going on within the States is that since the submerged ‘acts’ the materials were actually gifted to us and we’ve been dealing with them separately and as usual the status of our Preservation Office which came in late in Federal Law seems to be taking precedence over those of us who were put in 20 years earlier at the State level. So when the Federal talked to the States, it would be nice if the Federal actually did talk to the States at an earlier point rather than at a later point. That’s not your problem, just putting it out there so you can take it back to Washington.

Paul Mardikian: Jonathan, I think that we could really raise that point and discuss it during the panel discussion. Let’s talk about the technical problems right now and we’ll bring up this important issue during the panel discussion if you don’t mind.

Jonathan Leader: Sure

Paul Mardikian: I want to see if there is anyone here who wants to discuss some technical issues here about the stabilization of aluminum or any other issue?

Peter Northover: In wet environments – the examples you have shown us seem to have been mainly marine – how important with aluminium corrosion is chlorine or is it things like the amount of oxygen that would be more important? So if something is in an anoxic environment in a freshwater lake, is it in reasonably good order?

George Schwarz: I think it is a case-by-case basis really depending on the amount of oxygen, what the burial sediments are like, the site formation process. I think doing archaeological studies on individual cases will help answer that question. Obviously aircraft in saltwater is definitely more pressing often times – it is the chlorides that are generally going to break down materials but in the freshwater you have sulphate reducing bacteria and other organisms and there are other things that are going to attack the aircraft as well. So I think it is a case-by-case basis.

Peter Northover: A separate thought on the question of restoration and replication: different areas of particularly military archaeology or industrial archaeology have particular requirements and we are part of a consortium that is developing procedures for the school of conservation for historic military vehicles and at the moment the conservation of tanks. The centenary of the First World War is approaching and we have the only working First World War tank in the world. But because of the nature of its structure and it is about 90 years past its design life it really should not be used again. There are some very serious cracks developing in it, as these things basically didn’t have any suspension. But it has been very useful in demonstrating to the public exactly what the experience was. They are fairly simple beasts and the same thing has happened with First World War aircraft and more recently in Britain with steam locomotives, the way to convey the experience is to just build another one. Is this approach being thought about in the States?

George Schwarz: I imagine it is different everywhere you go. I think that is one of the discussions people should get together and talk about. I have a tendency to think that if you have all the information there why not build a replica and operate it vs. trying to fix one that could be considered an artifact – it is definitely an original and will be considered an artifact at one point. And using it continually is going to cause irreparable damage.

Peter Northover: Another case is, the Tank Museum has the only working King Tiger in the world. To get it working, 3 main back engines were cannibalized but regimes changed at the museum – that would not happen now, but they do want to keep the one they got working, going. And of course WWI tanks are a lot simpler than WWII, same with aircraft.

David Hallam: Most of these issues were covered last week in '*Big Stuff*' so if you have a look at the proceedings from that you'll see some interesting comments. Particularly on that Tiger.

Paul Mardikian: I think that the issue of marine aluminum has nothing to do with freshwater and it is always the case for every material. I remember the case of the Focke Wulf 190 that was conserved with electrolysis in France and I remember Christian [Degrigny] was heading that project. I don't want to minimize that work but when you don't have chlorine it is much easier. So we have to be aware that there is no real technique right now to stabilize these big marine composite objects made of aluminum. And when it gets to an entire artifact, an entire airplane, this is just hell on earth. I think we are all aware of that and your paper was very interesting because you are putting together those nuts and bolts that we needed to have somewhere written down, showing that there is a lot of work to do and we have to be careful with what we raise.

David Hallam: I should point out that the Australian War Memorial treated a complete aircraft that was in the marine environment and it was treated successfully using electrolytic techniques in a citrate solution in a swimming pool.

Paul Mardikian: And it has been stable over the years?

David Hallam: Yes, it's been stable – it was treated over 10 years ago.

DISASSEMBLY OF USS *MONITOR'S* COMPLEX MECHANICAL COMPONENTS

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Abstract

National Oceanic and Atmospheric Administration (NOAA) archaeologists have recovered numerous complex mechanical components from the wreck of the USS Monitor*, including the ship's vibrating side-lever steam engine, condenser, and auxiliary machinery. These mechanical items are being conserved at The Mariners' Museum (TMM) in Newport News, Va. After thorough consideration, TMM conservators have opted to disassemble complex mechanical components from the* Monitor *to allow for more thorough cleaning and effective removal of chloride salts. Disassembly also allows for separation of iron, copper alloys and organic materials for material-specific treatment. Experience working with* Monitor *artifacts has shown that disassembly requires careful planning and is made more difficult by the corrosion processes that have occurred during 140 years in seawater. The challenges and limits of disassembling complex artifacts made of deteriorated metals and organic materials will be discussed with examples.*

Keywords: USS *Monitor*, ironclad, marine archaeological metal, composite artifact, disassembly, stabilization, steam engine, industrial artifacts.

Introduction

The Mariners' Museum (TMM) and the National Oceanic and Atmospheric Administration (NOAA) have partnered to conserve over 200 tons of artifacts recovered from the ironclad USS *Monitor* (1862). The artifacts, which range from small buttons and fragments of glass to large, complex mechanical assemblies, such as the ship's steam condenser and vibrating side-lever steam engine, require differing treatment strategies and practices.

Conservators at TMM face many challenges when treating large complex mechanical artifacts. Chief among these are the logistics and difficulties of disassembling large components composed of different material types to facilitate more effective mechanical cleaning, desalination, and treatment. Whenever possible, conservators attempt disassembly of *Monitor*'s artifacts in support of conservation. Successful disassembly allows each object to be treated by material type. For example, copper alloys are treated separately from wrought and cast iron. Surviving rubber gaskets and the remains of wood components are also treated individually for optimum results.

Disassembly of highly corroded artifacts that may also have sustained damage during a shipwreck is a very serious undertaking. Conservators discuss and plan each step of the process prior to beginning any invasive activity. Disassembly should only be attempted if conservators determine the artifacts and components are structurally sound and capable of sustaining various forces during disassembly. Conservators must weigh the benefits of disassembly and separate treatment of components with the possible negative consequences of incurring damage. If damaging a small rubber gasket or seal allows conservators access to the interior components of a significant structural iron piece, like an engine cylinder, TMM conservators deem this is a necessary sacrifice.

In contrast, attempting disassembly of a structurally weak assembly may prove more harmful than not gaining access to every surface of every component. In this scenario, TMM conservators might opt to treat the complete artifact as thoroughly as possible and provide added protection through specialized display environments after treatment, rather than doing unnecessary harm.

Why Disassemble Artifacts?

Disassembly of complex mechanical artifacts excavated from marine archaeological sites during conservation treatment has a number of advantages over treatment of intact assemblies. Chief among these is the ability to remove calcareous concretion and marine sediments from all surfaces and allow the treatment of internal and external surfaces. This is particularly important for the successful removal of chlorides, which, if left in the artifact in sufficient concentration, can cause destructive corrosion when the artifact is dried (Memet 2007). Iron artifacts, and cast iron in particular, are particularly vulnerable to destructive chloride corrosion, and as iron makes up the majority of recovered metals from the *Monitor*, effective desalination is a primary consideration.

Disassembly also reveals details about an artifact's construction, tool marks, maker's marks, and other technical details not initially apparent when examining an intact artifact. There is specific evidence that interior spaces of similar historic machinery from marine sites may remain tightly sealed, and thus impervious to immersion in treatment solutions even after long periods (MacLeod 1999). The experience of conservators working on the steam engine from the *SS Xantho* is an important parallel for conservators working on the *Monitor*'s engine and complex auxiliary machinery (McCarthy 2000).

Treatment incompatibility is a common issue with composite artifacts. *Monitor*'s composite gun carriages are difficult to treat because they consist of iron, copper alloy, and wood components that require different treatment methods. Pursuing a strategy of disassembly is important in order to isolate each material for more effective and thorough treatment. Desalination treatment of iron and copper alloy components with high pH alkaline solutions is detrimental to the overall integrity of the wood carriage components, which are best treated with other methods.

Decision Making

Conservators on the *Monitor* do not assume that disassembly of mechanical components is the best and only treatment option in every case. Rather, each complex artifact is considered on a case-by-case basis and a treatment plan is developed after information from original plans, historical engineering studies, and non-destructive testing, such as computed radiography (see Figure 1), have been reviewed (Peterkin 1985, Hanley 2009).

TMM conservators collaborate with marine archaeological conservators, structural engineers, non-destructive testers, and corrosion scientists, and with NOAA archaeologists and historians responsible for the management of the *Monitor* National Marine Sanctuary. This collaborative framework provides the maximum amount of information for inclusion in every disassembly decision. A disassembly plan is then produced, taking into account the condition, morphology, material composition, and practical challenges in handling, conserving, and disassembling the object. This process guarantees that human and artifact safety and stability are the highest priorities when considering invasive activities like disassembly.

Figure 1. Port Worthington pump photograph and x-radiograph taken before treatment.

TMM conservators and NOAA personnel ultimately determine which path to pursue for each complex artifact. For example, *Monitor* conservators developed a rotation and disassembly plan for both Dahlgren gun carriages excavated from the revolving gun turret (see Figure 2). The plan was reviewed and approved by NOAA staff. The rotation plan called for the fabrication of a steel framework and pivot rig designed to safely 'grasp' each carriage while they were pivoted to their original upright position. This major logistical step allowed conservators to remove additional concreted sediment and copper alloy roller wheel assemblies from their iron frames, as well as examine the other wrought iron and copper alloy structural components to plan additional disassembly.

Other practical factors to include in decision-making are material fragility, size, weight, composite nature, bi-metallic corrosion, and need for specialized tools or techniques. These factors alone may not determine whether an artifact will be disassembled, but together they often determine the amount of time and effort required. This is useful in conservation planning, especially when specialized equipment may be needed.

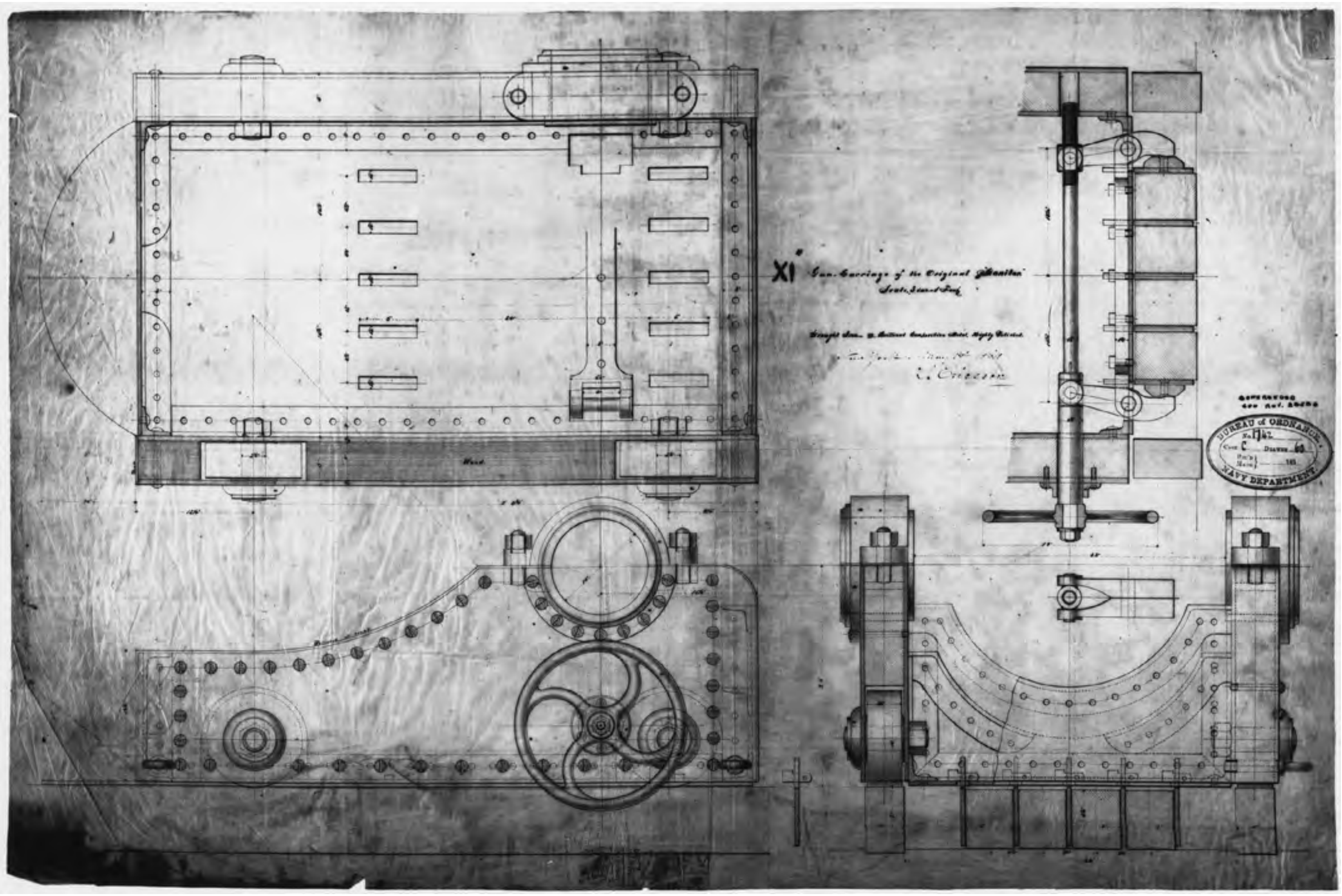

Figure 2. USS *Monitor*'s gun carriage engineering drawing.

Disassembly Tools

Conservators at The Mariners' Museum utilize a variety of tools and equipment to disassemble complex, composite artifacts after performing initial deconcretion and developing a disassembly plan. When possible disassembly preparations include physical molding of fasteners, conservators use an alginate molding material and Forton casting compound. This preserves a physical record of the fastener should any damage occur and aids in the production of replica fasteners.

The most commonly used tools are modern pipe wrenches and chain wrenches. Conservators typically apply a protective material, such as thin rubber padding or canvas, over the surfaces of a mechanical artifact's nuts and bolts. This protects the original surfaces from the potential damage caused by steel wrenches. Force is then applied until the fasteners turn. If a nut does not move under force, conservators will apply a 'cheater' or pipe on the end of the wrench to increase leverage and power. Conservators closely watch the nut or bolt for twisting or distortion rather than loosening. Upon initial loosening, conservators use their hands to remove the fasteners.

Modern screwdrivers are also adapted to fit artifact screws. Recently, *Monitor* staff used standard size flat-head screwdrivers to loosen copper alloy screws on the side cheeks of a gun carriage. The most important concern was maintaining a tight fit to reduce the possibility of the screwdriver slipping from the slot and scraping the artifact's surface. Conservators also constructed a wide screwdriver from modern hardened steel stock and welded it to a specially designed handle. This custom tool facilitated fastener removal from a braking wheel assembly.

If deconcretion and initial disassembly of complex mechanical artifacts fails, *Monitor* staff utilizes electrolysis to help reduce corrosion products and 'loosen' assemblies. This has been quite effective, and with one exception, has not resulted in any damage or separation of the graphitized layer on cast iron. Following periods of electrolysis, artifacts and assemblies are sometimes subjected to flame deconcretion and heating (Carpenter 1990). An oxy-acetylene torch is used to heat the surface of the concretion on certain copper alloys. Heating causes minimal expansion of the material, but with enough effect to loosen components for removal with methods described above. Small wooden wedges are used to carefully apply controlled pressure to aid in deconcretion and disassembly. Various blades, scalpels and other devices are used to help loosen corrosion products and remove gaskets. Artifacts are sometimes subjected to ultrasonic immersion to help facilitate disassembly.

More forceful methods are sometimes required to disassemble large industrial artifacts. *Monitor* project staff have utilized hydraulic pressure to push bolts from bolt holes where tight construction tolerances were required. A Torin hydraulic ram, typically used for auto repairs and restorations, was used to push copper alloy axles from gun carriage wheel assemblies with no damage to the artifact. Other hydraulic devices were successfully used in conjunction with custom-fabricated steel frames to evenly apply large forces over larger surface areas.

Cranes and other industrial equipment support disassembly activities. For example, the proposed disassembly of the reversing gear assembly of *Monitor*'s steam engine is very simple and straightforward on paper, however, the reality is quite different. Heavy wrought iron valve arms and shafting must be disconnected from adjacent components. The wrought iron reversing assembly shaft must be supported overhead by a chain hoist attached to a steel I-beam by a rolling sled. The sled will guide the heavy shaft as it is pushed forward by a hydraulic press. The chain hoist will allow conservators to incrementally raise or lower the shaft as it is pushed through the engine bed. Each step must be planned and rehearsed when dealing with multi-ton composite assemblies.

The port and starboard Worthington steam-powered bilge pumps have been successfully disassembled using the methods above, with the exception of the water plungers, which proved difficult. Alternative methods utilizing penetrating lubricants are now being explored.

It is important to note that no single, modern tool can accomplish every disassembly objective related to complex historic artifacts. Conservators must adapt existing tools, create and develop new methods, and consider all options when discussing disassembly. Additionally, working on such projects is sometimes dangerous. The first priority is personnel safety. The second priority is the safety and condition of the artifacts.

Disassembly Process

Once the attempt to disassemble the artifact has begun, there are a number of possible outcomes:

1. Complete disassembly of all fasteners, components, and gaskets is achieved with little or no difficulty.

2. Complete disassembly is achieved with some difficulty, and some minor damage occurs to elements, primarily gasket material.

3. Complete disassembly is achieved and some damage occurs to elements, including gasket material and metal components. This is not necessarily a desirable outcome.

4. Partial disassembly is achieved, but some elements present problems and minor damage occurs during attempts to complete the disassembly process. After available solutions are tried, a decision is made that disassembly should not proceed because more damage will likely occur.

5. No disassembly is possible. Attempts to begin disassembly encounter difficulties and it is determined that disassembly should not proceed as damage to the artifact will occur.

How do conservators effectively determine the likelihood of damage occurring? This difficult question has no single answer. *Monitor* conservators consider many factors and utilize various methods to evaluate the likelihood and degree of damage. Conservators are developing plans to measure stresses placed on artifacts during disassembly via stress and strain instrumentation, and stress imaging technology used in modern industry.

Monitor conservators also are adapting three-dimensional scanning techniques to evaluate artifacts and components before and after disassembly, and after reassembly to evaluate dimensional change and document the entire process at various intervals. This is a costly and time-consuming technique, but it thoroughly documents the entire process. Accumulated experience is perhaps the most important factor when determining the likelihood of damage. Conservators who work with the same artifacts and materials year-after-year develop great understanding and a 'feel' for the materials and methods used during disassembly.

Limits of Disassembly

An important ethical consideration in conserving marine-recovered metallic mechanical components is whether or not it is justified to risk damage to the artifact during disassembly in order to more thoroughly stabilize the artifact through effective chloride removal. *Monitor* conservation personnel seek a middle ground by adopting a philosophy of causing 'no undue harm'. The conservation team utilizes all methods available to disassemble components and is willing to accept there is some risk to the integrity of the material in the process. However, disassembly may be halted due to tangible visual, tactile and audible cues, as well as cumulative experience and judgment indicating that damage may be imminent if disassembly efforts continue.

There have been a number of instances when conservators stopped disassembly when it became clear they were not achieving the desired results and that damage was likely to take place. The effort to disassemble *Monitor*'s packing seal assembly is a perfect example of modifying or halting disassembly (Nordgren et al. 2009).

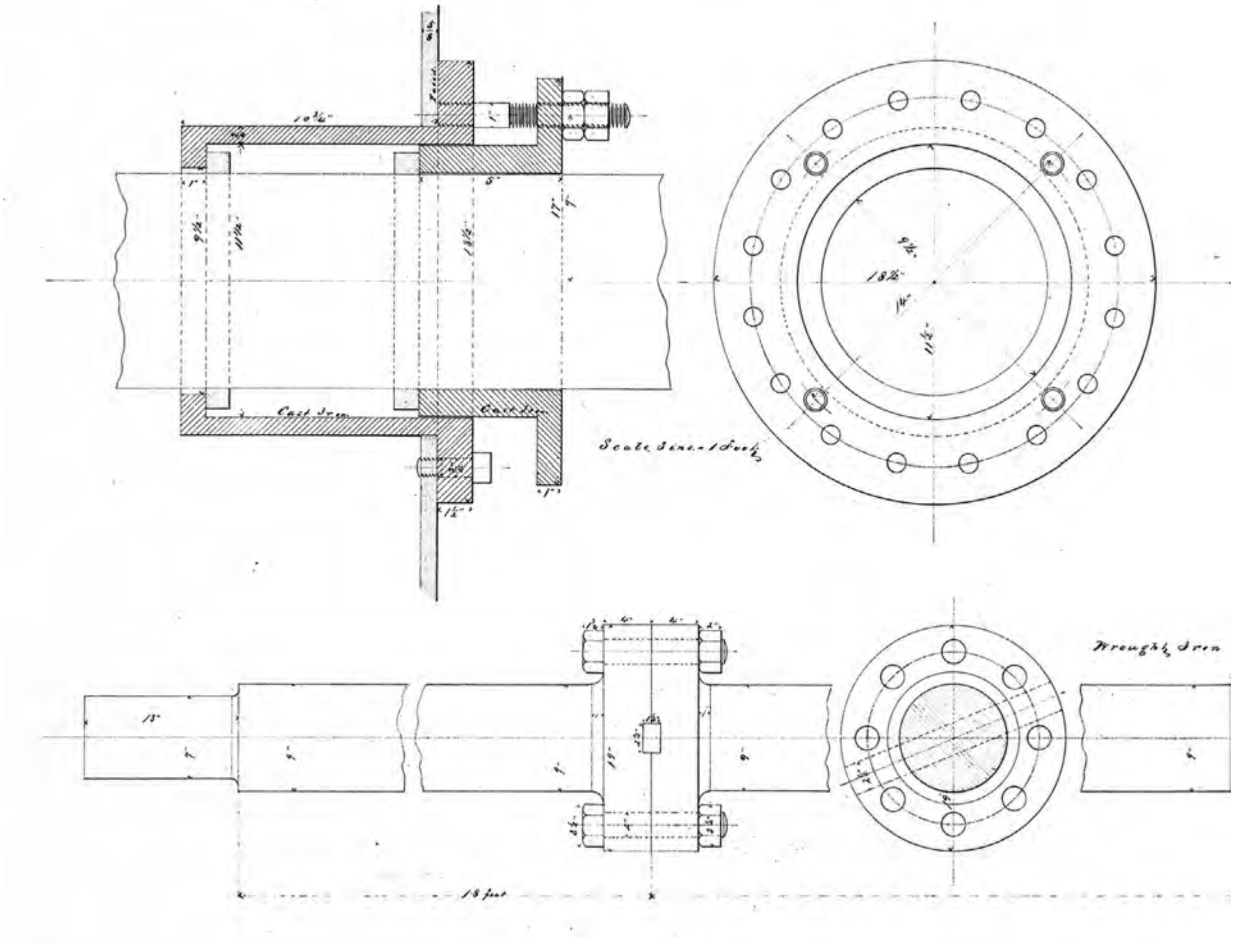

Figure 3. USS *Monitor*'s packing seal assembly.

The packing seal was an important watertight component of the ship's propulsion assembly. It was designed to allow the propeller shaft to rotate freely but prevent excess water from entering the hull (see Figure 3). The cast iron packing seal surrounds the 9-inch diameter propeller shaft, which is flanged and fastened with eight 2-inch bolts to an additional section of shaft that connects directly to the engine.

During deconcretion, conservators revealed an important detail. The 9-inch diameter wrought iron shaft was bent a few degrees off centerline. This likely occurred when the *Monitor* slammed stern-first into the seafloor. The force of this impact fractured a 6-inch by 8-inch section of the aft cast iron packing sleeve and revealed the aft packing ring and packing material. After thorough examination of the cracked packing gland, conservators opted to halt full disassembly. The fragile condition of the damaged cast iron packing gland indicated the artifact would be unable to undergo complete disassembly without suffering additional damage.

Conservators initially planned to remove the entire cast iron sleeve assembly to promote more thorough desalination, but opted for partial disassembly for fear of causing greater damage to the graphitized, cracked casting. The conservation team focused on removing eight wrought iron nuts that secured the bolts to the flanged assembly. After reviewing original packing seal engineering drawings, they used modern pipe wrenches and a chain wrench to successfully remove the nuts. The bolt threads were so well preserved that after loosening the corrosion seal with a wrench, conservators removed the nuts by hand. Removal of a single bolt revealed shiny metal surfaces that appeared unaffected by over a century of immersion in the ocean. But several factors, including minor twisting of the bolt head and the extreme amount of force used to remove the bolt, led conservators to cease further disassembly of the fasteners.

Partial disassembly was considered an acceptable alternative to risking excessive damage during complete disassembly. The artifact is composed of a single material type (iron) that can be treated in the same solution, as opposed to a composite assembly (iron, copper alloy, organic) that requires disassembly for thorough treatment. This situation is a good example of using visual clues and accrued experience to cause no undue harm. Conservators successfully removed artifact components, but halted activities when it became apparent that additional disassembly posed risk of irreversible damage to the fragile cast iron packing sleeves and badly corroded bolt heads.

In such cases, when conservators decide to stop disassembly efforts to prevent damage to the artifact, treatment of all accessible areas is completed. The object is then monitored closely in storage or on display, with particular attention paid to any outbreaks of chloride related corrosion or dimensional change.

While all *Monitor* metal artifacts are stored in stable environmental conditions of 20 degrees Celsius and ≤ 50% Relative Humidity (RH), objects that could not be disassembled and thoroughly treated may require additional measures, such as modified atmosphere (argon or nitrogen) or very-low RH display environments (≤ 20%RH) (Watkinson and Lewis 2004).

As indicated above, it may not always be possible to separate all components or all materials. In such cases, the artifact is treated with a compromise procedure that is safe for all the elements. It is possible to treat wrought and cast iron composites together as in the case of the packing seal, and several inseparable brass and cast iron components of the Worthington pumps are currently undergoing desalination.

In the case of metal-organic composites, small caliber lead ammunition rounds with copper casings and textile wadding were successfully treated with electrolytic reduction in pH-buffered potassium nitrite (MacLeod et al.1993).

Artifact Reassembly

Artifact reassembly must also be carefully considered while disassembling and treating component pieces. In some cases, such as that of a small copper alloy valve from the port Worthington pump in an excellent state of preservation, re-assembly is as simple as fastening the original parts together (see Figure 4). In others, such as large portions of the *Monitor*'s engine or Worthington pumps, the original iron fasteners may not have survived the archaeological environment and the cast iron components are fragile, but still retain substantial weight. Such artifacts must be given adequate physical support, which may involve the fabrication of special mounts or supporting frames. Replica fasteners may have to be fabricated out of metal or a synthetic material and fastened just to the point of safely holding the part, but not so much that excess pressure is applied that could cause damage.

Many of these issues are illustrated on a small scale by the conservation and re-assembly of the mechanical movement from *Monitor*'s engine room clock (see Figure 5). The movement was crafted of high quality brass, steel, and copper-nickel alloys. Following archaeological recovery, X-radiography and investigative cleaning revealed that while the brass and copper-nickel parts were in excellent condition, the steel springs, screws, and shafts (arbors) were completely lost due to galvanic

Figure 4. Worthington pump steam cylinder drain valve, exploded view.

Figure 5. Reassembled engine room clock movement.

corrosion. In order to properly re-assemble extant parts of the movement after stabilization, conservators worked with horologist Roger Conner to re-create the missing parts in modern steel and reversibly integrate them into the clock. This course allowed re-assembly of the object and rendered it considerably more readable for museum display.

Conclusion

The Mariners' Museum conservation department continues to pursue a strategy of disassembly in support of artifact treatment when working on the USS *Monitor*'s complex mechanical components. Each artifact is considered on a case-by-case basis, and the primary tenets are to maintain human safety and cause 'no undue harm' to the artifacts. TMM conservators gained invaluable knowledge and experience by initially focusing disassembly efforts on smaller components, like Worthington pumps (400 pounds) and other auxiliary steam engines. The tools and methods developed during this early phase of the project are currently being scaled-up and applied to the ship's condenser (8,000 pounds) and vibrating side-lever steam engine (60,000 pounds) in support of overall conservation treatment.

Materials

Forton MG
The Compleat Sculptor, Inc.
Vandam Street
New York, NY 10013

Alginate
Darby Dental
NE Industrial Park Van Buren Building, Bldg. 27
Guilderland Center, NY 12085

Torin hydraulic ram
Northern Tool and Equipment
2800 Southcross Drive West
Burnsville, Minnesota 55306
http://www.northerntool.com/

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Authors

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Eric Nordgren is Senior Conservator with the USS *Monitor* project at The Mariners' Museum, Newport News, Virginia, USA. In his current position he focuses on the conservation of metal artifacts from marine archaeological sites. Eric studied Archaeological Conservation at the Institute of Archaeology, University College London, UK, and has worked as a conservator for a wide variety of museums and archaeological projects in the US and overseas including the National Museum of Beirut, Lebanon, the Institute of Nautical Archaeology, Egypt, and the *Queen Anne's Revenge* project in the USA.
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Q & A SESSION

Tim Foecke: How are you going to work with NASA and NTSA on imaging stresses?

David Krop: Eric [Nordgren] is actually the one that's familiar with that equipment but what we've done is talked about using cameras that will essentially be able to measure stress or strain as activities are being pulled and placed. We tried to get this project up and running about a year ago. As some of you are sure, NASA's had some differences in long-term planning but again it is one of those things we've discussed with them briefly. We're going to bring them to the lab, review their equipment and see if it fits some of the activities that we are actually doing.

Tim Foecke: Our lab actually has that exact same equipment and also if you have a smaller piece that you need to measure stresses in and you want to bring it to Gaithersburg, MD, we could use neutron diffraction. We have measured stresses inside railroad rails for example with 1mm resolution through the thickness and if you have a piece and you want to bring it up we'll be glad to help you.

David Krop: I'll be talking to you right after this, thank you Tim.

Paul Mardikian: I think it's a wonderful paper because it outlines the decision tree. And when we are confronted with those big artifacts, it is extremely difficult to make decisions. What you've shown is how you gradually understand gaining knowledge of your artifact and try to make those decisions and whether or not to disassemble, and take the risk assessment. So I think it is a wonderful paper.

David Krop: Thank you. We've had a lot of pressures, both internal and external about 'what are you going to do with the engine – it came up in 2001' or so on. What we've tried to do over the past few years is to start this process on a smaller scale, consulting with Dr. MacLeod, refining our techniques, methods, equipment and tools and then starting to scale that up, and I think that's been really beneficial. One of the other things is, when you're facing 200 tons of artifacts, it's easy to be paralyzed and to just think: 'there is so much here, where do I start?' Well, you just have to start and we grabbed the lowest hanging fruit from the tree and gathered our early successes and learned from that, continued to scale things up and there is no guarantee that we will be able to completely disassemble the engine. Thank goodness we had a guy like Ian who had already been through a lot of this. His engine is 1872 so it's pretty close to 1862 and he's been forthcoming with information. Again, we don't know everything, but we want to be able to share this – what worked, what hasn't …

Paul Mardikian: And Ian's engine is 10 times smaller…so you are really dealing with a monster artifact here. Tell me, how did the blue prints help you with the disassembly?

David Krop: For the Worthington (pumps) we weren't as fortunate. We have later patent models and plans from the Worthington Company – the Worthington Company I think still exists but under a different name now. We have not found the exact patent for the original pump. An 1848 patent date in the cast iron is beautifully preserved. We did take later drawings for that artifact and learned more about it and matched that up with the x-rays to see what was similar and what was different. For something like the packing seal or the gun carriage – outstanding! Granted these are documents that are created, and potentially could be modified as the builders put these things together, but we know a lot more going into it, we're not working blind and they have been an outstanding help – very high resolution, we can blow them up, laminate them, take them into the lab, write on them – it makes a big difference.

A CASE STUDY OF IN SITU MONITORING ON AN ANCHOR FROM THE *QUEEN ANNE'S REVENGE* (1718)

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Abstract

North Carolina shipwreck 31CR314 is believed to be Queen Anne's Revenge, *the pirate Blackbeard's flagship that ran aground in Beaufort Inlet in 1718. Large iron artifacts, such as anchors and cannon, provide an excellent opportunity for corrosion potential studies. A preliminary in situ study began on Anchor 3 in the fall of 2008 to obtain an indication of the inherent stability. Research has suggested that attaching a sacrificial anode to improve the corrosion potential and begin conservation treatment by removing chloride ions can protect artifacts in situ. This study aims to provide an indication of how a changing environment may further affect preservation of artifacts in situ and provide the basis for continuing conservation in subsequent years. This paper will outline the processes, data obtained and conclusions drawn from this project.*

Keywords: *Queen Anne's Revenge*, in situ monitoring, corrosion potential, cathodic protection

Introduction

North Carolina's submerged archaeological site 31CR314 is believed to be the pirate Blackbeard's flagship, *Queen Anne's Revenge (QAR)* that ran aground near Beaufort Inlet in 1718. This shipwreck was discovered in 1996 by Intersal Inc. and has since been managed by North Carolina's Underwater Archaeology Branch (UAB). In 2003, the North Carolina *Queen Anne's Revenge* Archaeological Conservation Laboratory was established to conserve the artifacts recovered from the *QAR* site. In 2006, the UAB started full recovery excavations beginning at the stern portion of the wreck. To date, approximately 50% of the site has been recovered, with the majority of this work completed in the 2006-2008 field seasons. In October 2008, an in situ monitoring study of Anchor 3 (A3) began; this paper outlines procedures, data obtained, conclusions and recommendations for future studies drawn from monitoring the A3.

Site Description

Beaufort Inlet is a barrier island tidal inlet and the *QAR* shipwreck site presently rests in 7 meters of water on the shoals of the ebb-tidal delta, 1.9 kilometers from Fort Macon State Park (see Figure 1). The Beaufort Inlet shipping channel to Morehead City is currently maintained at a controlling depth of 14.3 meters and located less than 1.2 kilometers to the east of the *QAR* site. Geologists have estimated that sea level has risen about 0.5 meters since QAR ran aground (Wells 2001), and the total volume of sand making up the ebb-tidal delta has decreased 34% since extensive dredging began in the 1930's (Henry 2003).

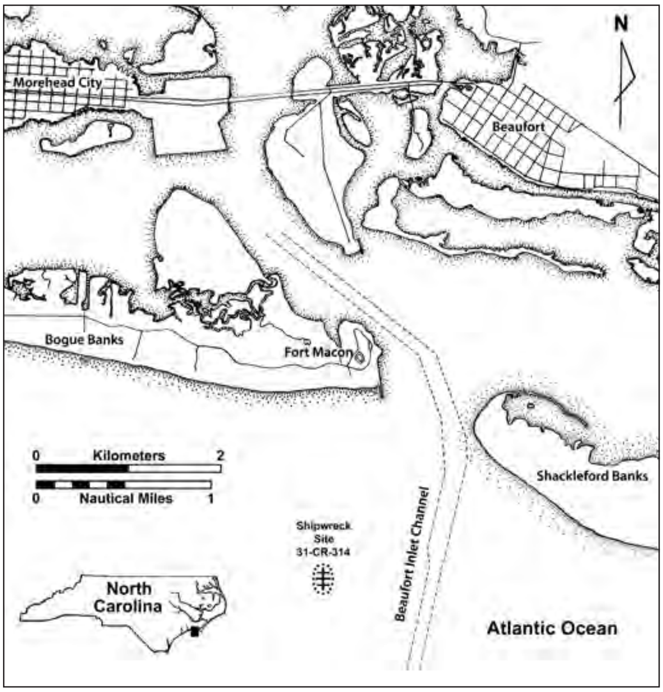


Figure 1. Location chart of the *QAR* site in relation to the North Carolina coast.

The hull structure dimensions and anchor sizes that represent a 250-300-ton ship coincide with the historical evidence reported about the nature and loss of the *QAR*

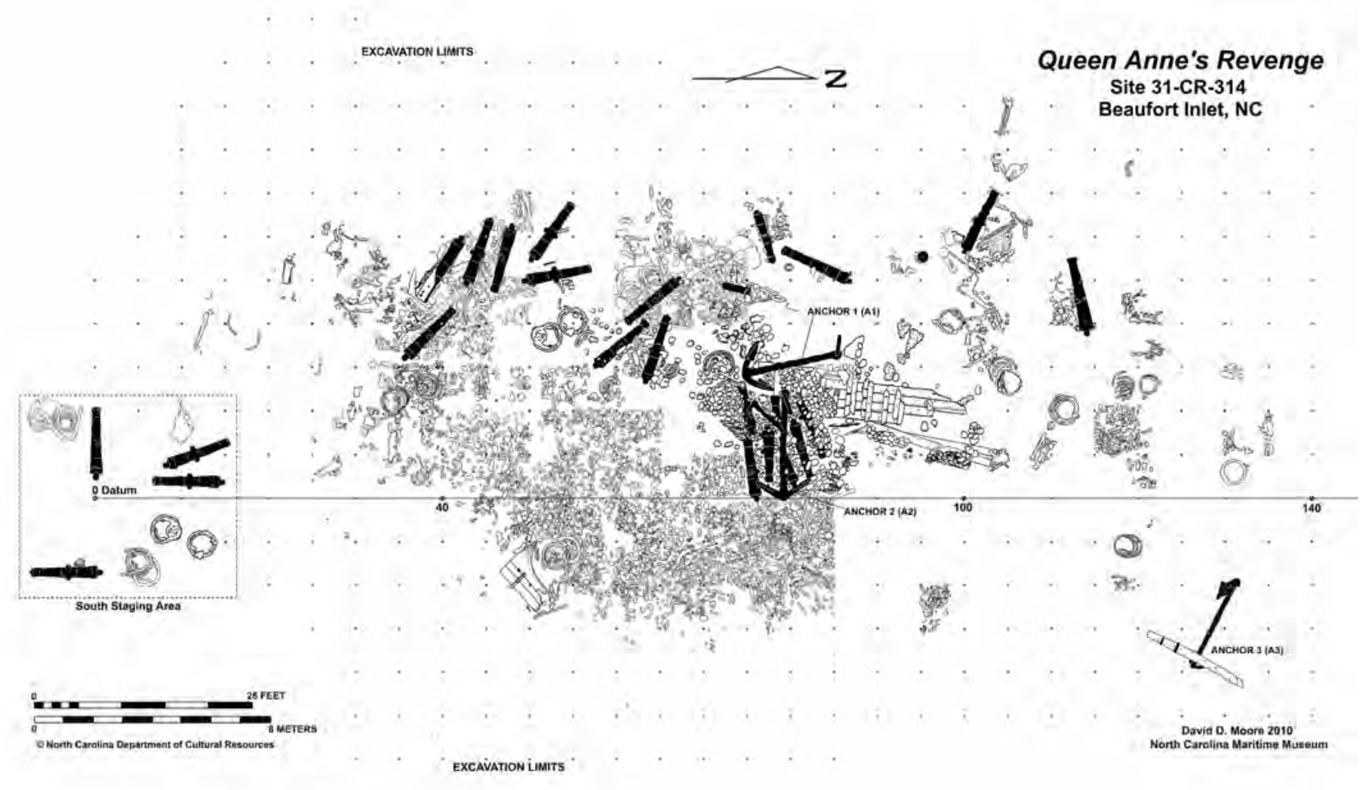


Figure 2. *QAR* site map.

(Moore 2001). Thousands of artifacts, including 24 cast iron cannon and four anchors, have been recorded within an area approximately 30 x 50 meters and most rest at the same depth (see Figure 2). The main feature of the *QAR* site is the 'ballast pile' that measures 7.6 meters by 4.6 meters and rises an average 0.6 meters above the seafloor. At present, it consists of two wrought iron anchors (A1 and A2), seven cast iron cannon, thousands of ballast stones, cannon shot, rigging assemblies and cask hoop concretions. A3 with wooden stock is located 15 meters north of the ballast pile with one arm buried in the sand and the other arm extending 1.5 meters above the sea floor. A fourth anchor possessing a wooden stock is buried beneath sediment approximately 125 meters offshore of the main site. Eleven cannon have been recovered and 13 remain on site, four of which have been moved from their original position to a staging area for later recovery. All anchors from the *QAR* remain in situ.

Site Environment

Core samples of sediment from the *QAR* site indicate the upper meter is composed of easily erodible fine to medium grain sand overlaying a layer of shell hash and debris (Gibson 2004). Geophysical studies indicate the site has historically been exposed to episodes of rapid scour and burial. The primary reason for exposure is a scour resistant sand layer that lies beneath the wreck site and restricts the burial process. This aerobic environment leaves artifacts that are perched upon the seafloor exposed to wave and tidal currents that threaten long-term site preservation especially during strong storms and hurricanes (McNinch 2006).

In 1999, biologists noted various forms of sea life, including encrusting bryozoans, corals, barnacles, and purple urchins on the exposed portions of the wreck (Wilde-Ramsing and Lusardi 1999). Coral growth studies indicated the wreck had been exposed for at least 16 years (Lindquist 1999). Since discovery, neither the ballast pile nor A3 have been fully covered with sand, resulting in nearly 30 years of exposure. In situ corrosion studies will be an effective management tool in determining artifacts most at risk, since many of the larger artifacts are likely to remain exposed.

The only water quality studies of dissolved oxygen and salinity at the *QAR* site were performed in October 1997 and 1998 (Gillman-Bryan 1998 and Monahan 1998). The Shackleford Banks' testing site is located 3.4 kilometers from the *QAR* site where water quality data has been collected since March 2008. Data utilized are averages collected below 6 meters (Dingle 2009). Dissolved oxygen, pH and salinity values used for this study are an average of measurements taken on site and from Shackleford Banks, (see Table 1).

Beaufort Inlet Water Temperature	5.6°- 28.7°C (Avg. 20.42°C)
pH of Sea Water	7.8
Dissolved Oxygen	6.8mg/L
Salinity	34 ppt

Table 1. Seawater parameters around the *QAR* site.

In Situ Corrosion Studies

The corrosion mechanisms of iron submerged in seawater are described in detail by North (1982). The iron surface comprises anodic and cathodic areas that react with oxygen, hydrogen, and chloride ions in seawater. The corrosion reaction occurs when positively charged ferrous ions (Fe^{2+}) are rapidly oxidized to ferric ions (Fe^{3+}) as they move away from the solid metal resulting in Fe (III) oxide and hydroxide formation. A calcium carbonate layer begins to form on the surface with corrosion products that incorporate the surrounding sand, shell and sea life, eventually covering the entire surface separating the anodic and cathodic reactions. The encrustation or concretion grows over time and becomes very solid. This semi-permeable membrane is where an exchange of ions continues between the metal and the seawater and is also where the cathodic reaction occurs, which produces hydroxide ions (North 1982). A concretion can actually preserve iron artifacts, however, it also increases the concentration of chloride and hydrogen ions at the iron surface. Under the concretion, the pH at the surface of the metal is acidic (4-5) while the pH of seawater is 7-8 (MacLeod 1996b).

In situ corrosion studies on shipwrecks have become common practice in Europe and the U.S., in large part due to the research of Dr. Ian MacLeod and colleagues in Australia over the last 30 years (Weldon 1991, MacLeod 1995, Soerensen 1998, Gregory 2000, Matkinson 2002, Smith 2009,). Corrosion of metal in seawater is an electrochemical process and its rate is dependant on temperature, salinity, dissolved oxygen and water movement. To determine the corrosion potential (E_{corr}), of the object, an inert platinum electrode is placed directly in contact with solid iron and the potential is measured in relation to a silver-silver chloride (Ag/AgCl) reference electrode that indicates the difference in potential between the reference electrode and the object. Researchers have demonstrated that measuring electrochemical parameters, such as the corrosion potential and the surface pH of a corroding iron artifact, can give an indication of the inherent stability when referenced in a Pourbaix diagram. An artifact that stands proud on the ocean floor is exposed to dissolved oxygen in seawater and will have a higher corrosion potential (anodic) than an artifact that is buried in anaerobic sediment. The lower the corrosion potential (cathodic) the less the artifact will corrode due to a more stable form of iron. These studies have also shown that by attaching a sacrificial anode to iron artifacts in situ, the E_{corr} can decrease and chloride ions (salts) can be removed by changing the polarity of the iron (MacLeod 1987).

Cathodic Protection

> Sacrificial anodes for iron objects contain metals, such as zinc, magnesium or aluminium. Aluminum anodes contain about 5% zinc and a small amount of indium, and are recommended for use in seawater as the oxide film formed is non-passive. Wrought aluminum alloys used to fabricate items such as SCUBA tanks contain iron and copper that passivate the anode. Therefore, they do not work well as galvanic anodes (Johnson 2009).

Attached to a sacrificial anode, iron gains protection as the electrons released from the corroding anode flow to the artifact, effectively lowering the corrosion rate (Gregory 2000). As electrons flow into the concreted iron, hydrogen ions are reduced to hydrogen gas and the chloride ions begin to diffuse away from the degraded surface increasing the pH at the metal surface. This reduction in acidity promotes a redeposition of magnesium calcites and a deposition of the iron carbonate mineral siderite, which enhances the mechanical strength of the concretion (MacLeod 1996a). It has been reported that the corrosion rate and the time required for conservation of objects that undergo this type of treatment are reduced. These objects also appear to retain more of their original surface compared to similar objects that have not undergone the treatment (MacLeod 1987).

Limited funding and space in the lab has contributed to postponement of large artifact recovery, like the cannon and anchors. Conditions around these large iron artifacts vary providing an opportunity to study corrosion potential monitoring in a variety of environments. One objective of this preliminary in situ corrosion study on A3 was to establish a baseline for understanding corrosion parameters on the *QAR* site and the potential for future research. A second goal was to attach a sacrificial anode to improve the stability of A3, which in theory should initiate the conservation process while the anchor is still on the seafloor.

Methodology

Equipment Preparation

The flat surface pH electrode used in this project was extended with 15 meters of RG58 cable, joined with waterproofed BNC connectors. When calibrated, the meter read comparable to other pH electrodes in the lab. The pH meter was calibrated according to the manual with aqueous buffers 4 and 7 but was not adjusted for salinity. The platinum electrode was fabricated by soldering a small piece of platinum to 14 gauge wire (AWG). The connection was placed inside an empty pen casing and secured with epoxy; there was no resistance measured in the 18 meter electrode. The Staperm Ag/AgCl reference electrode was tested against a new Metrohm Ag/AgCl electrode to determine its relation to the standard hydrogen electrode (+249mV vs. SHE).

On Site Operations

Six site visits were made from October 2008 to December 2009 to monitor A3. During the procedure, the boat was positioned over the anchor, while both the pH and voltage meters were operated topside by a team of two who were in constant contact with the divers obtaining readings. The voltage meter was connected to a laptop that constantly logged E_{corr} data while the pH readings were manually recorded. The pH, platinum and reference electrodes had 15-18 meters of wire that extended from the boat to the anchor. A pneumatic drill on a 15-meter hose attached to a compressor was used to drill into the concretion with a 12.7 millimeter mason bit; this size was selected so that the pH electrode could fit into the hole close to the metal surface.

The crown of A3 was chosen due to the centralized nature of this feature and proximity to the seafloor. Challenging conditions on the *QAR* site require two people to obtain a pH reading, one to drill and the other to hold the pH electrode directly beside the test site to immediately situate the electrode into the hole to try to detect a pH change before currents sweep the corrosion soot away. When the concretion was drilled, a release of gas was observed; most likely a mixture of hydrogen, methane, nitrogen and carbon dioxide (MacLeod 1995). The thickness of the concretion was measured with a small millimeter ruler from the core metal to the outside of the concretion. The Ag/AgCl reference electrode was held adjacent to the test site and the voltage reading obtained with the platinum electrode held to the metal surface for two minutes to ensure a stable E_{corr} reading.

QAR Cathodic Protection Escapades

In October 2008, a sacrificial aluminum anode designed specifically for galvanic protection in seawater, was placed on a PVC frame and connected to A3. A 4.5 meter-long wire was connected to the anode with a band clamp. The wire was secured along the anode and frame with multiple cable ties. The frame was placed just north of A3 and buried so the anode sat about 0.3 meters above the seafloor. The 'G' clamp was a large band clamp modified by attaching an adjustable screw that connected the wire from the anode to the anchor (see Figure 3). Pro Seal 34, an underwater curing silicone based sealant, was placed on the wire connections on the anode and at the anchor test site to prevent corrosion; however, the sealant failed to adhere.

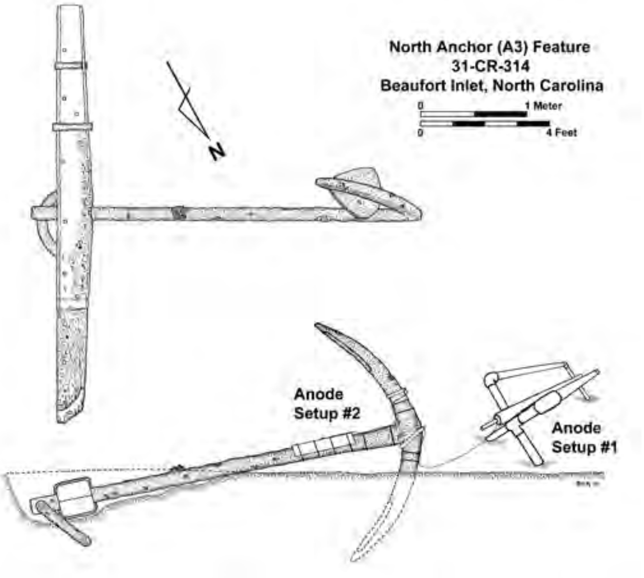


Figure 3. Illustration of anchor 3 in situ.

The anode and connection seemed to be secure, however after returning to the site a month later following a large storm, the anode frame had relocated about 2 meters to the northwest. The frame was flipped over and buried so that the anode was level with the seafloor. Extra wire attached to the frame allowed the connections to stay secure to both anchor and anode. The anode did not have any growth accumulation on the surface with the exception of the occasional barnacle. Subsequent E_{corr} measurements were made at the same test site in which the connection was positioned.

In June 2009, the connection to the anchor was found to be secure, with the wire leading into the sand and the anode appeared to be buried beneath a significant amount of sediment. In August, the sand levels were the highest yet observed on the wreck and the 'G' clamp to A3 was detached. In September, the detached wire was buried in the sand. However, efforts to locate the anode were unsuccessful. In October, as a temporary solution, a cut aluminum SCUBA tank was used as an anode and fastened directly to the shank of A3. A new hole on the upper arm of A3 was drilled for an easier connection with the 'G' clamp that permitted another concretion measurement. At this time a base reading for A1, located in the ballast pile, was also obtained.

In December, the temporary anode was covered with sea growth and consequently filed down to bare metal. The E_{corr} measurement was taken at the original test site that did not have a connection to the sacrificial anode. No secondary measurement was obtained on A1.

Results & Discussion

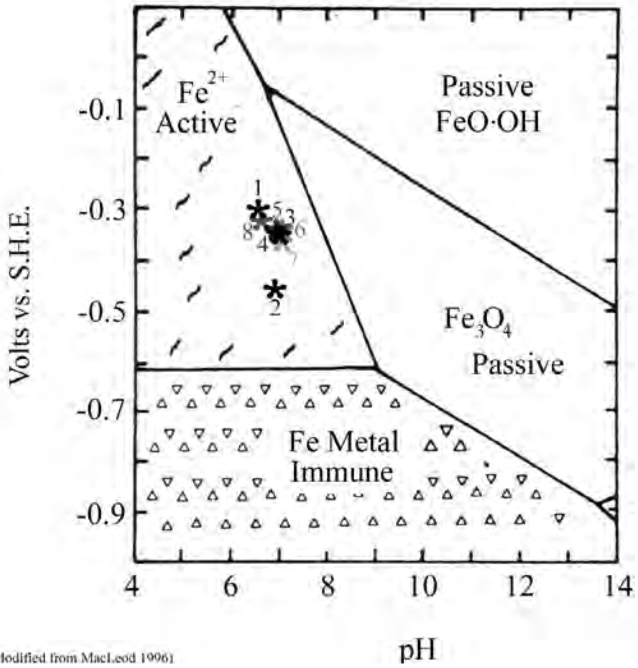
Results from the in situ corrosion study are given in Table 3. Concretion thickness divided by the number of years submerged is used to calculate a corrosion rate (Gregory 2000). Site conditions made obtaining pH readings difficult, and readings were not always attainable. The pH and E_{corr} results plotted onto a Pourbaix diagram for iron in seawater reveal that all of the readings are in the zone of active corrosion (see Figure 4). Pourbaix diagrams, also known as a potenial/pH diagram, are thermodynamic stability maps, which show whether a metal is in an active, passive, or immune region with regard to corrosion. It should be noted that the E_{corr} is

	Testing Site	Date (#)	Anode Location	Corrosion Thickness (mm) / Rate (mm/y)	pH at Metal Surface	E_{corr} Volts (vs Ag/AgCl)	E_{corr} Volts (vs SHE)
A3	first	10/08 (1)	0.3m above seafloor	17 / 0.058	6.6	-0.549	-0.300
	original	11/09 (2)	level to seafloor		6.9	-0.713	-0.464
	original	06/09 (3)	buried in sand		7	-0.615	-0.366
	original	09/09 (4)	not located		CNO	-0.603	-0.354
	original	10/09 (5)	secondary anode on shank		CNO	-0.595	-0.346
	second	10/09 (6)		14 / 0.048	7	-0.595	-0.346
	original	12/09 (7)			CNO	-0.615	-0.366
A1	first	10/09 (8)		21 / 0.072	6.7	-0.583	-0.334

*CNO-Could Not Obtain

Table 2. In situ data for anchor 3 and anchor 1.

not a true thermodynamic function and can only give an indication of the mechanism of corrosion and not of the corrosion rate (MacLeod 1996b & Gregory 2000).



(Modified from MacLeod 1996)

Figure 4. Pourbaix diagram for iron in sea water with A1 & A3 data.

Sacrificial anode placement and the type of anode used are important lessons learned from this study. Anode conditions can effect the corrosion of the aluminum, which also can effect the cathodic protection to the artifact. Inspection of the data from A3 is as expected considering the changing environment of the sacrificial anode. Of all readings taken, there was a significant improvement in E_{corr} when A3 was attached to the primary anode. The cathodic protection slowed when the primary anode was buried, although the E_{corr} remained above the baseline reading. Assessment of the anchor after two months of no cathodic protection indicates the anchor was close to pre-disturbance levels but did not reach initial readings. High sand levels observed in August could be a contributing factor to corrosion potential readings for A3 not falling to the initial readings. The secondary anode did improve the E_{corr}, but is not a long-term solution to cathodic protection as it would require constant encrustation removal, which is not practical.

The E_{corr} reading for A1 was not as high as the base E_{corr} reading for A3. However, the concretion is 7 millimeters thicker and the calculated corrosion rate is higher. A1 is part of the main ballast pile with large iron artifacts in close proximity, which could contribute to more concretion growth. A3 does not have the protection of other large artifacts in situ, and environmental conditions possibly affect more surface area of the lone anchor causing a higher base corrosion potential.

Conclusion

This preliminary in situ corrosion study has established a baseline for understanding corrosion parameters on the *QAR* site. Cathodic protection showed positive results providing the anode stayed attached to the anchor. However, removal of chloride ions was unlikely considering that the polarization of the iron was not always achieved. In situ corrosion studies are essential in determining management priorities for large iron artifacts and the possibility of initiating conservation on the seafloor seems an attractive strategy considering limited space and financial resources. Corrosion studies are imperative to decisions concerning which cannon and anchors to recover and which to treat in situ. The number of *QAR* cannons and anchors provide an opportunity to test the reproducibility of in situ monitoring and cathodic protection methods.

Future Studies

In situ corrosion studies will continue with A3, and other anchors and cannons from the QAR will be incorporated into this long-term project. Eventually, sufficient data will be attained to predict an accurate corrosion model for the *QAR* site. Mild steel coupons have been placed in various conditions on site to aid in determining the current corrosion rates. Additional studies are needed relating to aspects of the physical environment that are likely to effect corrosion rates, such as seasonal fauna, water quality and sediment testing for the presence of sulfate reducing bacteria. This study will also be incorporated into public educational programs.

Acknowledgments

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Materials

Orion pH Meter 210Aplus
Fisher Scientific
2000 Park Lane Drive
Pittsburgh, PA 15275
Tel: 1-800-766-7000
Fax: 1-800-926-1166
Web site: www.fishersci.com

Orion Aqua Pro Flat Surface pH Electrode
Fisher Scientific
2000 Park Lane Drive
Pittsburgh, PA 15275
Tel: 1-800-766-7000
Fax: 1-800-926-1166
Web site: www.fishersci.com

18m Extension RG58 C/U Cable for pH Electrode
West Marine Products
406 Atlantic Beach Cswy
Atlantic Beach NC 28512
Tel: 252-247-3356
Web site: www.westmarine.com

Aqueous Buffers 4.00 & 7.00
Fisher Scientific
2000 Park Lane Drive

Pittsburgh, PA 15275
Tel: 1-800-766-7000
Fax: 1-800-926-1166
Web site: www.fishersci.com

Precision MM570 Multimeter with BS85x Data Logging Software
Cole-Parmer Instrument Company
625 East Bunker Court
Vernon Hills, Illinois 60061-1844
Tel: 1-800-323-4340
Fax: 1-847-247-2929
Web site: www.coleparmer.com

Staperm AG-3-SW Ag/AgCl Reference Electrode with 15m Cable
GMC Corrosion & Electrical
2132 Grove Ave. Unit F
Ontario, CA 91761
Tel: 909-947-6016
Fax: 909-947-9430
Web site: http://glmcorr.tech.officelive.com/default.aspx

1 Inch Platinum Rod
Electronic Space Products International (ESPI) Metals
1050 Benson Way
Ashland, Oregon 97520
Tel: 1-800-638-2581
Fax: 541-488-8313
Web site: http://www.espi-metals.com/

Aluminum Sacrificial Anodes
Galvotec Corrosion Serevices, LLC
300 Bark Road, Bldg C-2
Harvey, LA 70058
Tel: 504-362-7373
Fax: 504-362-7331
Web site: http://www.galvotec.com/services.htm

Pro Seal 34 (Polycarbonate Sealant)
Pro-Seal Products INC
16541 Redmond Way Suite 363C
Redmond, WA 98052
Tel: 1-800-349-7325
Fax: 425-821-1006
Web site: www.prosealproducts.com

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Author

Wendy M. Welsh obtained her BA in Anthropology from Appalachian State University and is currently pursuing a second degree in Chemistry at East Carolina University. Welsh has worked as a conservator on the *Queen Anne's Revenge* shipwreck project since 2002 both in the laboratory conserving artifacts as well as an archaeologist on site during field excavations. Welsh will continue to develop the in situ monitoring project and eventually plans to utilize this research as a post-graduate thesis topic.

Q & A SESSION

Jean-Bernard Memet: You used the Pourbaix diagram for this potential and even if it is modified by Dr. MacLeod, I don't think it is a good way to see if your anchor is protected or not. In fact, when you do some cathodic polarization or protection, the important thing is the open potential of your artifact. How can you explain that your potential decreased and then increased in your measurements?

Wendy Welsh: That's a great question, I would like to know myself! I do know that whenever we initially hooked up the proper anode to it, it brought it up great and whenever we put the scuba-tank anode on it went back down. However it didn't go all the way back down to its initial state. Whenever we started this, the sand levels were really low. Also since we have put on the proper anodes after the scuba-tank anodes the sand level has gotten much higher. So the anode is on the shank which is now covered by a lot of sediment, so I'm guessing maybe that's what's happened to it and caused the differences in the corrosion potential. The complication is the amount of sediment movement which buries the anodes, and so they passivate and thus they are not able to corrode like it probably should. That is my thought.

Jean-Bernard Memet: How did you do your design of cathodic protection, because I'm wondering if it is not over-designed. Because the anchor has a specific area and designing a cathodic protection [system] is related to this area, and it is related to the current amount of metal. These 2 large anodes on a small anchor, I'm wondering if it is not overprotected. If you are overprotecting you can provoke some bad things on the anchor especially hydrogen bubbling – so we have to use it very carefully and design it very carefully. How did you do the design of this cathodic protection?

Wendy Welsh: Both of these anodes weren't hooked up at the same time. I've only ever had one anode hooked up to it at once. I did a lot of talking with our corrosion engineer at the Galvotech– what they do is create these big anodes for oil rigs out in the gulf – I told him the size, structure and material type and he sent me anodes he said would be fit for that.

Jean-Bernard Memet: One last question: by now is the anode covered by the sand or the silt?

Wendy Welsh: This one at A3 we had to dig this out. So all of that was totally covered with sand. A1 is still in the water column and is in a good place.

Ian MacLeod: Just an observation. The man who gave you the anodes was being very kind but aluminium anodes only work in free-flowing aerobic seawater. They are absolutely [no good] in sediment – what you should be using is zinc because zinc works in aerobic and in anaerobic [conditions]. And never use magnesium anodes, you'll blast your concretion off and you lose all your natural protection.

Wendy Welsh: When the sand levels were low – I thought the aluminum would have been good, and that's when we initiated this project. But in the year that has passed the sediment has just come into the site so much… so I will definitely need to change to zinc anodes – that will get me over the threshold maybe?

Ian MacLeod: There were similar problems on the *Xantho* engine. We put aluminium anodes on initially and then the seabed came up 2.5 meters in a year. They use magnesium anodes on the internal hulls of ships when they want to clean all the rust off – they just put magnesium anodes on, fill the hull with seawater and then it generates so much hydrogen it blasts all the scale off. They pump the seawater out and repaint the hull. It's much easier than sandblasting, but it does occasionally go wrong, and the hydrogen catches on fire and the ship then sinks!

Conservation Of Marine Archaeological Objects

Chair: Paul Mardikian
Panelists: Ian MacLeod, George Schwarz, David Krop, Wendy Welsh

Paul Mardikian: What is interesting with all those papers is the big responsibility in raising artifacts, and the burden when you have raised them and you have them in your lab. So the idea, the UNESCO convention and all those discussions about leaving artifacts in situ and trying to keep them – I know this is not good for the conservators, they would want to raise the artifacts and conserve them. But we also have to consider what is feasible with the amount of money we have, and sometimes be wise in leaving artifacts where they were found. So, I think what George [Schwarz] has shown is that airplanes are really extremely fragile and at this point we are not completely ready to tackle them and there is a lot of work and a lot of research needed in this kind of work. I do believe that marine airplanes are going to be the big challenge; I would hope that we could put funding into the research of the stabilization of aluminum and keep going with that, as it would be really great. But you will not find aluminum alone on an airplane, you will find different grades of aluminum, you will find numerous materials together, this is what makes an airplane such a complex object.

Jonathan Leader: I would like to thank the speaker for giving us insight into the interaction between the Naval Wreck Act, other federal legislation and the concern for preserving Navy aircraft. I understand the desire to use the Advisory Council for Historic Preservation's policies in the preservation of the historic built environment as a possible route for the preservation of Navy aircraft. My concern is that the ACHP's policies, while an interesting point of departure, may not adequately address the issues specific to Navy airplanes. It is clearly early days in this process, but I would suggest that whatever policies are formulated to address this important issue be folded into an extended version of the Naval Wreck Act. If I am not mistaken the current Naval Wreck Act doesn't address Navy property other than sunken vessels. This is an understandable oversight, but one that should be corrected if possible sooner rather than later. It would undoubtedly make your preservation efforts easier to accomplish.

George Schwarz: Well, again, I think that is what my and Peter's presentation was about, to get more discussion going on this topic, but as far as the US Navy is concerned, the Sunken Military Craft Act was designed to prevent unauthorized disturbance of sunken military craft. I think that the aircraft should be treated the same as the shipwrecks, I do believe that. Maybe not all of them, it depends, there are different opinions on what is considered an archaeological site. For example, if an aircraft fell off the back of an aircraft carrier, and it went straight down into Lake Michigan, is that considered an archaeological site? Versus one that was flying during the war in Jaluit Lagoon, Marshall Islands, and wrecked during battle? I am not really sure, I think that there is potential to study all of these as archaeological sites because there is still so much that we have to learn about it. So, I think it is a case-by-case basis, but I think that they all have potential for that kind of study.

Paul Mardikian: What struck me was to see how many years of work Ian you put into that research, and application of anodes on the seabed, and how different it is from what people do in the industry – because the artifacts are different from an oil rig so you have to really develop your own tools to be able to gauge those artifacts, and this is why is it difficult to go directly from the cathodic protection industrial setting to what you are trying to do on shipwrecks. This is what you have done Ian, and you have published extensively, but it's still difficult for you to apply that. It requires more collaboration and it's not trivial to just go underwater, drill holes and make sense of all of that, it's a lot of work, and Ian you have been championing that work over the years. Do you have projects like that in France too Jean-Bernard, do you have impressed current protection on cultural heritage?

Jean-Bernard Memet: Yes we have such projects in France and in Europe which are waiting to begin at the end of the year on shipwrecks, but the real need is to have the whole protocol of the approach to shipwrecks under the sea [figured out] because there are so many different parameters to know when you want to protect, and if you want to protect a shipwreck, starting with the environmental parameters, starting with the residual thickness of the shipwreck, the current demand on the metal because it is very, very important to have the whole of these parameters. We are starting a project dealing with metallic shipwrecks all around Europe and we want to have a common protocol from all of the countries. The main goal of this project is to know if you have to protect it or not, because sometimes it is better to leave the artifact or the shipwreck as it is than to protect it with sacrificial anodes for example. So, we have to think about it and we will have a lot of discussion with Ian because his huge experience with iron is fantastic for all the community.

Paul Mardikian: How do you make that determination? Is it only based on the potential of the artifact?

Ian MacLeod: You make the decision on what you will treat in conjunction always with the maritime archaeologist, because no matter how experienced you are, you have to take into account what the overall parameters of the site are, the historic significance of the objects, and also the viability of it, and we know now that because the corrosion rate is logarithmically dependent on water depth, if you have to recover a cannon, then you choose the one from the deepest part of your wreck site, because that's the easiest one to conserve – its less corroded. But also, similarly, if an object is lying proud of the seabed, and it's easy to excavate, that's the one you choose, because working underwater is always hard and you always risk damage to the artifact during excavation, so the other parameter is if you are going to recover a token object, pre-treat it, but do the one that is easiest to recover. It can be as brutal as that. But if you've done an underwater pre-disturbance survey, and you know the depth of graphitization of the cannon, then you know which is the best one for treatment and recovery.

Eric Nordgren: I have a question for Wendy. My understanding currently is that the plan or the decision was made to do a full recovery on the *Queen Anne's Revenge* so is that the case? And also given that, how does that affect these decisions in terms of prioritizing which artifacts you might try to protect and recover and in which order? Can you comment on those factors?

Wendy Welsh: Very good question. There was a decree by our Secretary stating that we are going to bring up the entire shipwreck in three years, however we are only given small amounts of money to do limited field work and there is no money available to actually build a facility to house all of these artifacts which is what we are in need of. You saw the picture of our warehouse, we are filled to the brim and we do not have any artifact storage space. We keep getting these small sums of money like $50,000, which we are grateful for but we are then expected to use that for lab operational cost as well as a 12-week field season. We want to see results so that's been quite difficult for us in the project to manage. We would like to take more of an initiative and study these objects on the bottom because we, as conservators, feel that it is a bit unrealistic if you are not going to put the money into a facility, so we want to try to see what we can start conservation-wise on the bottom of the ocean. So yes the excavation is supposed to continue however we do everything on a shoe-string budget and it would really be great to have some money put towards the project but that has yet to happen.

Claudia Chemello: I have a comment for Wendy to reassure you. I work on archaeological terrestrial material and this is a really big problem in our field as well and I am really pushing some of the archaeologists that I work with on site to rebury their stuff because we do not have really good storage facilities either. I work in Egypt as well as in Israel, and in Egypt, we have really, really desiccated material so different problems to what you are dealing with, but we do not have enough room to store all of this material. David Hallam just made a comment about the significance and assessing the significance and I can't make that decision on my own and I always have to make that in conjunction with my director who is an archaeologist who has a different mission to me, although we are all there to get information. But, we have six weeks, we have hundreds of things, we have limited resources, we are working in countries where it is very difficult to undertake a lot of conservation on the material. The conservation that we do often cannot be assessed again as and the objects may go to a storage facility where it is rather convoluted to actually ever get access to the objects again. So some of them are stored on site where I work and I was just thinking of this as you were talking how difficult it is because there's hundreds and hundreds of objects and I have very limited time or possibly a student with me or another conservator, and you have to choose really well what you are going to conserve and obviously that's the significance of the material as Ian was just saying or the rarity of the material or these kind of things, but it is also what you are able to do in that period of time. So we face the same things with terrestrial materials.

Wendy Welsh: That's definitely true, even just on our project, the archaeologist and the conservators have different views. The archaeologists have a decree to dig, dig, dig and we as conservators are like 'wait, hold on'. They want to get as much done as they can, however, it is really difficult for us as conservators to say 'no, we have to be smart about this and have a place for these things to go, before you go and pick these things up'. So, whenever you have all those different opinions on a site it is really difficult.

Paul Mardikian: For some materials such as waterlogged wood, we know for instance on the Red Bay shipwreck [Canada], you excavate the boat, you study the boat, you mold the surface of the wood, and eventually now you could even scan the surface of the wood, and then rebury in a perfect environment. That's something we do with waterlogged materials. With iron or with other materials, the access to the information is encrypted, you could possibly x-ray your iron objects and then rebury them. I don't know if it works in terrestrial archaeology, I don't know if anyone has reburied things in terrestrial archaeology. But the idea of studying and then maybe putting back, but I know that it sounds a bit difficult, but that's something we do to some extent in maritime archaeology.

Ian MacLeod: It's more of a comment and observation on Wendy's site. One of the other justifications for intervention on a site like that is being able to do the pre-disturbance survey and not ripping up all the cannon, but you can actually map the way in which the guns and other artifacts on the site have interacted with each other. On the American China trader the *Rapid,* which sank on Monday night Jan 7, 1811 when you look at the extent of the corrosion of the cannon, you can find that a gun that was placed between Mr. Scott and myself was much more corroded than the gun the distance between Wendy and him. And that is because of proximity corrosion, and you get this on shipwrecks, it's a form of galvanic corrosion when the things aren't in direct physical contact but they are communicating and feeling each other's vibe through the sediment, and over hundreds of years that can have a major effect. And so if the archaeologists were actually doing a systematic survey of the corrosion of the cannon, they would actually be able to build up a history of how that site has become buried and exposed and how different parts of it have done it, and you would be able to recreate a time lapse of how the site has formed, pulled apart and reformed. That is where I see the real value in a full excavation and analysis because it was only because Graeme Henderson had decided to recover all of the cannon from the *Rapid* that I was able to make those observations. So, sometimes there are questions that you don't know to ask, until you've got the artifacts there to treat and then as you're treating them you find the question you should have asked 30 years ago.

Wendy Welsh: One thing that I was wondering if you could comment on Ian, is the anchors around the pile [on the *Queen Anne's Revenge*], and I am sure there are a lot of parameters that affect this, but they had much more concretion on them and the corrosion potential was a little bit better than the lone anchor that was sitting out North of the site. So I was wondering if you could comment on maybe why this anchor that is alone out there and is still prominent above the seafloor, why the concretion is not as thick on as much of it in comparison to the two anchors which are in the main ballast pile, surrounded by a bunch of other anchors and cannon.

Ian MacLeod: What's happened I think with your anchor that's still got the wooden stock on it, because one fluke is sitting up in the oxygen in the seawater and the other one is buried, it's all one artifact but you've got two different environments on it. So the exposed bit is going to be mainly where the cathodic reduction of oxygen is occurring, while the bottom bit is also being anaerobically corroded. So, with the cathodic sites, the pH increases and it's much easier for the marine organisms to grow in the more alkaline environment. That's why you get much bigger oysters on a cathodically protected iron jetty and they are much tastier, and they are cheaper! You've got to remember that there are two halves to the corrosion cell and if you have an anchor that has lost its stock its going to be covered with a very different type of concretion than one that is half sitting out and half buried.

David Krop: I just want to make a point regarding recovery of so many artifacts and trying to minimize the amount of things that are recovered. In our lab [USS *Monitor*, Newport News, Virginia] we have about 1600 artifacts, roughly one fifth of the *Monitor* itself has been recovered and is in the lab. The archaeologists were really excited because it wasn't really a once in a lifetime opportunity it was a once in a 140 year opportunity to recover, with the assistance of the Navy, countless numbers of really high profile and high risk pieces from the bottom of the ocean. So, that was undertaken and now we are talking about decades to conserve these artifacts. One of the newer staff members at the National Marine Sanctuary Foundation office, who is now the Sanctuaries superintendent, he came from a different heritage preservation field and fortunately he was all ears for the first six months to a year and was very involved with how conservation directly impacted recovery. There came a time a few years later when the monitoring team for the wreck wanted to raise additional objects because they were within easy grasp. But the superintendent consulted with the three conservators and asked us our thoughts and the relevance of the recovery – is it important – and he decided to say no. That was nice, you could see his change in thought processes over time, of questioning the merit of recovering countless numbers of artifact just because there was an opportunity.

John Scott: In hearing about the issues of excavating and how much to excavate and whether or not to excavate, it occurs to me that in terrestrial archaeology reburial hasn't been found to be that protective on a lot of materials, so that reburial perhaps in a marine environment may not be as effective as we'd like it to be. And when we think about what archaeologists want from us and what we are getting by excavating or bringing things out, it occurs to me that in oil and gas discovery now, people are finding resources with great accuracy at very great depths with a lot of reduced risk in their recovery investments. I wonder if things like ground penetrating radar or Terahertz imaging or spectroscopy, has anyone been thinking about these techniques or computed tomography of the sites so that you could have three dimensional representations of your archaeological sites in the marine environment without having to excavate so much, perhaps doing some probes for confirmation of materials or states of corrosion. It could be that you could produce a lot of information for archaeologists without disturbing so much material.

Paul Mardikian: Something that is obvious for us in marine archaeology is that it is extremely difficult to decipher, understand, and read the artifacts unless you go through them. Very often you raise artifacts and then you understand that you've got several of the same artifact and you're not learning from those artifacts, you are duplicating what you have found. You cannot predict – very often we have lumps of concretion and we have to explore them and then we find out what we have. So, its hard when you just look at the material on a shipwreck to decide what is of interest or not, so it requires a collaboration with the archaeologists. The material is encrypted and it is extremely difficult.

Eric Nordgren: Paul, I very much agree with you there, in many cases when there is a time limit, and in the case of the recovery of a lot of the artifacts from the *Monitor*, especially the turret, the recovery conditions were difficult, there was very limited time and a very limited budget as well. In those situations you have to use the best judgment you have. In praise of recovery of certain things when a decision has been made and there are good reasons behind that, it does allow us to get as close as possible to ensuring that they will last as long as possible. If you think back to what we talked about this morning to eliminating a certain amount of the chlorides, that gives us the best chance of preserving something that might be an important part of history as long as possible. And that might also be the case in situ in some cases, but there are others where there are environmental factors or other causes, which means that that won't be the case. And so, I think that if we can make good decisions about when to recover things and then do the best conservation we can, I guess that is obviously the best case, but it's very good to consider before you excavate or recover something from a marine site. Think about the possibility that when we have a good treatment then we can make a difference in that way.

David Watkinson: If I could just raise a point which I think there will be quite a few different views on but maybe, when you are initially talking about whether you do or don't recover objects, are there different levels of recovery or not in that some of the objects we are talking about might be considered to be association objects in that you know how a Messerschmitt 109 was built, you've got all the plans and suchlike, and if it's lying there it's been recovered because it's been associated with an event, and it's not maybe entirely necessary to recover it. But in terrestrial archaeology, if you're excavating a site, you've no choice but to go down and everything that comes up you take out. And then the question becomes, everything that you take out – should you actually keep it, it should all be studied, it should all be recorded and if you can analyze as much as you can in financial terms. But then you have this very long lifetime drain of looking after the material in terms of cost etc, so I guess there are a whole range of really difficult decisions to make and those things need to be dialed in, so maybe there are views on that, I don't know.

Jean Bernard Memet: Just a few words, that's a very interesting point David, in France for example you don't have any right to raise the object if you don't have a really good project and if you don't have the budget to treat it, to analyze it. So now in France as the years pass, we are decreasing the number of artifacts which are extracted from the sea. And as part of a UNESCO convention about underwater cultural heritage this is a very important point - not to recover everything.

Paul Mardikian: I feel that in theory it would work well, what is the budget that you need to recover such and such artifacts and to conserve them, but how can you predict how long it is going to take you for a specific artifact, it is impossible to do. What the French are trying to do is to say that at least you need to have a budget for the conservation, and then you will address those problems, but at least make sure that there is money aside for that. But saying how much it is going to cost to treat a specific artifact when you are looking at it on the seabed is pretty difficult.

MATERIALS CHARACTERIZATION AND IDENTIFICATION

Session Chair: Andrew Lins

HOT-TINNING OF LOW TIN BRONZES

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Abstract

Identification of hot-tinning on corroded bronze is often a challenging task due to the various mechanisms by which shiny or grey surface finishes can be formed. The nature of intermetallic compounds formed during hot-tinning changes during use because of solid state diffusion of copper, or due to application of heat at temperatures above the melting point of tin. To identify their presence, a clear understanding of tinning microstructures must be combined with knowledge of their forms relative to corrosion structures developed from general corrosion of the underlying bronze. This study reports on the examination and identification of the intermetallic phases associated with tinning. Reported experimental work is designed to examine aspects of the formation and detection of intermetallic compounds that can be used to discuss the challenges associated with definitive identification of tinning on low-tin bronzes.

Keywords: Hot-tinning, low-tin bronzes, intermetallic phases, room temperature diffusion, X-ray diffraction

Introduction

Studies suggest that various tinning methods were used in antiquity to confer a silver color finish on copper alloys. Apart from work by Meeks (1986, 1993 a,b), there are only few published analyses of tinned archaeological bronzes in Europe. Scientific examinations focus on the presence of black or silver colored surfaces on high tin Chinese bronzes (Shoukang and Tangkun 1993), low and high tin Roman and Chinese mirrors (Meeks 1993b, 1993a), Bronze Age axes (Kinnes et al. 1979, Tylecote 1985) and various small objects reported to be dip-tinned (Oddy and Bimson 1985). Analysis often omits information on body composition and microstructure, or relies on scanning electron microscopy (SEM), backscattered electron (BSE) imaging and elemental mapping with little supporting diffraction analysis of phases. It may be significant that publications identifying hot tinning of bronze seem to report its occurrence on cast objects, yet tinning of worked bronzes is expected to have been extensively applied in antiquity. Is this because the production technology and the preservation mechanisms of tinning on worked bronzes influence the survival of evidence for tinning? More needs to be known about the preservation of tinning and its various corrosion paths.

While Meeks's experimental work (1986) reports extensive microstructural evidence that could be employed to identify tinning methods, this now needs to be viewed in association with current knowledge of copper/tin (Cu/Sn) interactions to better understand what constitutes evidence of tinning. Consequently, this study reports examination and identification of the phases associated with tinning, and it forms part of an ongoing investigation to further understand the formation, preservation and detection of tinning layers. Experimental tinning is used to establish the phases present and determine the efficacy of detection methods. This data is then used to examine corroded archaeological bronze microstructures, followed by a brief discussion of current hypotheses and scientific evidence on their identification.

'Tinned' surfaces on low tin archaeological bronzes

How is tinning defined and identified? Silvery or grey surfaces on archaeological bronzes appear deceptively similar to tinning or silvering and occur either intentionally or unintentionally during manufacture or corrosion (Meeks 1986). 'Tinned' surfaces with high relative tin concentration can be achieved in various ways that produce different microstructural evidence (Meeks 1986, Meeks 1993b).

In Europe, hot-tinning of low-tin bronzes is documented in the literature since Roman times (Oddy 1980). The two common methods of hot-tinning flux the object with rosin, followed by wiping tin over the surface over an open fire at a temperature above the melting point of tin (232°C), or immersion in a tin bath. The latter is unlikely to have been practiced on large objects, because of uneconomic use of tin and copper contamination of the tin bath (Meeks 1993b).

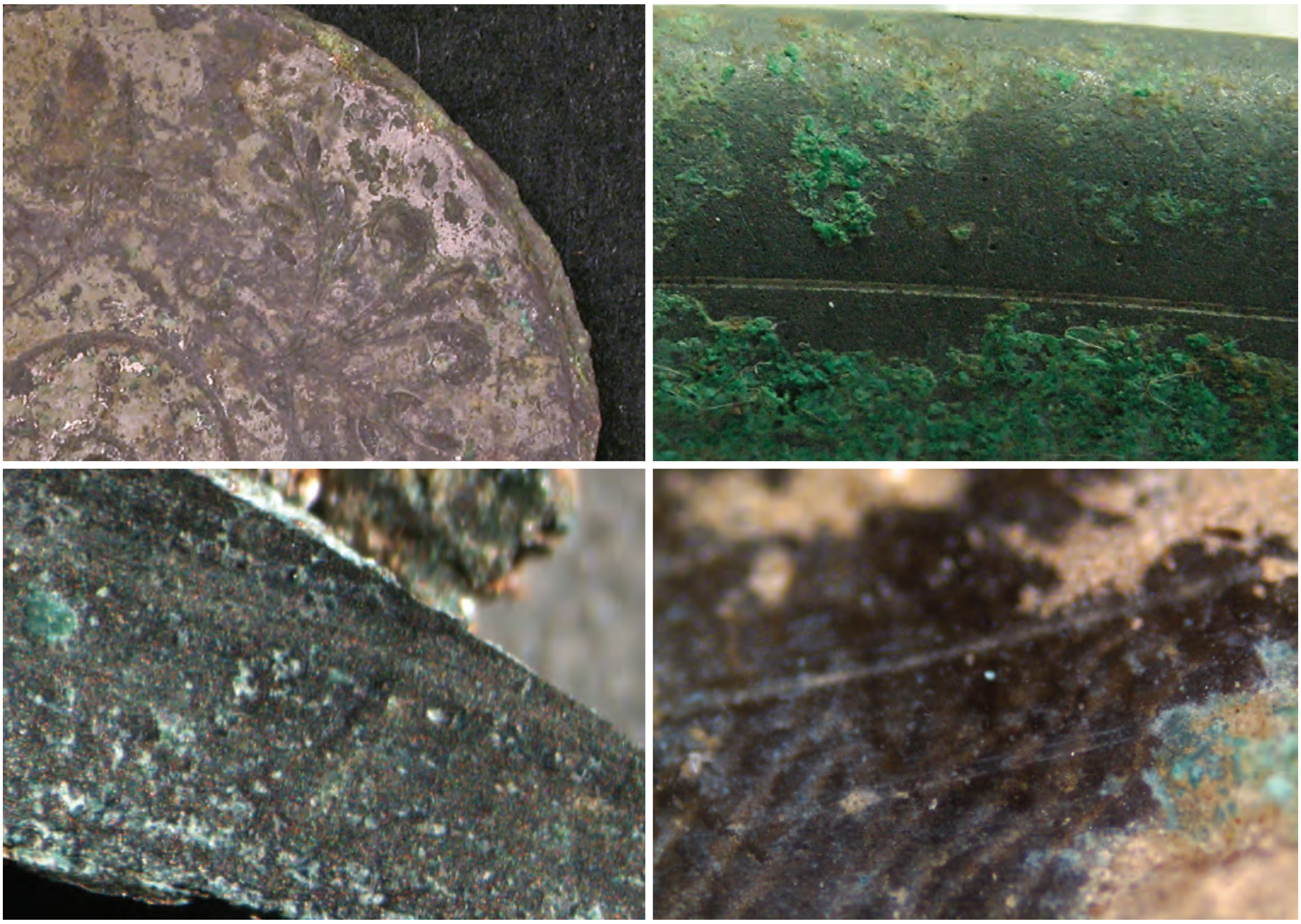

Figure 1. Tinned and silver/grey colour surfaces on analysed archaeological objects: Decorated tinned harness fitting from Brecon Gaer Roman fort (1-2 c. AD), National Museum Wales (*top left)*; Roman skillet with tinning remnants at incisions, Ceredigion Museum, Aberystwyth (*top right);* Fragment from Roman skillet from Manorbier (1st c. AD), National Museum Wales (*bottom left*); Detail of surface of Illyrian type helmet (mid 6th c. BC) from Archontiko Pella, Greece (*bottom right*).

Tinning at elevated temperatures involves diffusion at the tin/bronze interface to produce intermetallic compounds (IMCs), typically with a $Cu|Cu_3Sn|Cu_6Sn_5|Sn$ profile according to the Cu/Sn equilibrium phase diagram. Compositional variations at the interfaces of the IMCs are reported (Lee and Duh 1999). At equilibrium conditions, epsilon (ε-Cu_3Sn, 37.74-39.50 wt%Sn) and the low temperature transformation of η-Cu_6Sn_5, eta (η′-Cu_6Sn_5, 61 wt%Sn), are stable at room temperature. However, the high temperature η-Cu_6Sn_5 is also reported at room temperature because cooling following tinning can be too quick for it to transform into η′ (Laurila et al. 2005). The presence of ε and/or η (or η′) s considered evidence of hot-tinning on archaeological bronzes (Meeks 1986). Interestingly, research has shown that η′ can form and grow linearly at temperatures below 60°C due to solid state diffusion of copper atoms into tin at the Cu/Sn interface, whereas ε only starts appearing above 60°C (Tu 1973). Aging of η at room temperature turns it into η′ (Wang et al. 2009). Using compositional analysis for the detection of ε and/or η′ can be problematic because similar composition ranges are found on surface corrosion of archaeological low-tin bronzes (Oddy 1980, Scott 1985, Robbiola et al. 1998). Also, visual errors can occur because corroded homogenised low-tin bronzes and corrosion of α-bronze in the α+δ eutectoid of cast low tin bronzes can produce a metallic grey colour that looks deceptively like tinning (Oddy and Meeks 1982).

The following experimental work is designed to examine aspects of IMC formation and detection that can be used to discuss the challenges associated with definitive identification of tinning on low-tin bronzes.

Experimental

Tinning replication and analysed archaeological objects

Copper tokens (99.9 wt% Cu, 3.25mm thick) were tinned using a wiping procedure based on practical observation and an interview with a modern tinsmith (Mr Panagiotis). Following cleaning (50wt% hydrochloric acid, HCl), the tokens were individually heated over a Bunsen burner, then fluxed with rosin just before a tin wire (99.75wt% Sn) was passed over the surface and wiped across it with cotton pads.

Thermal aging experiments above tin's melting temperature (reflow experiments) were designed to examine the influence of temperature on the intermetallic compounds that formed from tinning. This offers insight into IMC microstructural changes as a result of applied heat during use in antiquity, such as cooking. Reflow temperatures of 250°C, 350°C, 450°C and 550°C were applied in an electric furnace on two different sample sets of tinned copper tokens for 5 minutes and 60 minutes.

Objects with visual and archaeological evidence of tinning were analysed for comparison. These included two Roman cast bronze skillets with evidence of a wrought microstructure in the bowl area, a cast, tinned, decorated bronze harness fitting, and a hammered Archaic Greek helmet (see Figure 1). Apart from the helmet, all objects contained small amounts of lead in the low-tin bronze alloy.

Instrumental analyses

All samples were examined using polarised light microscopy, SEM with secondary and backscattered electron imaging (SEM-SEI and SEM-BSE), in top view prior to mounting and in cross section after mounting in epoxy resin. Intermetallic phases on replica samples were revealed by dissolving excess surface tin using 5% aqueous HCl (Gagliano and Fine 2001). Compositional analysis employed a CamScan 2040 SEM (20 kV with 120x96μm spot area) with an Oxford Link Pentafet 5518 Dispersive X-ray spectrometer and Isis 300 software. The spectrometer's super thin atmosphere window (ATW2) permits X-ray detection of light elements ($Z>4$). Calibration involved pure elements, mineral and bronze standards (No. 4629, Micro-Analysis Consultants Ltd). Oxygen calibration used wollastonite ($CaSiO_3$), and showed 1.85% mean relative error of accuracy and 1% relative precision. Accuracy and precision are reduced when analysing corroded surfaces as micro-roughness is inevitably encountered after polishing due to hardness differences and some loss of material. X-ray diffraction (XRD) was undertaken using an XPERT-PRO PANalytical diffractometer. Flat samples were analysed in situ on a fixed stage with divergent beam footprint of 100 or 200mm^2 for 20-60 minutes acquisition time depending on sample. Data was analysed with X'Pert HighScore V2.1.2 using the PDF-02 database.

Results and Discussion

Experimental tinning

Thickness of the tin layers varied according to the amount of tin used and the dexterity and skill of the person applying it, which directly affected the type and thickness of microstructures observed in cross section (see Figure 2 a,b). SEM-BSE imaging of polished cross section profiles shows the presence of $Cu/Cu_6Sn_5/Sn$ for as-tinned samples (see Figure 2d). XRD confirms the presence of Sn and η-Cu_6Sn_5 (PDF 65-2303) as well as a small amount of ε invisible to microscopic observation (see Figure 2d). During tinning, Cu_6Sn_5 is the first phase to form (Tu 1973). The Cu_6Sn_5 is initially granular (see Figure 2c) but becomes elongated and angular in later stages of annealing (Gagliano and Fine 2001), which can be seen in this experiment at higher annealing temperatures (see Figure 3; S11).

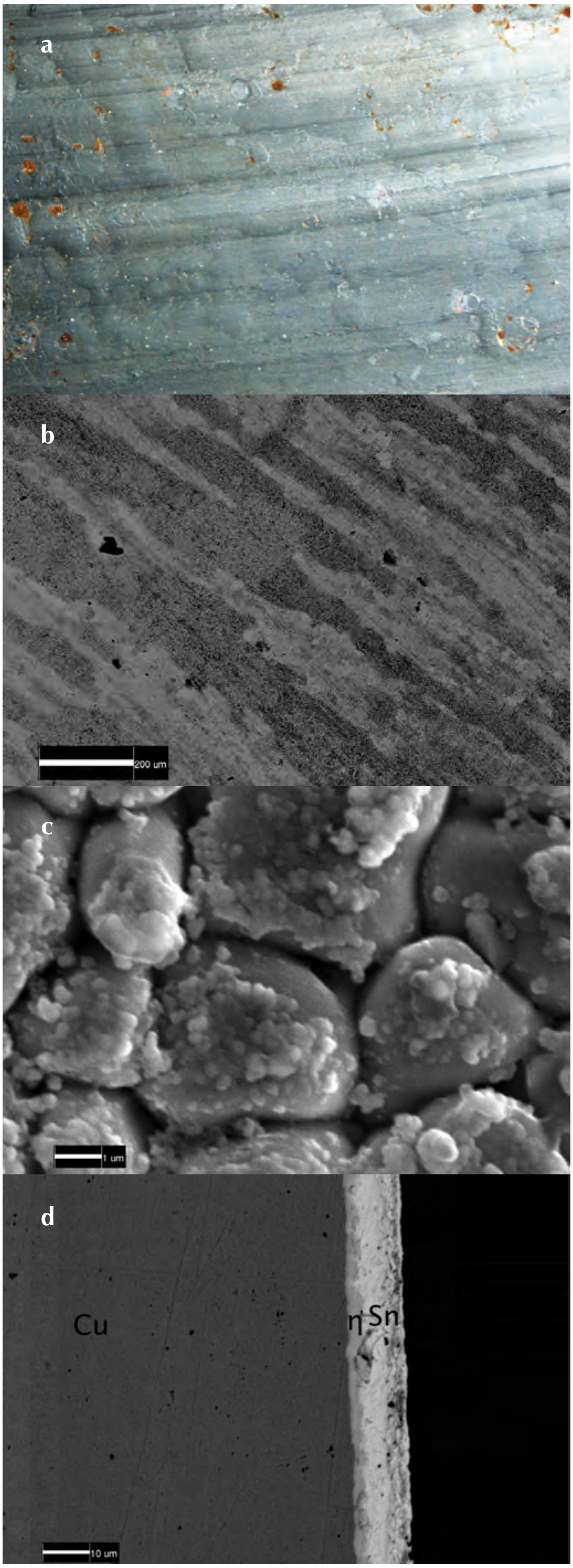

Figure 2. Observations of as-tinned sample (S1). a. Tinned surface exhibiting banding due to uneven application; b. BSE image of the same surface shows a dark granular surface under bright tin; c. BSE image of etched surface reveals Cu_6Sn_5 scallops; some tin is visible on their surface; d. BSE of cross section showing a thin Cu_6Sn_5 layer between Cu and Sn.

With increasing annealing temperature or time, diffusion phenomena result in further morphological change and growth of Cu_6Sn_5 accompanied with the growth of planar shaped ε-Cu_3Sn at the expense of Cu_6Sn_5 at the Cu/Cu_6Sn_5 interface (Prakash and Sritharan 2001). Consequently, the presence of ε is cited as evidence for tinning at relatively higher temperatures (Meeks 1993b). An increased amount of ε is visible using BSE imaging for annealing between one hour at 250°C and five minutes at 550°C, and is readily detectable by XRD (PDF 03-065-4653)(see Figure 3, S7, S11-S17). Growth of ε is reported to be parabolic with time and exhibits variable growth rates at different temperatures (Laurila et al. 2005).

Similar phase formation of Cu_6Sn_5 and Cu_3Sn is reported for Sn/Pb alloys, with Cu_3Sn being observed at higher temperatures (290-310°C) for a 27Sn73Pb alloy (Prakash and Sritharan 2001). Therefore, if a Sn/Pb alloy coating applied in antiquity has been lost due to polishing or corrosion, it would leave the same IMCs as those left behind after loss of a pure tin coating; this further complicates interpretation of tinning microstructures.

A small amount of δ-$Cu_{41}Sn_{11}$ (PDF 03-065-7047) is detectable only by XRD after annealing at one hour at 450°C (or 5 min at 550°C) (see Figure 3; S15, S17), with δ in a tin matrix being the only phase at temperatures above that detected with both XRD and BSE imaging (see Figure 3; S19).

Porous tin layers were formed at low aging temperatures/short time period due to the large amount of flux used (see Figure 3 S5, S7). Samples S11-S19 (see Figure 3) show Kirkendall porosity at the Cu_6Sn_5 /Sn interface. Kirkendall porosity is associated with atomic vacancy diffusion phenomena at the Cu/Sn diffusion couple because the diffusion rates of the two species are different (Nakajima 1997). Their nucleation depends on activation temperature and the addition of other elements (Laurila et al. 2005). Although these voids are generally observed at the Cu/Cu_3Sn interface or in the Cu_3Sn-matrix, their formation at the Cu_6Sn_5 /Sn is likely due to the elevated aging temperatures used here or impurities in the flux that increase this effect (Yu and Kim 2008). Kirkendall voids are detrimental to IMC mechanical properties and this causes reliability problems in the electronic industry (Lee and Chen 2002, Yu and Kim 2008). The voids could provide an additional explanation for the mechanical loss of tinning layers, alongside the current hypothesis of wear due to polishing (Meeks 1986). Crude polishing could perhaps lead to loss of the Cu_6Sn_5 (and Sn) leaving a firm and thin Cu_3Sn layer (1-2µm) on the substrate. Unfortunately, this will resemble compositions observed on corroded surfaces of low tin bronzes (Robbiola et al. 1998). A thin ε-Cu_3Sn layer is very easily missed in SEM-BSE observation unless it is still un-corroded metal, which could be detected by XRD. For example, a substantial ε layer found under an Cu_6Sn_5 layer was identified on mercury tinned samples (Qinglin and Scott, 2003).

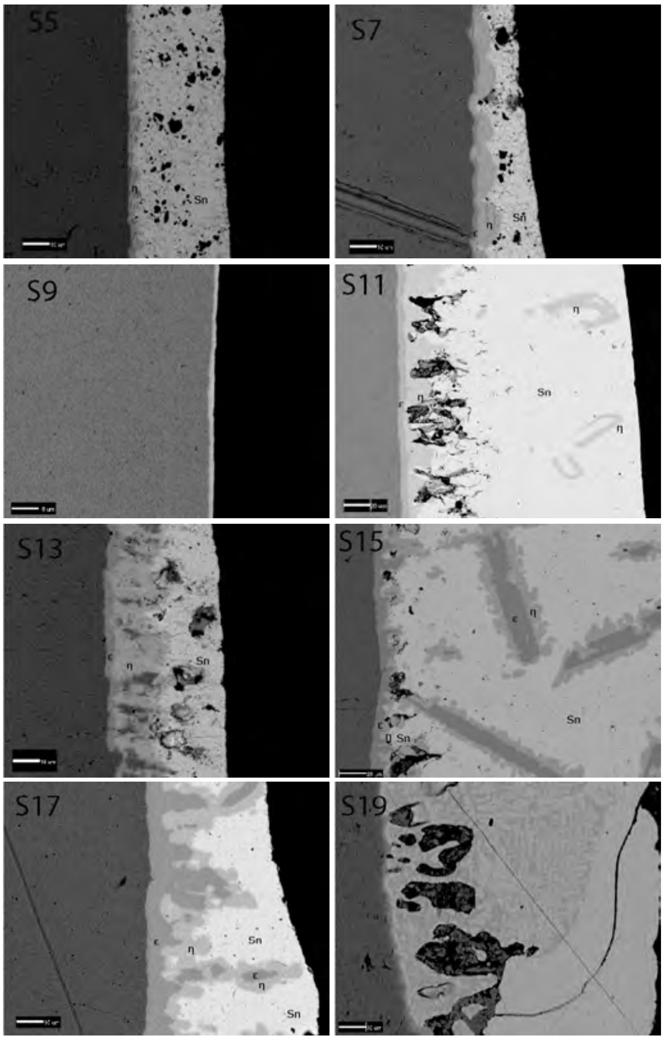

Figure 3. SEM-BSE images of annealed tinned copper tokens- *S5*: annealed for 5 minutes at 250°C. *S7:* 60 min at 250°C. *S9:* 5 min at 350°C. *S11*: 60 min at 350°C. *S13*: 5 min at 450°C. *S15*: 60 min at 450°C. *S17:* 5 min at 550°C. *S19*: 60 min at 550°C.

Archaeological bronzes

XRD and SEM-BSE detected η-Cu_6Sn_5 on the Brecon Gaer harness fitting (see Figure 4b), whereas Cu_6Sn_5 scallops were visible with BSE on the surface of the Ceredigion skillet (CER) (Figure 4a). No ε-Cu_3Sn was detected in either sample. Energy dispersive X-ray spectroscopy (EDX) elemental mapping of the Brecon Gaer cross section sample showed a complex core microstructure and a lead compound deposited locally on the surface rather than in association with the η (see Figure 4a).

Normalised (Cu+Sn+O=100wt%) EDX multiple spot analyses of Cu_6Sn_5 shows generally reduced Sn wt% and Cu wt% concentration relative to their expected concentrations due to the presence of oxygen (see Table 1). It is likely that composition reflects some oxidation of tin combined with copper dissolution from the η-phase due to corrosion. Corrosion behaviour of the IMCs is unknown. It is often deciphered by comparison to other high-tin phases, such as the preservation of δ in the α+δ eutectoid bronzes (Tylecote 1985). However, localised anodes can be formed and copper depletion from the copper-rich center of δ dendrites is reported (Scott 2002). Tin is theoretically anodic to copper and low tin bronze due to electrode potential differences (Wranglén 1972). Preservation of IMCs can be due to either the Sn/Cu bimetallic corrosion couple, where IMCs are reported to be cathodic to both copper and tin (Hedges 1960), or to the formation of thermodynamically stable tin compounds that delay corrosion rates of the underlying layers (Britton 1952, Turgoose 1985). Published analyses of corroded tin solder report its complete conversion to tin oxides (Piccardo et al. 2007), but with no reference to the presence or corrosion of IMCs. Overall, more work is required to understand the corrosion behaviour of IMCs.

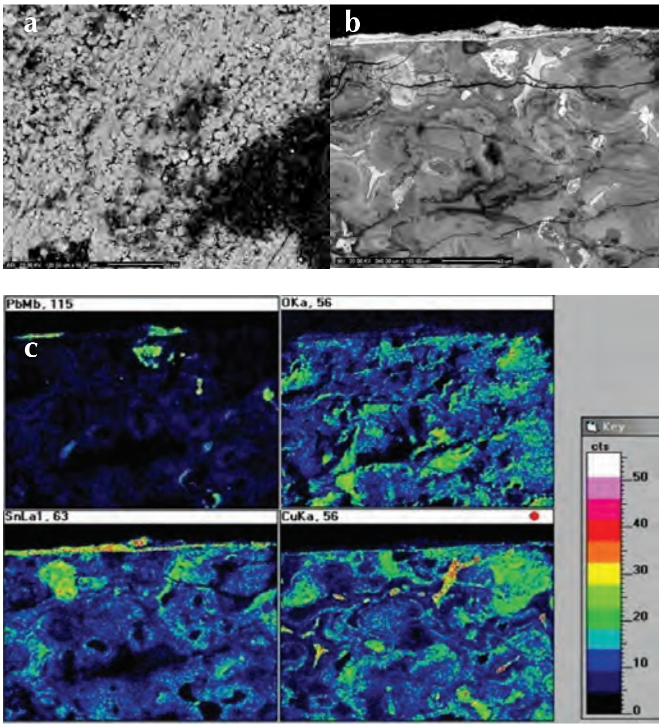

Figure 4: a. SEM-BSE of the surface of the Ceredigion skillet showing η scallops, locally overlaid by tin and corrosion deposits. b. SEM-BSE of a cross section from the Brecon Gear harness fitting showing a η scallopy layer on the surface covered by corrosion; η was confirmed by XRD. c. EDX mapping of the same sample for lead, tin, copper and oxygen showing that a lead compound is deposited on the tinning layer, and it is not associated with tinning. Oxidised tin covers part of the surface of η. The body of the bronze is oxidised with areas of increased Cu/Sn concentrations. The key indicates the counts of CuKα peak.

Conventional XRD of a sample from the Manorbier skillet and the helmet comprised mostly malachite deposits and ε or η were not detected. On the helmet sample, the surface microstructures can be characterised as a Type I corrosion structure (Robbiola et al. 1998). The surface of the helmet sample retains polishing marks and is rich in oxygen (30-50wt%) with increased tin (30-60wt%) and reduced copper concentration, fitting a Type I corrosion pattern. Similar composition ranges are detected at the surface of the Manorbier skillet, where surface colour is due to corrosion. In contrast to the Brecon Gaer harness fitting and the Ceredigion skillet where η-Cu_6Sn_5 was detected, the Manorbier and helmet samples exhibited a wrought and annealed microstructure in the core metal. Substrate texture is important for the growth of Cu_6Sn_5 (Wang et al. 2009) during tinning, so it could perhaps be significant for its preservation. Analysis of more samples is underway to examine whether cast or wrought microstructures can somehow influence the preservation of IMCs on low tin bronzes.

Object	**Position\Phase**	**Normalised Cu+Sn+O=100 wt%**		
		O	**Cu**	**Sn**
Ceredigion skillet	**Cu_6Sn_5**	19.7	31.3	49.1
Ceredigion skillet	**Cu_6Sn_5**	8.6	39.8	51.7
Ceredigion skillet	**Cu_6Sn_5**	26.6	14.3	59.1
Ceredigion skillet	**Cu_6Sn_5**	23.1	18.8	58.1
Brecon Gear fitting	**Cu rich**	35.7	55.6	8.7
Brecon Gear fitting	**Deposit**	33.3	7.6	59.1
Brecon Gear fitting	**Pb rich inclusion**	56.4	11.1	32.5
Brecon Gear fitting	**Cu_6Sn_5**	17.0	28.0	55.0
Manor Bier skillet	**Inclusion**	2.5	87.8	9.7
Manor Bier skillet	**Outer surface**	36.1	31.6	32.3
Manor Bier skillet	**Outer surface**	17.1	35.7	47.2
Manor Bier skillet	**Below outer surface**	33.7	36.0	30.4
Helmet	**Inner layer**	20.5	56.8	22.7
Helmet	**Outer surface**	30.5	23.3	46.3
Helmet	**Below outer surface**	25.0	45.9	29.0
Helmet	**Outer surface**	19.4	64.0	16.6

Table 1. EDX wt% composition analyses of archaeological samples. Each analysis is the averaged value of 3 spot analyses.

Conclusions

Laboratory experiments showed that η-Cu_6Sn_5 is the major phase formed during hot-tinning, and because of its granular nature it is easy to detect by SEM. Kirkendall voids formed on some samples, and it is suggested that these may contribute to future mechanical detachment of the tinning layers as a whole, or detachment of the Cu_6Sn_5 layer, leaving only planar ε-Cu_3Sn on the surface. Identification of thin ε layers using SEM-BSE or EDX is challenging, even for modern samples, and on corroded archaeological samples it will be very difficult to detect. This study has shown how useful XRD can be to identify evidence of tinning, while SEM analysis is of limited use.

A literature review revealed that the same IMCs are developed during application of Sn/Pb alloy coatings on bronzes. Therefore, where metal layers have been lost, it may be difficult to conclusively link occurrence of η to either tinning or a Sn/Pb coating. This can be further confusing, as analysis of archaeological samples in this paper showed that lead compounds on their surface were due to corrosion of the bulk alloy, rather than application of Sn/Pb coating.

Experimental work confirmed that heating following tinning changes IMC evidence, which means the life use of an object would influence evidence of tinning, with high temperatures eventually diffusing the tin layer into the copper alloy. Additionally, published work demonstrates occurrence of solid state diffusion at the Cu/IMCs/Sn interface at room temperature. Consequently, even prolonged exposure to hot sunlight could potentially change IMC morphology.

The overall lack of evidence for tinning on wrought low tin bronze in the literature is of concern, as it may be a result of detection limitations or corrosion processes.

For instance, our analyses of tinned archaeological samples show that some loss of copper and tin oxidation is possible in Cu_6Sn_5, but greater understanding of the mechanisms is required. Definitive identification of tinning can be very easy where an uncorroded metal layer remains intact, but will be challenging on heavily corroded bronzes.

Acknowledgements

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Materials

Elements and mineral standards Block No. 4629
Micro-Analysis Consultants Ltd
19 Edison Road, St. Ives Industrial Estate
St. Ives, Cambridgeshire, PE27 3LF, UK
Tel: (44) 1480 462626 Fax: (44) 1480 462901.
Email: standards@dial.pipex.com
Website: www.macstandards.co.uk

Tin metal 99.75wt%
Copper 99.9 wt% 3.25mm thick, half hard
Goodfellow Ltd
Ermine Business Park
Huntingdon, PE29 6WR, UK
Tel: (44) 1480 424 800 Fax: (44) 1480 424 900
Email: info@goodfellow.com
Web site: www.goodfellow.com

Hydrochloric acid
Rosin (or colophony)
Fisher Scientific UK Ltd,
Bishop Meadow Road
Loughborough, Leicestershire, LE11 5RG, UK
Tel: (44) 1509 231166 Fax: (44) 01509 231893
Email: fsuk.sales@thermofisher.com
Website: www.fisher.co.uk

Epofix Epoxy Resin
Struers Ltd.
Unit 11 Evolution @ the AMP, Whittle Way
Catcliffe, Rotherham, S60 5BL, UK
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CamScan 2040 Scanning Electron Microscope,
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X'Pert-PRO X-Ray diffractometer, with X'Pert HighScore v.2.1.2 search and match software which uses the PDF2, 2005 Release ICDD library. Housed at the National Museum of Wales, Cardiff.

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Authors

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Q & A SESSION

Aaron Shugar: Thank you for an excellent presentation, I'm glad to see your future work will include micro-structure investigation. I think that there is a program called LISPIX from NIST, it's free software and it is a quantitative mapping program. So it takes your pictures you showed of the maps – they are average maps, showing you what is above average and below average in color. This will actually take that data set and make it quantitative. So it is a free software package that you can download from NIST, and you can actually get data off it instead of just showing averaging maps.

Panagiota Manti: Excellent, thank you.

Peter Northover: I only look at these things through cross-section, and the epsilon-phase layers are often only very very thin. When you are detecting it with X-ray diffraction, you can usually see it in the cross-section optically with good enough sample preparation. But it can be very very thin. Another thought is that the tin dioxide corrosion layers can very often be nanocrystalline or amorphous. I think the last section, from what I could see with my poor eye sight from where I was sitting, looked like a very thick layer of tin dioxide corrosion, which was not particularly crystalline and was perhaps from excess tin. And it looked like a very thin layer of epsilon right up against the metal surface. It would be unusual to have a whole solid layer of epsilon as you might imagine. So I think [the thick layer] is mainly tin-rich corrosion products and there is a very thin layer of epsilon at the interface with the substrate. To me that would suggest it is tin-rich corrosion, or do you think that is corroded epsilon?

Panagiota Manti: I would expect to see epsilon here [points to thicker layer on slide]. Because this is inwards and so is unlikely to be just tin corrosion products.

Peter Northover: Yes, but there is always eta and tin on the outside of the epsilon and there can be a lot of tin and I would not expect to see epsilon as the outside layer.

Panagiota Manti: Well you can see here [points to slide] that this is a corrosion profile. Therefore this is the patina layer, this is the marker of the original surface.

Peter Northover: But that original surface might have been tin.

Panagiota Manti: Yes it could have been.

Peter Northover: What puzzles me also is that epsilon tends to be reasonably corrosion resistant.

Panagiota Manti: Is it more corrosion resistant than eta?

Peter Northover: Well delta tends to be the most corrosion resistant but epsilon is nearly as corrosion resistant as delta.

Panagiota Manti: So what about eta?

Peter Northover: Eta does corrode. If the tin corrodes, then the eta corrodes and then quite often – because there is a granular interface between the epsilon and the eta, the outside surface of the epsilon could be the first sound metal you see. I had a Master student do a dissertation on this in 1992 and you are very welcome to a copy of the thesis.

Panagiota Manti: Thank you. Can I just reply as well that you say about the epsilon and the eta phase but I think there is more that we need to know and we need to understand about the corrosion of these phases. Because we can see the eta-phase in several artifacts, but the epsilon – I just tried to point out how tricky it is to identify this phase, and especially if it is corroded. Now bearing in mind that during tinning we only have the eta phase, or we mainly have the eta phase present and a tiny little bit, a very thin layer perhaps of epsilon, which is planar in shape, it is extremely difficult to identify this phase. But that is why I think that if you have uncorroded epsilon, the best chance [of identifying it] is by x-ray diffraction. Because it just looks very very similar to corrosion of the metal.

CONSERVATION OF PIGEON CAMERAS: A COLLABORATIVE APPROACH BETWEEN CONSERVATORS AND SCIENTISTS

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Abstract

This paper presents findings from the examination and technical analysis of three small pigeon cameras from the 1930's belonging to the Swiss Camera Museum in Vevey, Switzerland. The analysis was undertaken in 2006 in preparation for a new exhibition 'des pigeons photographes' at the Museum. The small cameras were designed for attachment to the underbelly of carrier pigeons to obtain aerial photographs for military use. The components of the camera are very small and consist of different metal alloys, paint, textile and glass. Some of the components were covered by a thick later of white corrosion products. Compositional information was obtained using energy dispersive X-ray spectroscopy (EDS). The corrosion products were analyzed with micro X-ray fluorescence (XRF), micro Raman spectroscopy and micro Fourier transformation infrared (FTIR) spectroscopy. Results indicate that the alloys used in the manufacture of the camera are aluminium/magnesium, magnesium/zinc and copper/zinc alloys. The white corrosion products were found to be a mixture of magnesium acetate and magnesium carbonate hydroxide hydrate. Results also establish the presence of cellulose acetate, the likely cause of the corrosion.

Keywords: magnesium acetate, magnesium carbonate hydroxide hydrate, XRF, Raman, FTIR, XRD, aluminium alloy, magnesium/aluminium alloy.

Introduction

In 1908, aerial photographs of a castle in Bavaria, Germany, were taken by a camera developed for carrier pigeons by Julius Neubronner. However, Neubronner's invention was not made public at that time. More than 20 years later in Switzerland, Christian Adrian Michel, the head of a family business of watchmakers in Walde, Switzerland, heard about this idea, refined it and developed the first prototype camera intended for commercial production (see Figure 1). He adapted the camera to 16 mm films and without increasing the weight of the camera he introduced a miniaturised timer, which controlled the start delay as well as the time between the exposures.

After he applied for a patent, Michel proposed the use of the pigeon cameras to the Swiss army in 1937. In the same year, the first tests were carried out on aircraft at the Dübendorf (Zürich) airport. Further tests using different cameras carried by pigeons resulted in eight films of good quality. After writing a manual for the use of the camera, Michel approached various companies that could manufacture it. The outbreak out of World War II in 1939 ended the project and the pigeon cameras were never commercialised. In 2004, Michel's children donated the cameras, manuals, films and associated documents to the Swiss Camera Museum in Vevey, Switzerland (Bonnard Yersin and Bonnard Yersin 2007).

Figure 1. Historical photograph showing how the cameras were attached to the pigeon.

For decades, the cameras were stored in uncontrolled conditions in Michel's factory. By 2006, the collection was in a poor state of preservation and the Museum of Vevey sent a set of camera parts to Art Metal Conservation GmbH (AMC), a private conservation firm in Basel, Switzerland, for conservation treatment.

The complexity involved in treatment of these composite objects made a preliminary study of the cameras' materials a necessity. In order to choose the best strategies for restoration and preventive conservation, AMC approached the scientists at the Laboratory of Conservation Research (LCR) and the Laboratory of Inorganic Chemistry (LCI) at the Swiss Federal Institute of Technology in Zürich to assist with this project and to provide answers to several questions: Why were some parts of the cameras heavily corroded and others not? What were the corrosion products? Which of the materials contributed to the corrosion and what was causing it?

The pigeon camera collection

The collection of objects that were donated to the museum comprised three cameras and numerous spare parts. A visual study of these parts provided an understanding of the cameras and how to dismantle them. Examination also provided information about manufacture of the camera parts and their attachment to the camera body by methods such as welding, crimping, riveting, bolting with miniature screws and interlocking (see Figure 2 and 3).

Figure 2. Two examples of pigeon cameras.

Figure 3. The components of the release mechanism.

In comparison with common commercial cameras, the components of the pigeon cameras are like miniatures (see Figure 4; all parts of the camera referred to below are shown and numbered in Figure 4). To save weight, most of them contain holes or are made of lightweight materials. The cameras are complex devices with a small inner chamber that consists of a bottom part and an upper part made from two different, bright metal alloys (see Figure 4, number 1 is the lower part and number 2 is the upper part). The inner chamber contains the film reel that is painted black (number 3 in Figure 4), the film roll (number 4 in Figure 4), including the film itself (number 5 in Figure 4) and a reel cap (number 6 in Figure 4). The film roll and reel cap are made from a shiny, golden colored metal alloy. The interior of the inner chamber that contains the film reel is painted black, and has an opening for the attachment of an objective with lens (number 7 and 8 in Figure 4). The chamber is sealed with black textile (number 9 in Figure 4) against light. It fits into a casing that is also painted black (number 10 in Figure 4) and contains the automatic release mechanism (number 11 in Figure 4). These parts were partially dismantled for conservation.

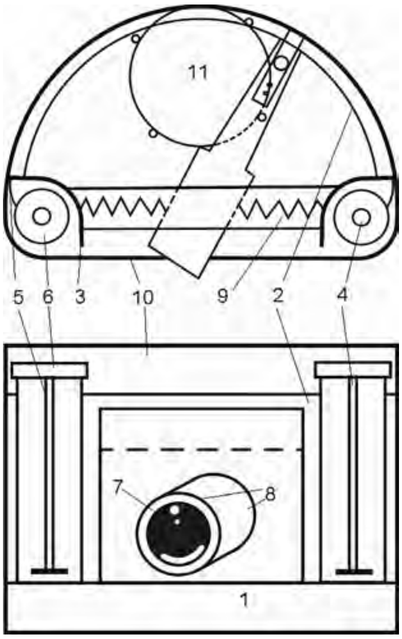

Figure 4. Schematic drawing of a pigeon camera; part numbers are referenced in the text.

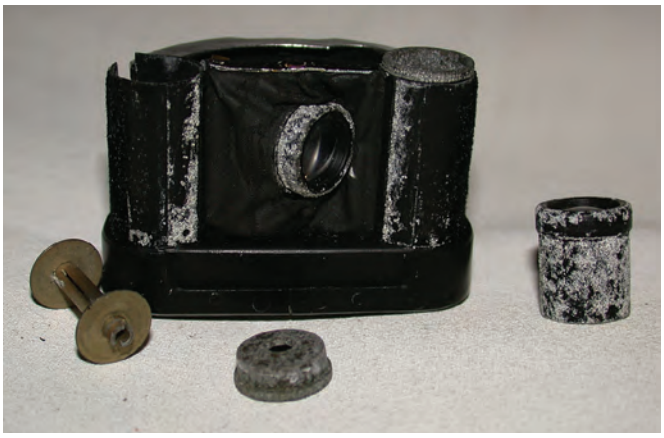

Figure 5. A pigeon camera, corroded objective and film reel before treatment. A thick white layer of corrosion is visible.

State of preservation and diagnosis

When examined, many of the cameras' parts appeared to be actively corroding with the corrosion spread over the entire camera (see Figure 5 and 8). A strikingly thick layer of white corrosion products were visible underneath the black paint and covered both the metal surface and the other materials associated with it. Another type of efflorescence consisting of light, microcrystalline powder seemed to affect only certain grey metal parts. A closer look revealed that these white corrosion products appeared only on components that were connected to other parts that appeared to be shiny and uncorroded.

Underneath the corrosion products, the metal surface was no longer smooth but appeared grainy and grey in color. It was obvious that one or more specific kinds of corrosion were occurring on the metal surfaces, a result of different metal alloys used in the construction of the camera. The corrosion affected only certain components of the cameras, such as the outer part of the lens ring, the tubes containing the film and the lids of the tubes. Some components were deeply corroded and others, such as the camera body and inner part of the objective, were immaculate.

Developing a treatment strategy

A close collaboration between scientists and conservators was essential in order to choose the best strategy for restoration and preventive conservation. It was crucial to find the possible causes and processes responsible for the corrosion and to characterise the corrosion products. Despite the fact that the cameras' parts are made from several different metals, there was no evidence of galvanic or pitting corrosion.

Given that identification of the type or types of corrosion visible on the various camera components would be the basis for devising a treatment plan, analysis began with the identification of the different white corrosion products. The next step was to determine why certain components of metal were corroding, while others appeared to be free of corrosion.

Methodology, results and discussion

The LCR works in close collaboration with curators and conservators, and specializes in the use of analytical technologies for the examination, characterisation and analysis of objects of cultural and historical interest, and conducts research on cultural heritage and historical materials. The LCR analysed the alloys and corrosion products from various camera parts using micro X-ray fluorescence (XRF), micro Raman, and micro Fourier transform infrared (FTIR). LIC carried out X-ray diffraction to characterize the corrosion products.

Metal alloys

The metal alloys of the different parts of the cameras were characterised by using an energy dispersive X-Ray fluorescence spectrometer Eagle III (EDAX, X-ray tube: rhodium target). This is a multi-elemental method (accuracy of the instrument is 0.01 % to 0.05 %) where the measurement accuracy depends upon the different elements and homogeneity of the samples. For elemental analysis, surface areas that are corrosion free are necessary for accuracy. Accordingly, very small areas (approximately 0.5 mm^2) were cleaned of corrosion using a scalpel. Approximately 30 areas with a diameter of 50 µm were analysed under the following conditions: Voltage 20 kV, current 100 µA and a dwell time per point of 200s. Because of the inhomogeneity of the alloys themselves, only a semi-quantitative evaluation was possible. Results are listed in Table 1.

Element	Bottom part of inner section (1)	Upper part of inner section (2)	Film reel (3)	Film roll (4)	Film reel cap (6)	Inner part of the objective (7)	Outer part of the objective (8)
Mg	0.7 ± 0.1	1 ± 0.05	**92.1 ± 0.2**	**93.2 ± 0.3**	**92.3 ± 0.9**	<LOD	**47.9 ± 0.2**
Al	**98.3 ± 0.2**	**94.2 ± 0.3**	**7.1 ± 0.2**	5.5 ± 0.3	5.7 ± 0.4	<LOD	<0.1
Cu	<0.1	<0.1	<0.1	0.3 ± 0.05	0.4 ± 0.1	11 ± 0.5	<0.1
Zn	<0.1	<0.1	<0.1	<LOD	<LOD	89 ± 0.5	**50.9 ± 0.2**
Mn	<LOD	0.8 ± 0.1	0.5 ± 0.05	0.6 ± 0.1	0.7 ± 0.2	<LOD	<0.1
Si	0.4 ± 0.1	3 ± 0.2	<LOD	<LOD	<0.1	<LOD	<LOD
Fe	0.4 ± 0.05	0.5 ± 0.1	<LOD	<LOD	0.4 ± 0.1	<LOD	<0.1
Cr	0.2 ± 0.05	<0.1	0.2 ± 0.05	<LOD	0.2 ± 0.1	<LOD	<LOD
Ti	<LOD	0.3 ± 0.05	<0.1	<0.1	<LOD	<LOD	<LOD
Ni	<LOD	<LOD	<0.1	<0.2	0.2 ± 0.05	<LOD	<0.1

Table 1. Semi-quantitative analysis of the composition of the metal from various camera components by means of XRF (w/w %, LOD: limit of detection)

Results indicate that the camera components are made from metals of four different compositions:

The film reels (number 3 in Figure 4), reel caps (number 6 in Figure 4) and film rolls (number 4 in Figure 4): a magnesium/aluminium alloy (Mg 92-93%, Al 5-7%), with traces of Ni, Cu and Fe. The outer part of the objective (number 8 in Figure 4): a zinc/magnesium alloy (Zn 51%, Mg 48%), with traces of Ni, Cu and Fe. The inner part of the objective (number 7 in Figure 4): a zinc/copper alloy (Zn 89%, Cu 11%). The upper and lower part of the body (number 1 and 2 in Figure 4): an aluminium alloy.

The magnesium/aluminium alloy is a relatively modern alloy that is a wrought or cast, lightweight material with a low density. These early magnesium alloys are not very resistant against corrosion because of impurities. Today, it is well known that copper traces, iron and nickel can promote galvanic corrosion of the magnesium matrix. It is now possible to produce very pure magnesium aluminium alloys that are less prone to corrosion (Oettel and Schumann 2005). The high strength-to-weight ratio of magnesium and aluminium base alloys made them attractive for applications such as the pigeon cameras.

Film material, textile and black paint

The examination of the film with a binocular microscope showed that it was made from two layers of different materials. For the FTIR analysis, a spectrometer Biorad Excalibur FTS 3000 coupled to an Infrared microscope UMA 500, fitted with a mercury cadmium telluride detector was used. Measurements were performed using a micro diamond anvil cell in transmission mode (4000-650 cm^{-1})). It was possible to take small samples (0.2 mm^2) of the carrier material and the surface of the film with a scalpel. The samples were pressed with a diamond cell in order to obtain thin films for the analysis. The spectrum obtained from the carrier material shows the characteristic peak of cellulose acetate, whereas the spectrum obtained from the surface of the film shows peaks that can be attributed to gelatine, normally used as film surface (Neumüller 1985, Socrates 1998, Derrick 1999). A sample of the textile was obtained for analysis using the same method described above. The FTIR spectrum of the textile shows that the main component was cellulose acetate.

The black paint was first analysed using XRF, however, the spectrum obtained did not show relevant functional peaks. The absence of fluorescence peaks indicates that this compound is most likely organic, that is, it may contain only elements with an atomic number smaller than 10. Another sample of the paint was analyzed by FTIR, however the spectrum also did not show relevant functional peaks. A third sample was analyzed by Raman spectroscopy and results showed that the paint was mainly composed of carbon black.

Corrosion products

Compositional analysis revealed that all of the highly corroded components are made of a magnesium/aluminium alloy, with small amounts of aluminium, or of a zinc/magnesium alloy. For the characterisation of the corrosion products by Raman spectroscopy, small samples were removed with a scalpel from the corroded parts of the camera. All Raman spectra were acquired on a LabRam Aramis (Horiba Jobin Yvon) equipped with a Peltier cooled open-electrode CCD (1024x256 pixel), fully automated grating system (600-1800 gr/mm), edge filter and laser selection between a diode laser at 785 nm, a He/Ne laser at 632.8 nm and a Nd:YAG laser at 532 nm. Each corrosion product was pressed on an aluminium plate and positioned on the microscope stage for analysis. Spectra were collected using the 532 nm laser, applying laser power between 0.084 and 0.84 mW (600 gr/mm). Measurement times varied from 100 seconds to 250 seconds. The results indicate that there are two different corrosion products present on the camera (see Figure 6). One is magnesium acetate ($Mg(CH_3COO)_2 \cdot 4\ H_2O$), the other a hydrated basic carbonate of magnesium, perhaps hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), dypingite ($Mg_5(CO_3)4(OH)_2 \cdot 5H_2O$), artinite ($Mg_5(CO_3)_4(OH)_2 \cdot 3H_2O$), or giorgiosite($Mg_5(CO_3)_4(OH)_2 \cdot 5\text{-}6H_2O$). With Raman analysis it was not possible to distinguish between the different hydrated basic carbonates of magnesium as their spectra are too similar (Canterford 1984, Frost 2008 and Twilley 2006).

For this reason, more specific results were sought by X-ray powder diffraction (Stoe STADIP, $Cu_{K}\alpha_1$-radiation, Ge-monochromator). The results showed that the thick white corrosion products were the same on all three parts of the camera (see Figure 7). This analysis did not detect magnesium acetate, most likely because of its non-crystallinity, but showed that the main component was in fact giorgiosite ($Mg_5(CO_3)_4(OH)_2 \cdot 5\text{-}6H_2O$).

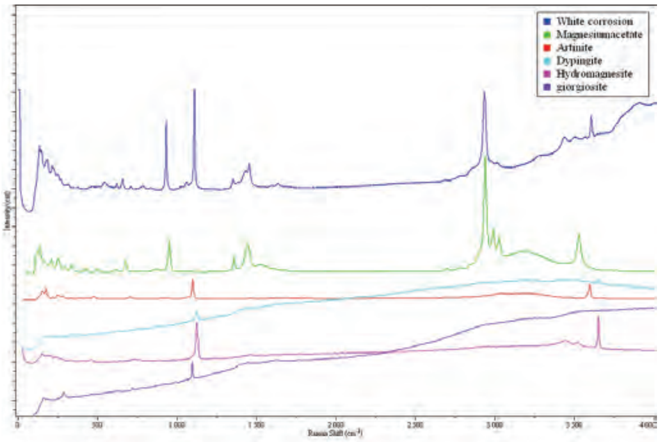

Figure 6. Raman spectra of the corrosion products analyzed from the cameras: unidentified white corrosion products and magnesium acetate were identified in 2006 (dark blue and green spectra), and artinite, dypingite, hydromagnesite and giorgiosite were identified in 2010 (red, light blue, pink and purple spectra), with a shift of circa +10cm-1 due to the aging of the laser.

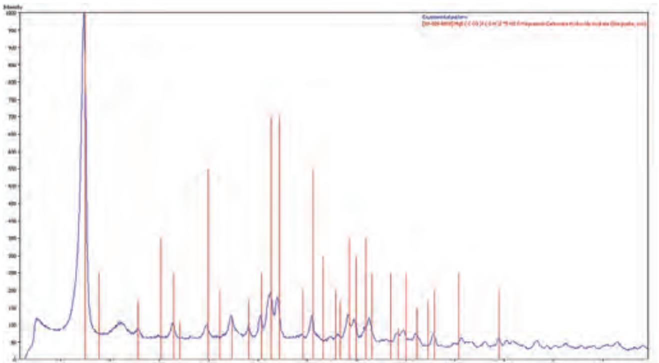

Figure 7. X-ray pattern of the thick white corrosion product, with major phase identification.

Discussion

The most probable reason for the formation of these corrosion products was acetic acid. In this case study, the potential sources of acetic acid are multiple. One possible source could be the cardboard box in which the cameras were stored, which was not acid-free. A second source could be the cellulose acetate contained in the photographic films and the black textile, which forms acetic acid by hydrolysis. This free acid can act like a catalyst for ongoing hydrolysis and reduction of the polymerisation degree. The degradation is promoted by increased relative humidity (RH) (Mills 1994, Waentig 2004).

A complete and detailed reconstruction of the corrosion process is difficult, because on one hand there are several potential sources of acetic acid (cardboard, films, textiles) and on the other hand, past storage conditions for the objects are not well known and could have changed several times.

Treatment

After determining the potential causes of the corrosion, a conservation strategy was developed. Because these objects were very unusual, no conservation literature about these objects was found. A search of the industrial literature for possible solutions was undertaken, and a decision was made to use a solution of 1g/dm^3 of sodium benzoate as a corrosion inhibitor (Rosliza 2007).

After removal of the thickest corrosion layers mechanically, most of the remaining corrosion was removed by means of compresses containing a mixture of ammonium citrate, ethylenediaminetetraacetic acid (EDTA) and phosphoric acid. The last corrosion layers were then stabilised with sodium benzoate.

Once it was established that acetic acid had contributed to the formation of the corrosion products that contained acetate, the project conservator used acid-free cardboard boxes to store the cameras, and removed the cellulose acetate films for storage in a separate box. To provide isolation, the black cellulose acetate textiles were separated from their metal support by a layer of acrylic (Paraloid B-72, 5% solution in toluene). In addition, a permanent acetic acid measuring device was placed in the showcase and the storage boxes (A-P-Strips, IPI, Rochester Institute of Technology, Rochester, NY) together with pollution absorbers (Zinc oxide and active charcoal textile).

In order to protect the most sensitive components made of magnesium/aluminium and magnesium/zinc alloys from an aggressive environment (organic acid) and humid atmosphere, the surfaces were coated with 5% Paraloid B-72 in toluene. All moving parts of the camera were coated with mineral oil, and mineral wax was used to coat the static components.

After conservation was complete (see Figure 9), the pigeon cameras were returned to the Swiss Camera Museum in Vevey and have been on exhibit there ever since with no corrosion problems noted (Berger 2008).

Conclusion

The conservation of three pigeon cameras was a close collaboration between AMC, LRC and LIC. The analytical results showed that different parts of the cameras were made from different metal alloys (magnesium/aluminium; zinc/magnesium, zinc/copper and aluminium). Only the magnesium alloys were covered with a thick corrosion layer. It is known that earlier magnesium alloys are not pure enough to be resistant against corrosion. The white corrosion layer turned out to be a mixture of magnesium acetate and magnesium carbonate hydroxide hydrate. The analytical study of the materials used for the manufacture and storage of the cameras showed that the corrosion was mainly due to the presence of acetate in films and textiles, leading to the release of acetic acid, combined with free acids originating in the cardboard boxes. These results were important for selecting the treatment and long-term preventive conservation strategy.

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Figure 8. A pigeon camera before treatment

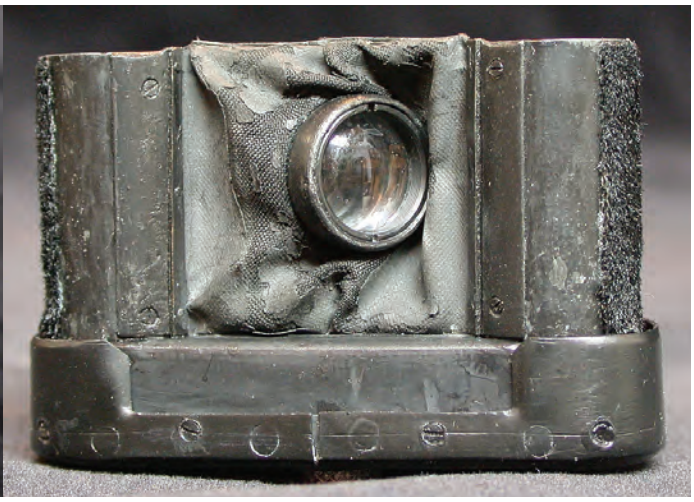

Figure 9. A pigeon camera after treatment

Materials

Paraloid B-72, Paraffin oil, wax Cosmoloïd H 80, EDTA and anionic soap

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Mobile: + 41 (0) 79 475 91 98
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AP strips and pollution absorbers
Long Life for Art
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Tel. +49 (0) 7663 608 99-00
Fax +49 (0) 7663 608 99-20
E-Mail: info@llfa.de
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Ammonium citrate, phosphoric acid, white spirit and sodium benzoate
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Fax: +41 44 745 13 38
E-Mail : info@ch.vwr.com
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Q & A SESSION

Tom Chase: How did the cameras work exactly? Did the lens move as they were shooting?

Olivier Berger: Yes exactly. You have a different way to program it, which means that you have the timer, where it will start, you can have maybe 24 h, where it will restart. And there is this movement so that between the different pictures you also have a timer so you can choose the times that you want. There are two types of cameras – there is one for 40 pictures and another for 7 pictures, which means that you have different lengths of the opening in front of the camera. And it is just done with springs and is fully mechanically operated.

Tom Chase: I have an observation too: the corrosion that you see in your photographs looks very much like what we see on Japanese lead objects in museum cases. I have dealt with a lot of that at the Freer Gallery in Washington DC- that sort of powdery deposit of the little spots – I think that may be a characteristic of a sort of gas-related atmospheric corrosion or something.

Olivier Berger: Yes, exactly. Elodie Guilminot told me: your problem looks like what we have on the lead – an acetic problem. And it was exactly that – it was the vapor of organic acids.

Paul Mardikian: How did you choose a corrosion inhibitor and how did you apply it?

Olivier Berger: As you can imagine there is no literature. There are not so many things on aluminum – for industry you have chromatization of the surface to stabilize the oxide and things like that but on chlorides you have nothing and for acetate, you really have nothing to act as a corrosion inhibitor. Basel is the center of chemistry in Europe and I have friends who are corrosionists, studying corrosion. One of my friends mentioned a publication in Malaysia from 6 years ago about a treatment of aluminum from seawater – this will interest Ian MacLeod as well for it was treated with benzoate, and I thought that is very interesting as we have no solution for lead [corrosion problems] either with regards to lead acetate. So we applied the benzoate, it is very easy to dissolve in water, the protocol was fully described in the article and we used the same protocol. We didn't have any background of course about this product, but it was our last chance! We applied it with a brush.

Dave Thickett: How damp was the basement that this was stored in? Did you get any humidity readings?

Olivier Berger: They were stored 70 years in a factory cellar. The paper components of the storage boxes were in good condition and there was no fungal growth, so I think it was quite a dry environment, but with cardboard boxes like that, very quickly you get organic acid formation. There was also the cellulose acetate textile which was inside and out, so the problem was internal and external (with two sources of acetic acid vapor).

Dave Thickett: I think that quite likely, even if the cellulose acetate was not there, the box almost certainly would have caused the corrosion. And another comment: although the boxes weren't acid free, even acid-free boxes give out quite a bit of acetic acid.

Olivier Berger: Yes, this meant that we also needed sorbents. This could be done easily with activated carbon in the cases.

David Hallam: A comment on the alloys you have there. One of the fascinating things about this project is the alloys you have are what I would call early prototype alloys. The Mg-Zn alloys really didn't prosper because they were such horrible alloys and they corroded so easily. The magnificent thing about this camera is that the crazy thing survived. Normally those alloys would have self-destructed, even if you think about moisture and a little bit of acetic acid, they would just self-destruct and normally through intergranular corrosion.

Olivier Berger: Yes, usually you could use them as a sacrificial anode on a boat or a submarine and at even minimal relative humidities they would degrade.

David Hallam: Yes. The problem with the Mg-Zn alloys is – quite often they have tiny amounts of lead in them and it is this that made them totally self-destructive.

Olivier Berger: We also had so many different alloys that they [the cameras] were galvanically corroding, and we were lucky to find them again!

TECHNICAL ANALYSIS OF MUNTZ METAL SHEATHING FROM THE AMERICAN CLIPPER SHIP *SNOW SQUALL* (1851-1864)

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Abstract

Sheathing materials from the American clipper ship Snow Squall *(1851-1864) were examined with polarized light microscopy (PLM), Fourier Transform Infra-Red (FTIR) Spectroscopy, x-ray fluorescence (XRF), scanning electron microscopy (SEM) electron probe microanalysis (EPMA) and metallographic techniques. Results indicate the padding beneath the sheathing is jute, with evidence of shellac and tar. Sheathing without a Muntz stamp is an alpha phase brass analyzed as 67.9% copper and 30.1% zinc. Sheathing with a 'Muntz's 24 Patent' stamp is an alpha phase brass on the verge of beta phase formation, analyzed as 64.5% copper, 37.4% zinc, 0.1% lead and a trace of iron. Patent stamped sheathing analyzed from the barks Petrel (1847-1853) and* Eglinton *(1848-1852) are contrasted with Snow* Squall's *analyses and together suggest a change in Muntz alloy composition occurred between 1847 and 1863. Muntz stamp designs and Muntz family patents are also briefly described.*

Keywords: *Eglinton,* nergandin, metallurgic analyses, Muntz metal, Muntz stamps, *Petrel,* punching machine, *Snow Squall*

Introduction

Analytical analysis returned unexpected results during an investigation to find suitable cleaning techniques for *Snow Squall*'s Muntz patent stamped sheathing. A literature search for analytical studies performed on sheathing with Muntz patent stamps returned little information, prompting a search for Muntz sheathing patents. These searches revealed that little is known about Muntz metal. This study reports information to encourage future Muntz metal research.

Historical Background

Brothers Alford and Cornelius Butler built the 742 ton clipper ship *Snow Squall* in 1851 in Maine, USA. The ship was condemned and abandoned in Stanley, the Falkland Islands in 1864.

Wooden ships were sheathed with copper, copper alloy or zinc sheathing to protect the hull from marine shipworms. *Snow Squall*'s last sheathing was in 1862 (*Registre* 1864), in New York during October (*Shipping & Commercial List* 1862). A final repair job is noted in May of 1863, in Singapore (Singapore Straits Times 1863). Over a 13-year sailing career *Snow Squall* likely experienced seven full sheathings, see Table 1. Today, the largest remaining part of the *Snow Squall*'s hull is at the Maine Maritime Museum in Bath, Maine. (Dean 2001). See Figure 1.

Figure 1. Port view of *Snow Squall*'s lower bow with its ship model in front.

Sheathing change	Sheathing Location	Date
1	Butler Yard, South Portland, Maine, USA	1851[A]
2	Shanghai, China or New York, USA	1853 or 1854[B]
3	New York Balance Dock, USA	Feb. 1856
4	Mare Island Naval Shipyard San Francisco, California, USA	Feb. 1857
5	James and John Dillon's Fort Hill Drydock, Boston, Massachusetts, USA	July 1858
6	Amoy, China	Dec. 1860
7	New York Sectional Floating Dry Dock, Pier 49, New York, USA	Oct. 1862
unknown	Singapore	May 1863[C]

A. It is speculated that Snow Squall was sheathed when launched in 1851, but no record has been found to confirm this. Her sister ship Warner was sheathed when launched from the same yard in 1852.

B. Speculation. No records have been found to verify when re-sheathing occurred.

C. *Snow Squall* was listed as repairing in Singapore.

Table 1. History of *Snow Squall*'s sheathing.

Physical Examination of *Snow Squall's* Sheathing

Ship sheathing practice has been published (Ronnberg 1974, Ronnberg 1980, Staniforth 1985, Jones 2004, McCarthy 2005). *Snow Squall*'s sheathing plates are 14 x 48 inches (35.5 x 124.9 cm) and 19 of her remaining 34 (55%) full plates bear double oval 'Muntz's 24 Patent' stamps. Muntz metal sheathing plate thickness was gauged by weight; thus, 24 gauge was a plate weighing 24 ounces per square foot (7.32 kg/m^2) (Butts 1858). This was sufficient to last three years (Ronnberg 1980).

The sheathing condition varies from intact plates to fragments retained only by lapping plates or fastenings. The plates are fastened to the hull with flat-head, cast copper alloy nails. The margin nail spacing is irregular, averaging 1.7 inches (4.3 cm), and likely was done by hand. The remaining 42 nail holes are arranged in five rows with an average spacing of 5.3 ± 0.1 inches (13.5 ± 0.25 cm) punched by machine (see Figure 2) or by hand using a template. Beneath the sheathing there is padding made of loose fibers with thick black residue on the side that once adhered to the outer planking.

Figure 2. A 19th-century sheathing punching machine, collected from mid-coast Maine. Courtesy of the Maine Maritime Museum.

Muntz Metal Stamps and Patents

The wreck of the Tasmanian-built 195 ton bark *Petrel* (1847-1853) resurfaced on Hope Beach, South Arm, Tasmania, in July 2006 (Knott, 2008). *Petrel*'s bow sheathing bears double oval 'Muntz's 26 Patent' stamps. 'Muntz' refers to Birmingham, England's, George Frederick Muntz Sr., the creator of the alloy called Muntz metal that was patented in 1832 (Flick 1975). See Figures 3 and 4 for examples of oval Muntz stamps.

Figure 3. *Snow Squall*'s 'Muntz's 24 Patent' stamp with a broken outer oval line and solid inner oval line. The number 24 (gauge) is repeated twice in the outer oval.

Figure 4. *Petrel*'s 'Muntz's 26 Patent' stamp with solid oval lines and the number '2' in the outer oval. The rest of the mark is worn off. Courtesy, Peta Knott.

Muntz patent stamp designs also included double circles with the gauge in the center ring and the outer ring words 'Muntz's' and 'Patent' separated by '40' or '41' (McCarthy 2005, Stanbury 2009). The '40' and '41' numbers remain a mystery, possibly some internal Muntz company code (Callcut 2010). A piece of ship sheathing recovered from the Eighty Mile Beach in Western Australia bears a double oval stamp with three crowns and the words 'PH Muntz 1872' (Stanbury 2009). A similar stamp on a copper alloy tambourine is viewable on Vin Callcut's[1] old copper website.

George Frederick Muntz's 1832 patent No. 6325 for sheathing allowed for a mix of copper and zinc 'in any proportions between fifty per cent. of copper to fifty per cent. of zinc, and sixty-three per cent. copper to thirty-seven per cent. of zinc', but 'I prefer the allow [alloy?] to consist of about sixty per cent. of copper to forty per cent. of zinc.' (Bruzelius 2008).

At 40% zinc content, the alloy would be two-phased

Patentee	Great Britain (GB) Patent date	Patent No.	Brief Patent Content summary (Cu=copper, Zn=zinc, Pb=lead; Sn=tin Ratios in %)	Source
George Frederick Muntz, Senior (GFM Sr.), creator of original Muntz metal.	1832, October 22	6325	Sheathing: Mixes Cu:Zn in preferred proportion of60:40. States Cu to Zn can vary from 50:50 to 63:37.	B.
George Frederick Muntz, Senior	1832, December 17	6347	Ship Fastenings: Same alloy specification as No. 6325.	B.2
George Frederick Muntz, Senior	1846, October 15	11,410	Sheathing: This formula reduces the copper percentage and adds lead. Cu:Zn:Pb=56:40.75:3.25; usual caveate that Cu and Zn percentage can be higher or lower.	C.
George Frederick Muntz, Jr. (eldest son of GFM Sr.)	1852, May 8	14,117	Tubes: Muntz metal tube manufacture Cu:Zn=60:38.	D.
William Henry Muntz, (son of GFM Sr.?)	1853, October 11	2,334	Improvement to paddle wheels for navigable vessels.	E. pg 214
George Frederick Muntz Jr.	1858, Mar 19	572	Sheathing manufacture: Melts alloys in closed vessel and then adds zinc.	A. pg 373
George Frederick Muntz Jr.	1858, May 21	1134	Sheathing manufacture: rolls hot until 5% of desired gauge, anneals, rolls cold to gauge.	A. pg 383
George Frederick Muntz Jr.	1861, March 13	620	Sheathing iron ships: yellow metal sheathing, India-rubber (electrical insulator) and iron sheeting is combined in heated press. Specific manufacturing details are explained.	C.
George Frederick Muntz Jr.	1861, August 20	2076	Sheathing iron ships: Yellow metal with India-rubber or gutta percha insulator layer is attached to iron sheathing so insulator touches iron. Non-conducting fasteners of ebonite or wood pegs specified.	C.
William Henry Muntz	1863, January 2	18	Attaching sheathing to iron or other vessels: India rubber etc. insulating material to vessels side, add sheathing by use of marine glue or adhesive material instead of nailing or riveting.	F. pg 506
Philip Henry Muntz (younger brother to GFM, Sr.)	1864, February 27	491	Sheathing: Uses the term "spelter" for zinc. New formula uses tin. Cu:Zn:Sn = 60.25:39:0.75	C.

A. Abridgements of the Specifications relating to Metals and Alloys (excepting Iron and Steel). 1861

B. http://www.bruzelius.info/nautica/Shipbuilding/Patent(GB6325).html

B.2 http://www.bruzelius.info/nautica/Shipbuilding/Patent(GB6347).html

C. Archives and Heritage Services, 6th Floor, Central Library, Chamberlain Square, Birmingham (England) B3 3HQ

D. The Mechanics' Magazine, museum, register, journal and gazette, Vol. 57 July 3 - Dec. 25, 1852 pg 416

E. Chronological index of patents applied for and patents granted… Oct., 1852 - Dec., 1953. Pub. 1860

F. Specification and Abridgements relating to Electricity and Magnetism… Part II, 1858-1866 pub. 1870

Table 2. A partial list of Muntz family patents.

with grains of alpha phase and an infill of beta phase[2]. Muntz rigorously defended his 60:40 (this refers to the weight percentage of the two principal components: 60% of copper and 40% of zinc) brass alloys' composition from piracy in a landmark 1844 court case and until his 1832 patent expired in 1846 (Flick 1975), the year his leaded 56:40.75 brass sheathing formula was patented (see Table 2). A leaded 70:28 brass Muntz alloy called nergandin[3] also existed but the time period is currently unknown.

Experimental

Snow Squall

One inch^2 (2.54 cm^2) samples were removed from the hull by Carlson and sent to Dr. David Scott of the University of California at Los Angeles/Getty Conservation Program for analysis.

An Olympus BH80 polarizing light microscope using bright field and polarizing light optical methods was used to identify the sample of sheathing padding material[4]. A Perkin-Elmer Fourier Transform Infra-Red Spectrometer (FTIR) using a diamond cell Attenuated Total Reflectance (ATR) accessory obtained a series of spectra from the padding[5].

A Bruker, Keymaster portable X-ray fluorescence (XRF) instrument[6] was used to analyze four samples, a degraded sheathing sample 'Port PO2', nail sample 'Nail PO2', a sheathing sample in good condition 'Port 80E', and nail sample 'Nail 80E'. Some XRF data was obtained from un-embedded, corroded, unpolished face surfaces. Other results are from embedded, mounted, ground and polished cross section surfaces so that no gross corrosion effects of the XRF data occurred.

Scanning electron microscopy (SEM) using a Joel Superprobe Electron Probe Microanalyzer (EPMA) [7] was used for microanalysis of four sheathing samples, two of 'Starboard 32C' and two of 'Port 80C', that directly bore the 'Muntz's 24 Patent' stamp.

Metallographic examination was carried out by mounting the samples in Buehler epoxide resin[8]. Photographic records were made using a Nikon epiphot metallograph with apochromatic infinity adjusted focus, employing a Nikon D300 camera body and Nikon Camera Control Pro 2 software.

Petrel

Knott removed 1 inch^2 (2.54 cm^2) samples of *Petrel*'s unstamped and stamped sheathing and sent them to the School of Earth Sciences, University of Tasmania (UTAS) where Simon Stephens prepared both samples as embedded and polished cross sections for subsurface analysis following *Snow Squall*'s protocol. Dr. Ron Berry photographed the samples using a Zeiss Axioskop microscope using a Spot Flex camera. Dr. Karsten Goemann (Goemann 2009) from the Central Science

Laboratory, UTAS, analyzed them using a Cameca SX100 EPMA with SEM wavelength dispersive spectrometry (WDS)[9].

Results and Discussion

Snow Squall

Snow Squall's sheathing padding comprises bast fibers, characterized as jute, *Corchorus* sp. Shellac and a degraded tree resin that best matched common yellow resin or *Pinus sylvestris* were detected by FTIR. Sheathing paper, canvas and felt[10] attached to ship planking by tar or pitch have been documented beneath sheathing (Staniforth 1985). Jute padding sized with shellac has not been previously reported.

XRF results are reported in Table 3. The 'Port PO2' sheathing face samples may show a loss of copper and zinc, with the result that some zinc is present in the corrosion products enhancing the percentage of detected zinc. The 'Port 80E' polished cross section subsurface sheathing sample 2.3 presented reliable composition data of 67.9% copper, 30.1% zinc, 0.8% lead and 0.39% iron. This is close in composition to a 70:30 copper:zinc alloy called cartridge brass and also suggests the alloy nergandin. The sample 'Nail-PO2' contained copper, zinc, iron and lead. Sample 'Nail-80E' contained the same elements, plus nickel, arsenic and tin that suggests it might have been an Admiralty brass, an alloy formulated with tin to resist dezincification.

SEM results of Muntz stamped sheathing composition are reported in Table 4. SEM backscattered electron images document 0.1% lead analyzed in each sample (see Figure 5). The average composition of sample 'Starboard 32C' from three analyzed matrix points was 64.3 ± 0.15% copper , 37.5% ± 0.10% zinc, 0.04 ± 0.03% iron and 0.1% lead. The average composition of sample 'Port 80C' from four analyzed matrix points was 64.5 ± 0.37% copper, 37.4 ± 0.24% zinc, 0.07 ± 0.02% iron and 0.1% lead.

Metallographic examination of the XRF samples revealed that both of the nail tips' microstructure are a cored dendritic cast morphology that was alpha phase, with no beta phase precipitate present. The unstamped sheathing samples are all alpha phase, confirming the impression from the XRF results that these are alpha phase brasses with a zinc content of about 30% (Scott 2008). Binary copper:zinc alloys of 30% zinc content can absorb all of the zinc into the alpha solid solution, and therefore there is no secondary beta phase.

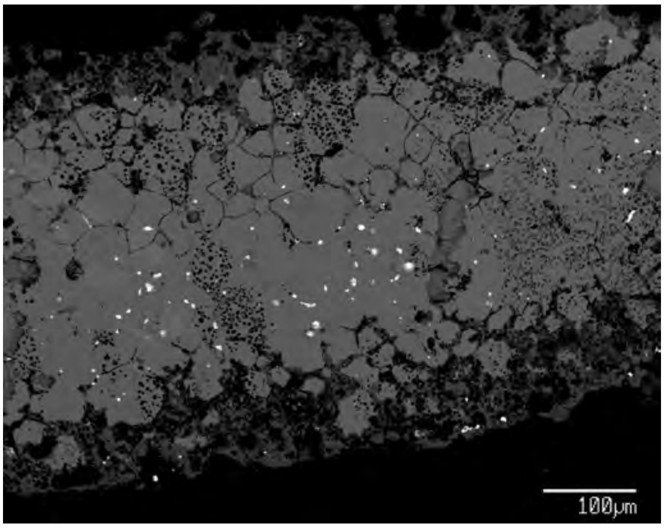

Figure 5. SEM backscattered photo of *Snow Squall*'s sample 'Port 80C'. The bright spots of lead and the corroded alpha grains are visible.

Material tested	**Elements Tested %** (no detection for Bi, Ag, Sb, Mn)								**Comments**
	Iron	Nickel	Copper	Zinc	Arsenic	Lead	Tin	Total	
Unstamped Sheathing									
Good Condition 'Port 80E' sample- (Subdivided into an unembedded face sample and an embedded cross section sample: Two matrix points for each subsample analyzed.)									
2.1 face section	4.50	0.40	67.50	16.50		2.00		90.90	This is an unembedded surface sample. Ingress of iron corrosion products is present on the surface of the sample. Low zinc levels reflect corrosion and dezincification.
2.2 face section	3.20	0.20	68.50	18.00		1.00		90.90	This is a duplicate surface sample.
2.3 cross section	0.39	trace	67.90	30.10		0.80		99.20	This is an embedded polished sub-surface sample unaffected by corrosion products and reflects the true composition of sample 'Port 80E'.
2.4 cross section	0.40		66.90	30.00		0.80		98.10	This is a duplicate polished sub-surface sample.
Degraded 'Port PO2' sample- (Two matrix points analyzed.)									
2.5 face section	0.40	1.20	59.80	37.00		0.80		99.20	This is an unembedded surface sample that is a very degraded alloy. Both copper and zinc loss may have occurred here, with the result that some zinc is present in the corrosion products, influencing the apparent zinc percentage.
2.6 face section	0.40	1.00	60.20	36.70		0.70		99.00	This is a duplicate surface sample.
Nails									
Nail PO2' sample									
2.7 head of nail	1.15		38.50	54.90		1.90		96.45	This is an unembedded sample that is heavily degraded with unreliable composition figures.
Nail 80E' sample									
2.8 head of nail	1.60	2.80	63.70	23.20	0.60	6.00	0.68	98.58	This is an unembedded sample. This alloy is closer to Admiralty brass due to the presence of arsenic and tin.

Table 3. X-ray Fluorescence analysis of Snow Squall's unstamped sheathing and nails.

Elements Tested %		Copper	Iron	Sulfur	Zinc	Lead	Total
Snow Squall (1851-1864, American built) **'Muntz's 24 Patent' stamp** The last sheathing was in 1862, New York, with repairs in 1863 in Singapore.	'Strb. 32 C' sample						
	pt. 1	64.20	0.05	0	37.60		101.85
	pt. 2	64.30	0.01	0	37.40		101.71
	pt. 3	64.50	0.06	0	37.50		102.06
	Average	64.33	0.04	0	37.50	0.10	
	Standard deviation	0.15	0.03	0	0.10		
	'Port 80C' sample						
	pt. 1	64.03	0.10	0	37.68		101.91
	pt. 2	64.53	0.08	0	37.25		101.87
	pt. 3	64.46	0.05	0	37.43		101.94
	pt. 4	65.03	0.06	0	37.13		101.22
	Average	64.54	0.07	0	37.37	0.10	
	Standard deviation	0.37	0.02	0	0.24		
Petrel (1847-1853, Tasmanian built) **'Muntz's 26 Patent' stamp**	'M2' sample						
	pt.1	63.90	0.045	<0.02	36.70	<0.06	100.70
	pt.2	63.70	0.042	<0.02	36.90	<0.06	100.60
	pt.3	63.40	0.042	<0.02	37.00	<0.06	100.60
	pt.4	63.60	0.046	<0.02	37.30	<0.06	101.00
	pt.5	63.30	0.042	<0.02	37.10	<0.06	100.50
	pt.6	63.10	0.047	<0.02	37.30	<0.06	100.50
	pt.7	64.70	0.034	<0.02	36.90	0.08	101.70
	pt.8	63.50	0.049	<0.02	37.10	0.09	100.70
	pt.9	63.90	0.038	<0.02	36.70	<0.06	100.70
	pt.10	63.50	0.037	<0.02	36.80	0.10	100.40
	Average	63.60	0.042	*	37.00	*	
	Standard deviation	0.40	0.005	*	0.20	*	
	3s precision +/-	0.40	0.01	0.02	0.30	0.05	

* statistical calculation not possible as some or all individual values below detection limit.

Table 4. Scanning Electron Microprobe analysis of Muntz-stamped sheathing from *Snow Squall* and *Petrel*.

Metallographic examination of the Muntz stamped sheathing samples 'Starboard 32C', 'Port 80C' and 'Port 70C', revealed identical microstructures, essentially an alpha phase brass but just at the boundary where the beta crystals are beginning to form. The beta phase is electrochemically anodic to the alpha phase in seawater, which results in the selective corrosion of the beta phase, the weakening of the structure and often the re-deposition of copper where the beta phase once was. See Figures 6 and 7.

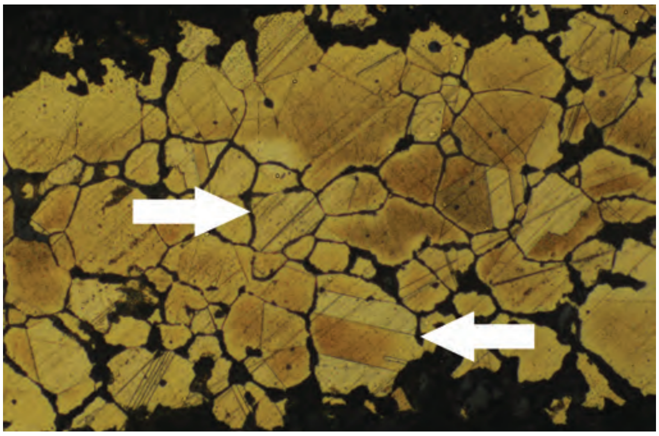

Figure 6. *Snow Squall*'s degraded 'Port PO2' alpha phase sheathing. Twin grains (*right arrow)* are visible with slip lines (*left arrow)* in some areas showing cold-working of the sheet after final annealing of the brass. This could reflect George Frederick Muntz Jr.'s 1858 patent No. 1134. 80x.

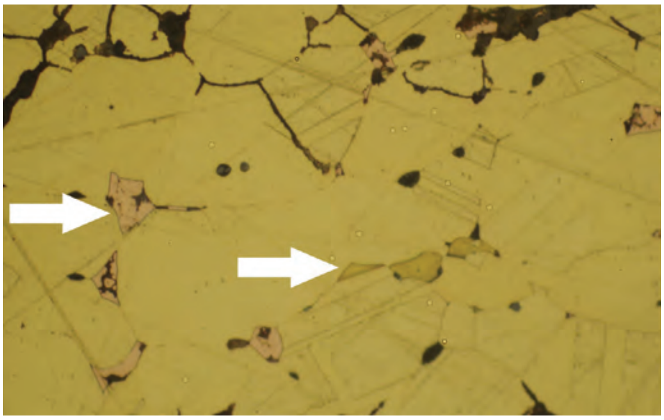

Figure 7. *Snow Squall* sample 'Port 70C' showing the small islands of the beta phase within the alpha grains (*right arrow)*. Some of the beta phase is preferentially corroded and replaced by re-deposited copper (*left arrow)*. 300x.

According to Scott, *Snow Squall*'s 'Muntz's 24 Patent' stamped sheathing 'is essentially a Muntz metal, but care may have been taken to try to prevent excessive precipitation of the beta phase, as the two-phase alloys are more susceptible to general corrosion' (Scott 2009).

Petrel

Scott reviewed and compared metallurgical micrographs from *Petrel* and *Snow Squall* and concluded that 'the microstructures are broadly comparable to each other but that slightly more of the beta phase (See Figure 8) was originally present in the *Petrel* sheathing' (Scott 2010).

SEM-WDS analysis of five random matrix points on *Petrel*'s unstamped sheathing returned an average composition of 63.5% ± 0.3% copper, 36.9 ± 0.2% zinc with a trace of iron and lead. Analysis of 10 random matrix points from *Petrel*'s stamped sheathing returned an average composition of 63.6 + 0.4% copper, 37.0 + 0.2% zinc with a trace of iron and lead. *Petrel*'s 1847-1853 era sheathing does not reflect the 1846 Muntz sheathing patent No.11,410 that specifies a leaded brass with 56% copper.

Figure 8. Microstructure of *Petrel*'s 'M2' sample of 'Muntz's 26 Patent' stamped sheathing. 50x Courtesy, Peta Knott.

Sheathing chronology

The Quebec-built bark *Eglinton* (1848-1852) was contemporary with *Petrel*, and its sheathing, dated to 1849, bore an oval stamp 'P. Grenfell & Sons 26 oz'. The sheathing was analyzed as 59.9 ± 1.1% Cu and 40.8 ± 0.9% Zn[11] (McCarthy and Stanbury 2003). Pascoe Grenfell and George Frederick Muntz were bitter ex-business partners (Flick 1975). *Eglinton*'s Grenfell sheathing reflects Muntz's original 60:40 brass formula while *Petrel*'s Muntz sheathing suggests a Muntz metal alloy change during the same time period. This change is further confirmed approximately 10 years later in *Snow Squall*'s 1862-1863 era Muntz stamped sheathing (See Table 5).

Conclusions

Snow Squall's sheathing varies greatly in condition, retains many double oval 'Muntz's 24 Patent' stamps, and the sheets were punched by machine or by hand using a template except at the margins where they were punched by hand. Compositional analysis of *Snow Squall*'s sheathing padding revealed it is unusual since it is jute containing evidence of shellac and of *Pinus sylvestris* tree resin (tar), used as fiber adhesives. Analysis of two sheathing nails from the *Snow Squall* revealed that they were cast and have two distinct compositions. Technical analysis of *Snow Squall*'s unstamped sheathing suggests an alpha phase cartridge brass or the Muntz alloy nergandin.

Petrel and *Snow Squall* both bear double oval Muntz

Vessel	Time period	Last sheathing	Stamp	Composition	Microstructure
Petrel	1847-1853	unknown	Double oval 'Muntz's 26 Patent'	63.6 ± 0.4% copper, 37.0 ± 0.3% zinc with a trace of iron and lead.	Alpha phase brass with small islands of beta phase present.
			unstamped	63.5 ± 0.3% copper, 36.9 ± 0.2% zinc with a trace of iron and lead.	Alpha phase brass with small islands of beta phase present.
Eglinton	1848-1852	1849	Oval 'P. Grenfell & Sons 26 oz'	59.9 ± 1.1% Cu and 40.8 ± 0.9% Zn.	not recorded
Snow Squall	1851-1864	1862 with repairs in 1863	Double oval 'Muntz's 24 Patent'	(Starboard 32C) 64.3 ± 0.15% copper, 37.5 ± 0.10% zinc, 0.04 ± 0.03% iron and 0.1% lead.	Alpha phase brass at the boundary where beta phase begins to form.
			Double oval 'Muntz's 24 Patent'	(Port 80C) 64.5 ± 0.37% copper, 37.4 ± 0.24% zinc, 0.07 ± 0.02% iron and 0.1% lead.	Alpha phase brass at the boundary where beta phase begins to form.
			unstamped	(Port 80E, sample 2.3) 67.9% copper, 30.1% zinc, 0.8% lead and 0.39% iron.	Alpha phase brass

Table 5. Sheathing Chronology.

patent stamps of different gauges.

Analytical investigation of *Petrel*'s stamped sheathing revealed an alpha phase alloy with islands of beta phase while *Snow Squall*'s stamped sheathing is an alpha phase alloy right at the edge of beta phase precipitation. This similarity of sheathing composition and microstructure in samples from two vessels approximately 10 years apart suggests a change in the Muntz sheathing metallurgy between 1847 and 1863 towards a superior, more corrosion resistant product for ship sheathing.

A metallographic examination provided essential corroborative microstructure information. Muntz stamps are iconic in design and potentially patent or time period specific.

This small sample set cautiously raises awareness of alloy changes in sheathing manufactured by the Muntz family. Further patent research and analysis of patent- stamped sheathing from know time-periods is encouraged.

Acknowledgements

In memoriam: *Snow Squall*'s Nick Dean and Al Gordon. Thanks are due to Vin Callcut for metallurgy discussions, Peta Knott, Tasmanian Maritime Museum for *Petrel*'s sheathing tests, Brad Duncan, Metropolitan Heritage programs in Melbourne and Myra Stanbury, Western Australian Museum, for sheathing information.

Endnotes

[1] www.oldcopper.org see marks list.

[2] As a molten binary alloy cools from the liquid stage, the microstructure will be an alpha phase if one component is completely soluble in the other. A change in the proportion of alloying elements, that exceeds the solubility of the materials in each other, can result in the additional formation of the solid second beta phase. See the reference Scott 1991 for more information.

[3] Nergandin is a (Philip Henry) PH Muntz & Co., Ltd. term for the alloy comprised of 70% copper, 28% zinc with 2% lead. It is listed in Woldmans Engineering Alloys, edited by John P. Frick, American Society of Metals, 8th edition (1994) 786, as being used for condensing tubes and being resistant to seawater corrosion. No patent for this alloy has been located to date.

[4] The fiber sample was mounted in Melt-Mount thermoplastic mounting material with a refractive index of 1.662.

[5] The spectra are the sum of 32 scans at 4 cm^{-1}.

[6] XRF used direct excitation for an acquisition time of 200 seconds at 30 kilovolts (kV) and 20 microAmps (mA) and brass alloy reference standards. The range of errors associated with XRF is ± 5% for major elements and ± 20% for minor elements. Embedded samples were mounted and ground like metallographic samples and polished on a diamond-impregnated wheel with mineral oil lubricant using six, one and one-quarter micron diamond powder.

[7] EPMA was carried out operating at 50 kV 20 mA, employing wavelength dispersive analyses and pure element standards. The equipment was operated by Dr. Frank Kyte at the UCLA Geology Department. Samples were coated with carbon to the same thickness as the standards. Results obtained by EPMA give data with a margin of error of ± 0.5% or better, depending on the element concerned.

[8] The resin molds were 1.25″ and ground on wet silicon carbide grit papers of grit size 200, 320, 400 and 600. Samples were polished on Buehler 'Mastertex' synthetic napped cloth using six micron and one micron diamond polycrystalline water emulsion polishing compounds, and etched with alcoholic ferric chloride for five seconds followed by rinsing in pure ethanol and drying.

[9] SEM-WDS operated at 20kV, 15mA. Analysis times on peak and background were 20s for Cu, 30s for Zn, and 60s for the other elements. Copper was calibrated on pure copper metal. Natural sulfide minerals were used to calibrate all remaining elements (zinc, iron, lead and sulfur). Certified reference material was un-available to validate the analytical method thus the absolute values have to be used cautiously.

[10] Felt: 'Fabric made of wool, or wool and fur, or hair, compacted by rolling and pressure, with glue and size. Patent felt, mixed with tar, was formerly put between the sheathing and the ship's bottom'. Definition from 1884 A Naval Encyclopedia, republished by Gale Research Col, Book Tower, Detroit, 1971.

[11] Analysis of two samples (EG 1447) by MacLeod, I.D. and Chan, M.A., 1983, using Atomic Absorbtion Spectroscopy on nitric acid-hydrochloric acid digested samples. Western Australian Museum Conservation Report, File MA-461/71.

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Q & A SESSION

John Scott: If we look at probability distributions and statistics of how an alloy can vary from another one – do we know enough about the quality control factors in manufacturing and the time, and do we know enough about the random aspects of which parts of a deteriorated sheet are being analyzed to make even more than qualitative assessments to see the differences in these alloys that you are showing? It is very interesting.

Molly Carlson: Thank you for that, that's a great question. I bet Peter [Northover] has an answer to the first one, so I may defer to him. I don't know. The research question I would have is: what do we know about that industrial manufacturing time period and how good as metallurgists were they at that time, and did they know (what they were doing)? I know that when you added zinc to the molten copper you would have a problem of volatilization of the zinc which affected what your composition would end up as. I know that they had patents addressing some of that – they would have a closed vessel and they would melt their copper in and then add zinc. So perhaps they were addressing that. We have a very small sample set and we need more samples.

John Scott: The other thing I meant to say also in patent work in general at the end of the day people give wide ranges as to compositions in order to normally not disclose their best composition, but to cover possible ranges of compositions, not just in metals but in all kinds of technical patents. You'll see when you read them people say the proportions will be within the range of this and this, when their actual product that they are patenting is very specific – but it is not disclosed specifically in patents. When you see that I'm sure it goes back to the earliest times of patents. People are required to show a range in order to get the patent and protect against competitors, but they will not normally disclose the exact proportions in the patent itself.

Molly Carlson: Yes, I think that happened to Mr. Muntz Sr. because everybody, before his patent ran out, was making sheathing to his 60:40 blend and he had to sue them. So in all that court proceedings he is very adamant and rigorous that it is this blend that will do the job. And as soon as his patent runs out, 'oops, just kidding!'… Here is another patent that drops the copper content but still has that caveat that it can be higher or lower. And that is common, but what is he really doing? And that's the question.

Peter Northover: The key to Muntz's patent was that the brass was hot-rolled. Because it really cut down the manufacturing cost by about 75% in the energy cost of producing/rolling the metal. And to hot-roll it, it has to be in the beta-phase region at a particular temperature – that's why you have the 37 – 50% range, that's what does it. And I suspect his preferred 60:40 was because he avoided any complications of losing zinc in the melting. It meant it was well inside the beta-phase range and it was not too high in zinc to run into other problems when handling the metal cold. So that's the key thing. As you see from the micrographs the redeposited copper really replaced the beta-phase pretty exactly, so it actually stays mechanically sound. And there is no way the worms can get through. Also, besides protecting against ship-worm, it is also anti-fouling and the leaching out of the zinc is the antifouling part. So you do actually want to keep in that sort of regime. Going down to 29-30% is probably something you would have to cold-roll. And you need to have more than a certain amount of arsenic in to inhibit the dezincification of that [composition]. So it is in fact not such a good metal for sheathing. There are impurities that can survive very well. We have some brass boiler tubes from some locomotives which were shipwrecked on their way to Canada in 1857. They are about 28% zinc, and they are surviving very nicely. They have just got enough impurity in to stop them dezincifying. A general comment to the audience is that because we are well into the era of ship classification for insurance by Lloyds of London and such-like, by going to sources such as Lloyds Register, we know now so precisely the history of these ships so we know exactly when they were sheathed, where and very often what with. I've been working on a shipwreck from the Eastern Sutherland, which was originally unidentified but because of the composition of the components including yellow metal sheathing, brass sheathing from 1851 sank in 1852, it is possible to get a precise identification for the wreck. And a final comment, in the course of a Master student project last year, Ian MacLeod and colleagues kindly sent me their collection of various analyses of copper and copper alloy components from ships and I am just in the process of consolidating it with Alice to return the compliment and if you would allow me to incorporate from your publication – include yours into our database then we are going to end up with a substantially improved picture of sheathing and copper bolts, brass bolts and so on from about 1780s onwards. One last quick question: what are the sheathing nails made of?

Molly Carlson: There is some information about that in the paper, I didn't put it in here. I do want to say, that Brad Duncan has a collection of samples that he's collected over 20 years from maritime archaeology, of sheathing samples with stamps, that have not yet been analyzed but it has always been a research goal of his. So he would be a good person to perhaps talk to.

Materials Characterization And Identification

Chair: Andrew Lins
Panelists: Panagiota Manti, Olivier Berger, Edith Joseph, Molly Carlson

Karen Stemann Peterson: I have a question for the last presentation [Carlson], there was a lot of good information on the copper brass, more or less brass sheeting, but I wanted to ask - you started off saying that you were interested in cleaning the surfaces and you have quite composite layers with the padding and everything behind and of course cleaning processes can start off a lot of corrosion. What, what did it end with?

Molly Carlson: Well, to make it simple it never began. The economic downturn has stopped any further research in pursuing a cleaning option, but we have a poster back there that talks about a dry ice-dusting technique that we were actively investigating before we lost the funding to come up with a final solution of a recommendation. So, the trouble with the Snow Squall is not only the surfaces but because it is in an uncontrolled relative humidity and temperature environment and the temperature can go down to 0 degrees Fahrenheit and the relative humidity can be up as high as 80-90% because we're so close to the river. So, from the metallurgic work David Scott recommended not to clean it at this time until a better environment solution could be procured for her.

Karen Stemann Peterson: The corrosion products can be a protection on copper, yes.

Molly Carlson: Yes, we also did a lot of X-ray diffraction work to identify the material, the corrosion products, we're also looking at toxicity issues for people who would clean them, and I'm happy to find that we didn't find any lead on any of our varied colored corrosion products. But a lot of work would have to continue before you would come up with an actual viable solution.

Lisa Young: I have a question about the pigeon cameras and if you guys could elaborate on the cleaning methods that you used for the aluminum magnesium alloys before you applied the corrosion inhibitors, or if you did any cleaning, mechanical cleaning of the surfaces?

Olivier Berger: No it was really the first time I had worked on this alloy, yes. It was a surprise for us to find this alloy, yes.

Lisa Young: Did you clean the surfaces?

Olivier Berger: Yes sure, we removed all of the corrosion product mechanically. We tried different methods with diluted, very diluted phosphoric acid complex, EDTA, citrate but mechanically was the best way to clean them, to clean it to have a good result, before applying [the corrosion inhibitor] it will not dissolve your corrosion product, you have to remove all the corrosion product before.

Lisa Young: Were you able to remove all the corrosion product down to a clean surface or…

Olivier Berger: Yes, yes.

Shelley Sturman: This is not a question as much as a comment on those terrific pigeon cameras, and it seems that people have to make the same mistakes over and over again. We were confronted with a situation and perhaps some people know about it already, of the contemporary artists Frank Stella who makes some very large painted structures on primarily aluminum panels, but for some reason, and I am not sure why, someone suggested that he do a series on magnesium alloy panels, and it's a time period that he doesn't like to discuss, it's very hard to get him to talk about this, but a series of his painted pieces were going to Australia, so David your question about humidity, there was certainly plenty of humidity and by the time the panels reached Australia all the paint had been popped off from the corrosion. Some of it was still a form of corrosion but it was a whole series of that and he had to completely repaint them, he will never use magnesium alloy panels again, but is just was something that I thought was very appropriate to what you discovered completely unexpectedly and most people wouldn't even know that Stella had used a different alloy on that small time period.

Tom Chase: About the pigeon cameras and the corrosion - the lead acetate that we saw on the lead inlay in lacquer boxes in the Freer. I think that that formed in 50% relative humidity. It would be interesting to go back and look at the records but that storage was conditioned to 50% plus or minus 5 since 1956. We did the cleaning work on this stuff in 1990, so it was not forming in a high relative humidity, it was forming in a relatively, in a moderate relative humidity and we weren't so concerned. Somebody said that we should be trying to chase down where the acetate was coming from, but with so many materials in the storage and making the storage cases we just decided that would have been a waste of time for us to try to figure it out so we just rolled and in that case we removed it mostly with hot water because it was soluble enough and then waxed to fill in the pit holes and present an even corrosion resistant surface.

Olivier Berger: I just want to add, we have done the same for the movable parts [of the cameras] we used oil because wax.. after that you will fix everything and it has to work again, and for the fixed parts [of the cameras] we used wax. But in this case I would say that to act on the environment around, to absorb the pollution, the organic acid, it's really the best way. You have different kinds of absorbers [available], it's really the best way to preserve them.

Paul Mardikian: I have a question for Panagiota, when it comes to conserving those artifacts what are your recommendations, because it's very difficult for us to gauge how much of those surface layers we might remove during treatment. So have you thought about the implication of your research conservation-wise not just on the analytical side of things but how it may affect the way conservators look at those objects and conserve them?

Panagiota Manti: That's down to each individual professional I guess, but knowing that at least, you know, being in a position to identify and to know that we might have these traces of coatings, metallic coatings, clearly help us following a more careful cleaning method perhaps mechanical method as normally one would use for retaining the patina on the surface. So I guess that apart from being interesting in technological terms, it raises like a red flag you know like hang on a minute, I have be ultra extra careful here, you know like not remove these traces by a cleaning method.

Paul Mardikian: What about chemicals? We all use chemicals, would you want us to try not to use chemicals. When it comes to certain artifacts you know I always come back to my field, which is maritime conservation. You know we are in a liquid and we keep going very often into liquid solutions and chemicals for treatment and cleaning and electrolytic and all kinds of…

Panagiota Manti: Well, strong alkali will definitely dissolve any tin from the surface, so that is why honestly as well, identification before this type of treatment is necessary, because strong alkali will dissolve tin. Now the actual effects that alkali treatments have on the phases themselves, this is yet to be investigated, and especially how they interact in terms of as an electrochemical couple you know like as a galvanic [cell], this is still…we need to find out.

Paul Mardikian: And you think that even under cathodic protection there is a risk to lose those layers?

Panagiota Manti: It's likely but it just depends on the choice of treatment and the condition. I don't know, did I answer your question?

David Hallam: Two things: one is with the storage of the camera, one of the things you may want to look at is a really finely ground copper product called corrosion intercept which is useful for absorbing things like acetate. On a more general thought is that when you are dealing particularly with magnesium and aluminium alloys from the period of the camera, the surface that you actually normally see is not the metallic surface, it's a thing called a corrosion conversion coating, so quite often what they would do is they'd dip something like that in one of the many goops that they were using at the time. Now that could be chromates, it could be phosphates, you know there were a whole…. because it was an experimental period, there were a whole batch of these. Now the Americans used acid processes for their magnesium and aluminium alloys, the Germans used alkaline processes, and these processes and technologies disappeared in immediately after World War 2, some of them existed for some time in the USSR which is where they ended up. But the critical thing is that the surfaces of the objects were not the base metal, and so, the way that you treat it, you've really got to think of the surface and the body separately and look at the technology of the conversion coatings as being an integral part of the object. So now sort of a question, how do we ensure, particularly when we don't understand the technologies, but we're concerned with conserving that kind of thing?

Peter Northover: It's a thought promoted by Molly's paper but is a more general comment on quite a few – you were mentioning the very small amounts of lead, 0.1% lead and 0.06% iron, or something which would, I expect, be the normal natural impurities in the brass accompanied by the copper and zinc and while certainly not put there on purpose, it leads to a more general thought about analysis and a lot of people in this room have access to a scanning electron microscope with EDX. The problem with that is that the information is gives you about impurities is just not sufficient to answer some of our questions. For instance, if you're thinking about the inhibition of dezincification of brass by arsenic, you've got to be able to detect 600 parts per million arsenic, and you know I am lucky and I do my analysis on the microprobe and we're going to 100 parts per million or better, but to understand the metallurgy of a variety of the metals that have been talked about today and yesterday, you do need that level of analysis because depending on the alloy, that level of impurity of a trace element has an important effect either on its behavior in service or its behavior in corrosion, so we do need to really to go to that level of analysis as much as we possibly can.

Molly Carlson: That's a good point Dr. Northover. I think in the paper David Scott and also Dr. Goemann, they do publish the trace elemental analysis, they looked for them and I know on *Snow Squall* no arsenic was detected and some of the other elements so I think that information was looked for...it will be in the published paper.

Peter Northover: That is important.

CASE STUDIES

Session Chair: Andrew Lins

THE EXAMINATION AND CONSERVATION OF A 17TH CENTURY INDIAN HORSE ARMOUR

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Abstract

In 2006, an opportunity arose for conservators and curators from the Royal Armouries to conserve and study important horse armour from India. The armour is one of the earliest acquisitions from the Indian subcontinent in the museum and is usually on display. The armour is formed of iron and copper alloy plates joined by links of mail, and retains a lining of quilted textile. Study and treatment revealed unknown details of the construction and restoration of the object, including an unusual type of mail link not widely published. Conservation treatments included cleaning using Melinex barriers that allowed both textile and metal to be cleaned without separating the lining from the armour, the selective removal of previous restorations to balance aesthetics, non-destructive reinforcement of weight-bearing plates, and localised humidification to relax and reshape the lining.

Keywords: Indian horse armour, mail and plate, textile, display, restoration, conservation, decision-making, preventive conservation

Introduction

The Royal Armouries owns an important example of Mughal horse armour, which dates from the 17th century (accession number xxvih.18) with an unusually well documented history (Richardson 1987). Its documented provenance begins in the early 19th century in William Bullock's private museum in Liverpool with its rider — a standing figure of a 'Norman Crusader', wearing what is now known to be Indian armour of mail and plate (Bullock 1808, Cripps-Day 1925).

The first reference to the horse armour was made when the successful Liverpool Museum collection was transferred to the London Museum and Pantherion in 1809, and the 'Crusader' had acquired an armoured horse (Bullock 1812). The London museum was not a commercial success, and it was sold, along with the 'Crusader' in 1816 to Mr. Gwennap for his Oplotheca (Greek term for armoury) on Bond Street, London (Oplotheca 1816). This exhibition was removed to the Gothic Hall on Pall Mall, and after the exhibition finished it was put up for auction in 1821 (Gothic Hall 1818). The auction was never held, and the collection was re-housed as the Royal Armoury on the Haymarket (Royal Armoury 1821).

The armour was most probably purchased by the Board of Ordnance for the Tower Armouries at the auction by Robins in 1833 (Cripps-Day 1925). At the Tower of London it continued to be displayed initially as an example of a Crusading knight (Henry 1834, Hewitt 1841), but was eventually identified by the armour historian Hewitt as an Indian armour (1845, 1859, Dillon 1910). In fact, its Asian origin had already been suggested: 'the very curious and ancient armour which covers the horse is most probably eastern' (Oplotheca 1816).

In 1917 it was transferred with the rest of the Tower Armouries' Asian collection to the British Museum, where it remained until it was returned in 1961 for the new Oriental Gallery at the Tower of London (Robinson 1967). From 1996 the armour has been displayed in the Oriental Gallery in the Royal Armouries Museum in Leeds (see Figure 1), alongside the museum's elephant armour of the same type and date (accession number: xxvia.102, Richardson and Stevens 1996).

A partial redisplay of the gallery in 2006 presented the conservation department with an opportunity to thoroughly assess its condition. After 10 years on open display and routine in-situ cleaning, which included dusting with soft brushes and dirt removal with a vacuum cleaner — areas of light corrosion were evident. The subsequent removal of the armour from its mount revealed several tears to the quilted lining in addition to broken and poorly aligned plates and mail. There were no full records of conservation treatment, aside from records indicating the routine cleaning.

Figure 1. Horse armour on display in the foreground.

Examination

The armour is constructed of small iron plates with decorative copper alloy plates that overlap and are secured with iron mail links. The original mail links are predominantly constructed of alternate rows of riveted and forge-welded links. The plates are held together and made flexible by the mail, which mostly run in vertical strips. There are several decorative circular bosses, which are slightly convex and decorated with scallop-edged copper alloy rims riveted to the surface. Small ferrous plates radiate outwards from these circular bosses and these plates are attached by mail.

The mail links, which are attached to the circular bosses and the outer edges of the mail panels, are unlike others found on the horse armour. The ends of these links are flattened and overlapped, they are not riveted or welded closed, and are perhaps designed to mimic the appearance of the riveted links (see Figure 2). At first it was thought that these links might be from a previous restoration, or that the armour was recycled. However, when compared to other contemporary pieces such as the elephant armour and armour from Jungargh Fort in Bikaner, Rajasthan, India, it became clear that this type of mail was quite common[1]. It has been hypothesised that this design enabled the plate armour to be easily disassembled for cleaning and maintenance (Bottomley and Stallybrass 2000).

Figure 2. Detail of armour construction, showing overlapped links next to the circular plate, welded and riveted links radiating outwards, and mail restoration that is butted rather than riveted, at the top right hand corner.

Previous analysis of the Bikaner armours by the Royal Armouries using XRF (X-ray fluorescence) found evidence of a zinc coating on some of the plates and mail (Stallybrass 2000). The zinc coating was probably applied by the hot dipping process, and these Indian armours are the earliest known evidence of galvanising. The first European patent for galvanising was not until 1836 in France by Sorel. As the horse armour from the Royal Armouries is so similar in date, style and construction to the Bikaner armours (and may indeed originate from Bikaner), it was necessary to assess the armour for a zinc coating to ensure that treatment strategies did not remove traces of zinc. Although XRF analysis was not possible at the time that this project was undertaken, close inspection of the surface using low magnification identified that the surface of the metal had never been prepared for hot dipping because it was rough and had not been chemically treated[2].

During examination, previous repairs of the mail and plate construction were noted. Some are most likely to have occurred during use, such as riveted repairs to plates. Other repairs of a much later date include plates of rolled steel and thick, butted links of bright wire with remains of copper plating, which were thought to have been made from welding rod.

The armour is backed with a textile lining that is composed of two layers, an earlier layer made from a fine weave textile (possibly cotton), which is dark brown in colour and quilted with cotton wadding. A coarse weave textile (possibly rough calico) of a later date is stitched on top of this quilted lining as a support to which the edges of the armour are attached (see Figure 3). Whether the armour was originally attached to a textile lining in this way is not known, although the current method of attachment does not appear to be robust enough to endure action. The survival of a textile lining on armour is quite rare since ferrous ions from corrosion contribute to the textile deterioration via oxidative degradation of the fibres (Daniels 1999). As a consequence, conservation of the armour has to be carefully planned to minimise further damage to the textile.

Figure 3. Textile lining before conservation.

Discoloration of the earlier lining suggests the positioning of original straps, which may have been used to fasten the armour to the horse. There are also two iron stains at the front proper right edge and the positioning and shape of these stains suggest that metal fastenings, perhaps buckles, were once attached here. There is also a tail of horsehair attached to the later lining, which is most likely a later (perhaps Victorian) addition.

Condition of the armour

The horse armour had been on open display for 10 years and several factors had contributed to its deterioration. Although the galleries are air-conditioned, the entrances are not sealed or protected from the adjoining open museum environment. As a result, dust, dirt and pollutants are carried into the galleries, and dust had accumulated in between the metal plates causing corrosion due to the hydroscopic nature of dust particles. A build up of old protective coatings such as natural grease, oils and waxes, originally applied to prevent the armour from corrosion, were evident in between the plates, and this had exacerbated corrosion as the old coatings degraded over-time. The armour is displayed on a plinth, but the barriers are inadequate and do not prevent the public from touching the armour. This has lead to corrosion in accessible points, such as the shaffron (head guard). The horse mannequin was not custom-made and it was too short for the armour, resulting in uneven stress on the mail and plate and creasing in the textile around the horse's haunches.

The mail appears to have been extensively damaged and repaired. The old mail repairs of welding rod were not sympathetic; they did not achieve a good match with the original mail in diameter or patina. Many of these links were placed in the wrong orientation preventing the plates from lying flat and confusing the pattern of the mail. The old repairs were haphazardly placed, preventing several areas from hanging evenly, and were causing undue stress from poor weight distribution. Many of the original mail links were missing and some were tangled due to lost rivets and distortion. A number of plates were poorly supported and creased or bent under the weight of the armour (see Figure 4); one plate had even ripped under stress where the metal was very thin.

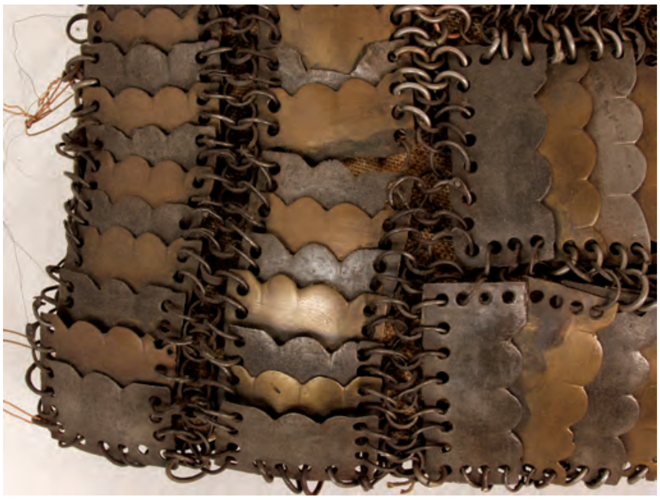

Figure 4. Dirty, greasy and corroded plates out of alignment due to the loss of links, before conservation.

The textile lining was creased, dirty, and stained with grease and iron corrosion from the armour. There were also several small tears and a large rip, approximately 30 cm long. Losses to the lining edge exposed the earlier quilted lining, which left it vulnerable to handling and risk of further tearing. The textile was particularly creased in areas where it was torn and across the proper left side of the horse's back where it was attached to its newer lining.

Conservation aims

Conservation treatment had to be sympathetic to the undocumented history of the horse armour and lack of information regarding its extensive previous restorations. It was therefore decided that evidence of past restoration would be retained as far as possible without sacrificing the structural or aesthetic integrity of the armour.

The goals of the conservation treatment were:

- Carefully document repairs and alterations to the armour using annotated photographs and written descriptions.
- Ensure the structural stability of the armour and lining.
- Retard chemical deterioration of the metal and textile by cleaning to remove dirt and corrosion.
- Improve the aesthetic appearance by the partial removal and replacement of poor restorations.

Treatment — mail and plate components

Due to the construction of the armour, it was not possible to detach the lining from the armour without destroying the stitching so the cleaning of the metal plates and mail was limited to a very time-consuming, labour-intensive method. Melinex® was inserted between the plates and the mail to prevent dirty solvent and loose corrosion coming into contact with the textile. The metal components were cleaned with IMS (Industrial Methylated Spirit) on cotton wool swabs to remove dirt, grease and any previously applied protective coatings. Once cleaned of grease and dirt, fine grade wire wool (Grade: 0000) swabs and soft glass fibre brushes were used to remove loose surface corrosion on or between the plates and mail.

Where possible, the damaged plates were removed (when the riveted links had lost their rivets or were replaced with the butted welding rod). The removal of the broken plates allowed them to be thoroughly cleaned of grease and loose corrosion in preparation for a textile support. Once degreased, the backs of the plates were coated with three applications of 10% Paraloid B48N® in acetone, which consolidated the surface and prepared it for a new support. Reemay® (random weave polyester) was cut to size and adhered to the back of the plates using 25% Paraloid B48N® in acetone (see Figure 5). To provide structural support, a thin (1 mm thick) mild steel plate was cut to the same size as the original plate, and holes were drilled to match the original configuration. The new plate was attached by the mail under the original plate. It was not possible to repair all of the structurally damaged iron plates as some were still held in place by original riveted links. The removal of the links would only have been possible by cutting them open — causing irreversible damage.

Figure 5. The right plate is supported by a textile backing, the left plate is new and will be included under the old plate as a structural support.

The structural treatment of the mail involved the rearrangement of some original links where they had been previously replaced or aligned in the wrong orientation. These were reshaped and re-linked to the metal plates, using pliers with protected jaws. The next stage of treatment required careful consideration, as the retention of physical evidence of restoration had to be balanced against the aesthetics of display. It was also necessary to add links to ensure the structural integrity of the mail and these additions had to be carefully documented. The decision was taken not to remove the bulk of the modern restorations, and to only remove the more randomly placed links that disrupted the lie of the mail or were particularly conspicuous. Where replacement links were necessary, mild steel wire of matching section was formed as a butted ring, patinated to blend with the original mail, and stamped with RA (the Royal Armouries identifying stamp) in order to distinguish new additions (see Figures 6-7).

Treatment – textile component

The iron staining in the textile could not be removed with a wet treatment as it might have adversely affected the amour by causing corrosion. The drying of the textile would also be problematic due to the many layers and wadding. Therefore, textile treatment was limited to being vacuum cleaned, followed by cleaning with a smoke sponge to remove greasy dirt, and finally, vacuumed again. The torn, creased areas of textile were relaxed by introducing localised humidity. This was carried out by inserting a Melinex® film behind the relevant area (to prevent humidity penetrating the wadding below) and diffusing humidity through Gortex® with damp blotting paper. A further layer of Melinex® was placed on top of the blotting paper to keep it from drying out. Once relaxed, the tears were aligned, pinned in place with entomological pins and couched with 100% polyester thread onto an industrially dyed cotton fabric (the fabric was boil washed to ensure colour fastness and to remove manufacturers finishes)

Figure 6. Mail before conservation.

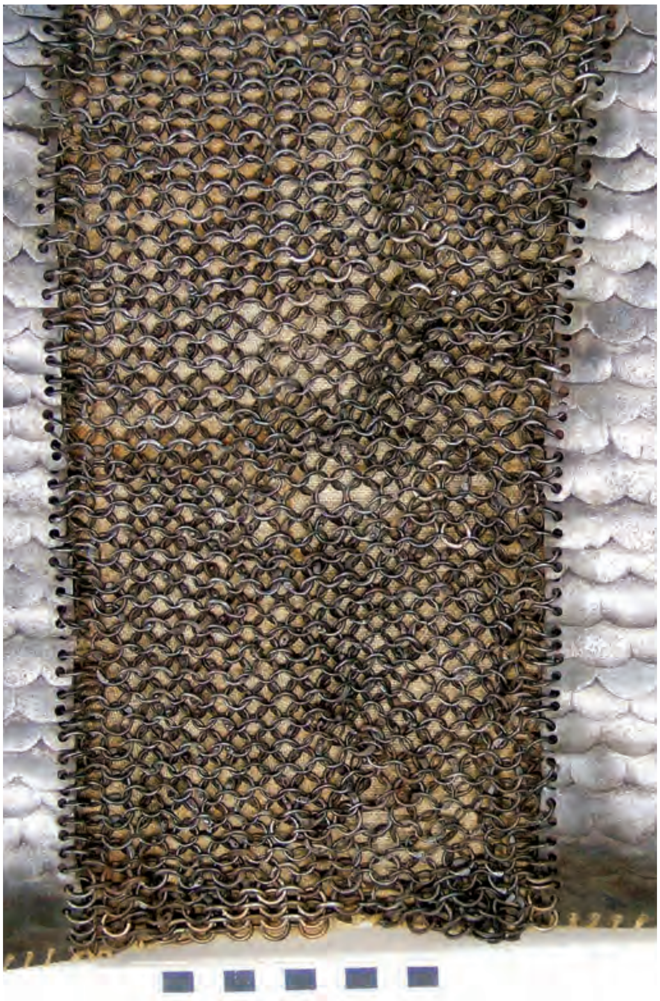

Figure 7. Mail after cleaning, conservation and adjustment of links.

Figure 8. Detail of couched and adhered repairs in the textile lining.

(see Figure 8). Losses at the edges of the fabric were supported by adhering support fabric with a thin film of Beva 371® and a heated spatula.

Protective coating

As the armour was to go back on open display it required protection from the inherent problems of dust, fluctuating humidity and wandering public hands. Melinex® was inserted in between the armour and textile in preparation for a hot application of Renaissance® microcrystalline wax. This was brushed onto the mail and plates and heated with a hair dryer. This method has been found to achieve greater coverage than cold waxing and enhances the effectiveness of the protective coating (Schmuecker 2004). When cool and hard the excess wax was removed by buffing with stiff hog hair brushes and lint free cloths.

Redisplay

The mannequin on which the horse armour was previously mounted was found to be inadequately sized for it to offer satisfactory support, so Plastazote® was used to bulk out the length of the mannequin. To prevent visitors touching the armour, a more robust barrier will be installed as part of the museum display redevelopment. The gallery environment is controlled to ensure that the relative humidity does not exceed the limits of 40-60%. This level of control will prevent the armour from corroding and will protect the textile from further contact with iron ions.

Conclusion

The detailed examination, documentation and conservation of this horse armour from the collection of the Royal Armouries Museum in Leeds, has led to a greater understanding of its construction. Due to a lack of documentation with regards to its restoration history, the Royal Armouries conservation and curatorial team decided to retain, where possible, some of the previous repairs. The comparison of the horse armour to contemporary pieces with better provenance, has led to a clearer understanding of manufacturing and construction techniques of 17th century plate and mail armour. In particular, findings such as the unusual overlapping links and the possible presence of a zinc coating were significant. This case study highlights the importance of research and knowledge of manufacturing techniques as an aid to conservation decision-making and to assist with the selection of appropriate treatment methods.

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Endnotes

[1] The Bikaner armours have excellent provenance and predate 1680 when Anup Singh, the Maharaja of Bikaner, captured the fort of Adoni in Andhra Pradesh, Southeast India, and brought a trophy of armours back to Bikaner. Many of the armours are inscribed with details of this event.

[2] The general procedure for galvanising steel using the hot zinc dipping process is: removal of soil and grease using a hot alkaline solution; pickle with either hydrochloric or sulphuric acid to remove surface rust or mill scale and provide a chemically clean surface; fluxing, where the steel is immersed in liquid flux (usually zinc ammonium chloride) to remove oxide and prevent oxidation; and, finally galvanising, a process in which the steel is immersed in a bath of molten zinc (435-455ºC)

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Q & A SESSION

Ingrid Gerritsen: How long did it take you to restore the whole piece?

Emma Schmuecker: Quite a long a project. It was a year's project. And an intern and myself worked on the actual body armour for about 6 months and then I treated the crinete and the chanfron separately so it was a very lengthy project just because we couldn't separate the two pieces. So that was just the compromise we had to make with the conservation of this object.

EXAMINATION AND TREATMENT OF THE CEREMONIAL WAGON OF STRETTWEG

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Abstract

In 1851, a small copper alloy wagon was found in an early Iron Age grave near the village of Strettweg, Austria. Since its discovery, it has undergone several restorations, some of which have resulted in damage to the wagon. In 2006, the Universalmuseum Joanneum in Graz, Austria, approached conservators at the Römisch-Germanisches Zentralmuseum (RGZM) in Mainz, Germany, to restore the wagon for a new exhibition on prehistory. This provided the first opportunity to fully examine the wagon's condition and observe technical details, particularly regarding casting and construction methods. Technical examination included the minimally invasive techniques of X-radiography (X-ray) and X-ray fluorescence (XRF). The wagon was dismantled, cleaned and reassembled using reversible methods. Carbon fiber was used for in-fills on the wagon and in areas that required additional physical support.

Keywords: Iron Age bronze wagon, technical examination, conservation, XRF, X-radiography, carbon fiber

Introduction

The ceremonial wagon of Strettweg is one of Austria's most famous archaeological artifacts from the early Iron Age of central Europe, dated to approximately 600 BCE. The wagon was discovered in pieces in 1851 by a farmer leveling his field in Carinthia, Austria, near the village of Strettweg. Soon after its discovery, it was deposited in the Graz Museum, Austria, by the chaplain of Judenburg, a city near Strettweg.

In 2006, conservators at the RGZM were asked to undertake conservation work on the carriage in preparation for a major renovation of the Archaeology Museum of the Universalmuseum Joanneum in Graz. New exhibits about prehistory, featuring the ceremonial wagon, were planned for the museum. This was the first opportunity for conservators at the RGZM to undertake a detailed examination of the wagon. The project comprised two main components: A technical examination to determine the method of manufacture of the wagon. This component included compositional analysis of the metal by XRF[1], and examination of the wagon with X-ray[2]; and the disassembly, conservation treatment and reassembly of the wagons' numerous parts in preparation for display.

This paper details the complex restoration history of the wagon, and the recent conservation treatment of this remarkable archaeological object, including a brief discussion of in-fills, supports and joins made with carbon fiber. It also describes the technical analyses undertaken on the wagon and results from analytical techniques employed.

Description of the Wagon

The wagon is 34 cm long, 30cm wide and 34 cm in height, and depicts a large central female figure, (approximately 24 cm in height), with a shallow bowl raised over her head. The bowl is secured by four twisted rods that are riveted onto the underside of the bowl and the platform. The bowl was probably carrying a vessel, but little of this vessel was found. Although fragmentary, the existence of the bowl or vessel groups it with the ceremonial wagons known from the Urnfield period (1300-800 BCE) (Egg 1996).

The female figure is surrounded by nine smaller human figures (both male and female), four horses (three with riders), and two stags. The group of a male and a female pair, referred to as the *sacrificing couple*, is located directly in front of the central figure. The male figure is holding an axe to sacrifice a stag in front of him, which is restrained by two asexual figures, referred to as the *deer group*. The longest sides of the wagon support two horses and riders with helmets, spears and shields.

The figures stand on a base, which is constructed from one piece of copper alloy sheet in a latticework pattern. The sides of the wagon terminate in axle bearings that are decorated with the head of a doe, and support the axles for the four large spoked wheels with a maximum diameter of 13.6 cm. The rear wheels are slightly different in size and appearance and may be the result of an ancient repair.

A fibula and other objects found within the grave area date the wagon to approximately 600 BCE. The wagon, or *Cult Wagon of Strettweg* as it is now known in archaeology, is unique in its complex and delicate figural presentation. It is without parallel among ceremonial wagons of the Hallstatt period (800-450 BCE), (Pare 1987, Egg 1996) found in the area of the Southern Alps and south Europe.

Previous Restoration

Soon after being deposited in the Graz Museum in the 1850's, the wagon was carefully cleaned. The wagon was washed in water, and no acid was used to clean the metal, possibly due to the presence of very little corrosion crust. The wagon's base was broken, but the figures were still riveted in place. Some of the arms and legs, and three of the four twisted rods supporting the bowl were broken. Many pieces were missing altogether, notably, one of the wheel hubs and the two axle blocks. One original axle fragment remained intact. (Robitsch 1852).

During the 1850s, the fragments of the base were joined with copper wire, using small holes and grooves drilled and filed into the original metal surface. A wooden board placed underneath the base provided support to the heavy and extremely fragmented base platform, as well as the wheels (see Figure 1) (Anon., unpublished photograph, Universalmuseum Joanneum 1873)

In 1862, a foundry in Graz cast the first replica of the wagon in bronze for the RGZM in Mainz. This replica, and a drawing of the wagon from 1862 (Anon., inventory RGZM, unpublished), proved to be extremely helpful during examination, conservation treatment and reassembly of the wagon. In 1873, the wagon went on display for the first time at the world exhibition in Vienna, see figure 1.

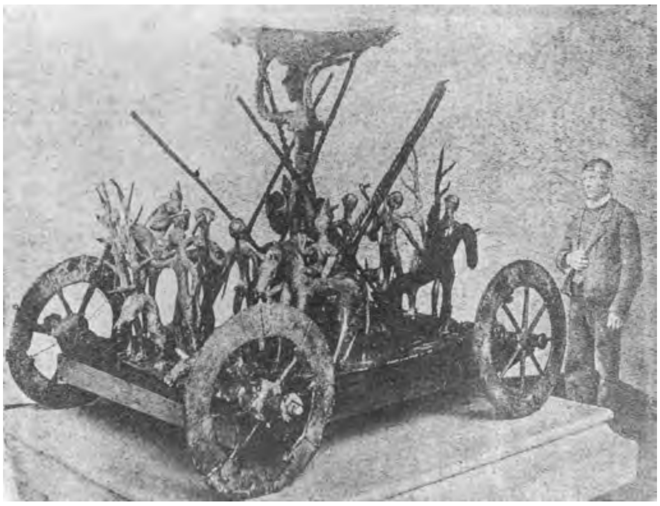

Figure 1. The Ceremonial Wagon of Strettweg on display at the world exhibition in Vienna, 1873, not to scale.

In 1881, a trained metalworker and engraver named Mr. Rennert, carried out restoration work on the wagon. After removal of the wire bindings, missing parts were cast in lead and joined to the original pieces using tin solder. Holes were drilled into the bronze material, and brass screws and pegs were used to support the joints before soldering (see Figure 2). In order to solder the corroded pieces, the original surface patina, and some of the metal, was removed around the joints with a file (Rennert, unpublished letters and documents, Universalmuseum Joanneum).

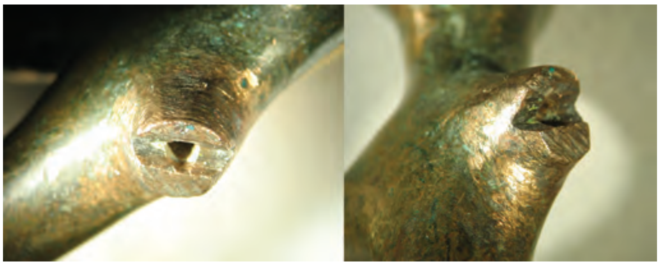

Figure 2. Detail on the arm of a male figure showing drilled holes and areas where metal was filed down during restoration work undertaken in 1881.

The wagon was again displayed in 1889 in Vienna, after which it was returned, damaged, to the museum in Graz. According to records from that time, the wagon fell and broke after it was on display (Rennert, unpublished letters, 1889, 1890?). The wagon then remained in storage until 1901-1902, when Mr. Rennert worked on it a second time. During this second restoration, for reasons that remain unclear, the configuration of the figures was rearranged, and a thick lead plate was soldered onto the fragmented base for support. Before soldering the base onto the lead plate, pieces were cut off and parts of the metal filed down to fit into the new arrangement. All of the original rivets were removed and brass screws were used to reattach the figures in a new configuration onto the base.

At this time, the wheels also were rearranged; the small, undamaged pair were placed in storage to be kept as 'spare parts'. New axles were constructed from iron and fitted into the system to replace those that were missing. The intact axle fragment found on the wagon, with a diameter that fit the larger wheels, determined which wheels were used and the size of the iron axles required. To create similar wheels, the pair of large wheels, which were broken into three fragments and one hub, were remodeled into three new wheels. Each of the new wheels included a piece of original wheel fabric with missing parts in-filled with lead. The fourth wheel was cast completely in lead. To join the original hub with one of the newly created wheels, all the remaining spokes of the hub were removed, see figure 4, and replaced with brass rods. Finally, the wagon received a coat of green paint.

Following restoration, the wagon remained in storage in Graz. In 1980, the Universalmuseum Joanneum in Graz approached the RGZM to produce a resin copy of the wagon for exhibit purposes, an occasion that provided the first opportunity for conservators to examine the artifact. In 2006, Dr. Markus Egg, head of the conservation department of the RGZM, and Dr. Thieter Kramer, then director of the archaeological department at the Universalmuseum Joanneum in Graz, finally succeeded in convincing the relevant authorities to send the wagon to Mainz for a full technical examination and conservation treatment.

Technical Examination

After the wagon was dismantled, information concerning the technological aspects of its construction, such as fabrication, casting and joining methods, the extent and type of previous restorations, the most likely order of construction, the presence of ancient repairs, and the wagon's current condition were obtained from visual examination, using magnification, and X-radiography. The examination was undertaken by conservators Ulrike Lehnert and Rüdiger Lehnert. X-radiography was undertaken by conservator Steffan Patscher at the RGZM. To aid conservators during restoration of the wagon, a drawing of the base of the wagon was made by graphic designer Michael Ober of the RGZM, using the wagons data, as shown in Figure 3.

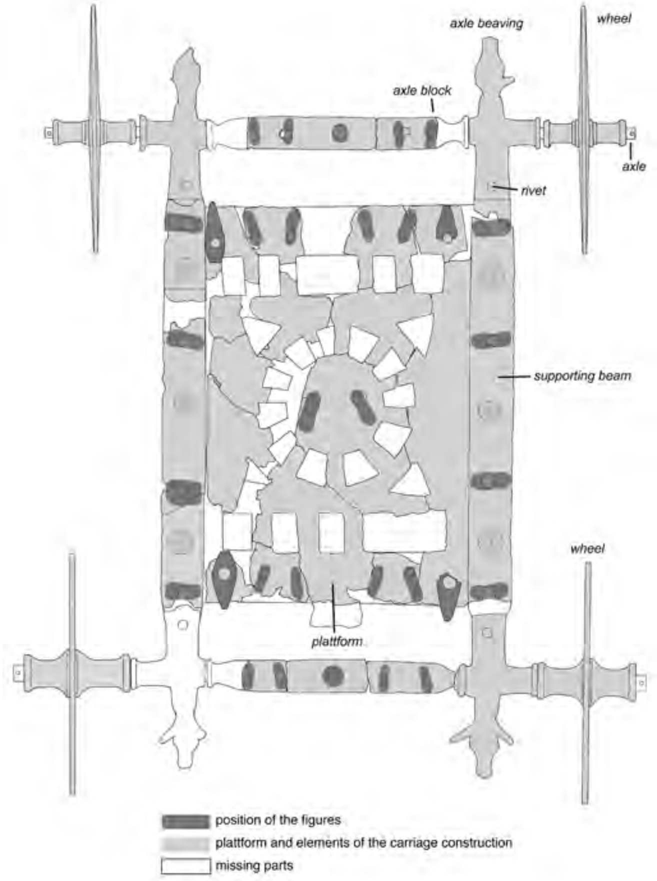

Figure 3. Detailed drawing showing the base of the wagon, the position of the figures, and the location of existing and missing parts.

X-ray fluorescence analysis (XRF) also was employed to determine the composition of the metal, and to assess whether cast-on elements and previous restorations had the same composition as the rest of the wagon. XRF was carried out by the materials scientist Songard Hartmann at the RGZM. The XRF at the RGZM is non-portable but has an extra large sample chamber that accommodated various parts of the wagon during analysis.

Wagon construction

The base is constructed from four main copper alloy elements: a thin platform of latticework metal, two additional supporting strips of metal along two sides riveted to the base and to the axle bearing, and two axle blocks supporting the wheels. Examination revealed that the rectangular area in the middle of the base was probably forged. Traces of the marks made by the forging tool are visible on the underside of the plate. The latticework decoration appears to have been chiseled through the plate after forging, as characteristic marks from a blunt tool or chisel are visible on the underside. Technical details, such as the join between the axle bearing and the base, and the holes in the axle bearing and wheel hub, as shown in Figure 4, were clearly made in the wax model prior to casting. Due to their location on the wagon, neither of these details could have been added after casting.

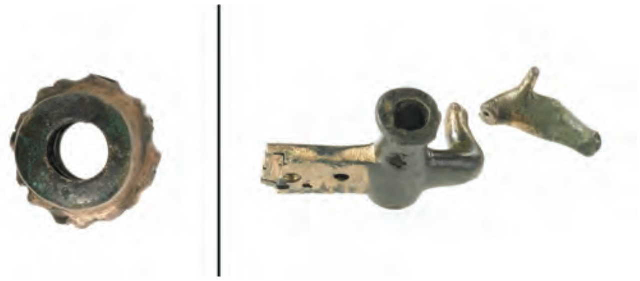

Figure 4. An axle bearing and wheel hub from the wagon during conservation.

Visual examination confirmed that all of the individual cast elements of the wagon are joined by copper alloy rivets, and some of the rivets are further reinforced with washers (see Figure 5). The wheels are secured to the body of the wagon with iron pins. Traces of iron corrosion are still visible on the exterior surface of the hubs on the smallest pair of wheels.

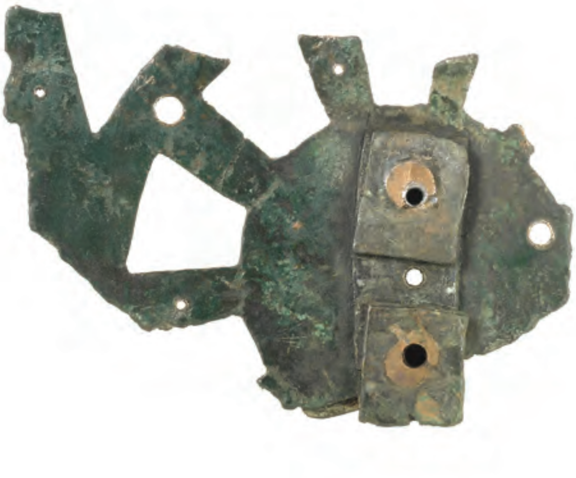

Figure 5. View of the underside of the goddess figure, showing original copper alloy washers.

Decorative elements, such as the nostrils of the animals and mouths of the human figures, were first created in the wax model. These areas are soft-edged in appearance, and traces of the modeling tool are visible as indentations on the surface of the metal. Light surface scratches indicate that these elements were slightly reworked after casting. Further details, such as the eyes of the human and animal figures, and the nipples of the figures flanking the stag, appear to have been added after casting, probably using a punching technique (see Figure 6). Flattened areas, visible on the back of the heads of the human figures, supported this theory. In addition to the punched decoration, an example of drilled decoration was found during examination. One of the horses (with its rider missing) has circular decoration on each side of its neck, which probably was made by drilling, as shown in Figure 7. Radiant scratches on the surface in the area around the circles, and a circular mark in the center of each circle provide clues for the drilling technique.

Examination of the metal surface indicates that it was highly polished, probably with fine sand and a polishing tool made from iron. Less accessible areas, such as those between the legs of some of the figures, still retain traces of the rough casting skin.


Figure 6. Punched circular decoration on a figure of the deer group.

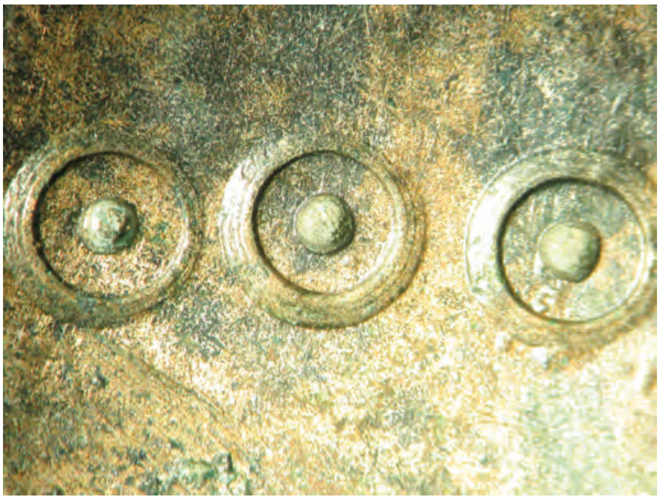
Figure 7. Decorative circles made by drilling, visible on a horses neck.

Casting techniques

XRF results determined that the wagon was cast from a copper/tin alloy, containing 88%-89% copper, 10%-11% tin and 3% lead. All areas analyzed on the wagon had the same composition, including elements that were cast-on. These results indicate that the metal was a copper alloy commonly used for casting in the Bronze and Iron Age (Greiff, personal communication 2008).

Technical examination revealed that the figures on the wagon were cast by the lost wax technique. For a description of this technique, see Bol 1985, Formigli 1985, and Mattusch 1988. The casting-on method, a common technique in practice since the Bronze Age, particularly for bronze swords and helmets (Drescher 1958), also was employed. This term describes a process whereby two pieces of already-cast metal are joined. To do this, a small mould is built onto the metal piece and new molten metal is cast into the mould in-situ. The heat from the molten metal fuses the pieces, and once the metal has hardened, the mould is then discarded.

The probable sequence of manufacture and casting-on of the figural group referred to as the *deer group* is described as follows: The antlers were cast first, and then the stags were modeled in wax and fitted onto the antlers prior to casting. The X-ray film of this area shows a faint shadow in the region around the join between the head and the antler, most likely from the union of hot and cold metal. Next, the human figures holding the antlers were modeled in wax and then cast-on to the antlers. The porosity, visible on break edges, indicates that casting conditions were less than optimal, and suggest that the molten metal was cooling at the time these figures were cast (see Figure 8).

Visual and X-radiography examination also revealed that the manufacture of some parts of the wagon did not go smoothly. The casting-on of a hand for a figure in the *deer group* appears to have failed. In Figure 9, the repaired hand is visible in the image at left; it was hammered flat and then mechanically bent to fit around the antler, resulting in a loose hold on the antler. The image on the right of Figure 9 shows an example of a *deer group* figure where casting-on of the hand was successful.


Figure 8. Detail from a male figure of the deer group showing a porous structure in the cast metal.


Figure 9. Detail showing different methods of construction used on the carriage. The hand on the left was mechanically formed around the antler; the one on the right was cast-on.

Conservation

Conservation treatment of the wagon was undertaken by Ulrike Lehnert and Rüdiger Lehnert in the conservation laboratory at the RGZM. Damage and lead in-fills were partially visible beneath the green paint that was applied during the 1901-1902 restoration. The inferior solder, and the screws that joined the lead plate to the base plate and the figures, made dismantling easy. To ensure correct orientation and allow access during the work process, the pieces were numbered and set into a Styrofoam bed, as shown in Figure 10.

Figure 10. Conservator R. Lehnert from the RGZM, dismantling the wagon.

The coat of green paint was removed using distilled water, alcohol, acetone, and petrol ether on cotton swabs. Considering its age, the metal was in excellent condition. Most of the pieces were broken or fragmented, with a thin, brownish-green, stable (copper oxide) patina and very little thick corrosion crust. Poorly soldered joins made it easy to remove the brass pegs and lead in-fills by hand, with minimal heat required from a hot air gun. Remnants of tin solder came off easily with the aid of a brush and scraper. Once removed, the old in-fills and the lead plate were retained as an example of an historical restoration treatment. A conscious decision was made not to cover or hide the damage from previous restoration attempts, and to take a minimal approach to loss compensation, in-filling only where stability was needed. Mechanical cleaning of the metal surface removed the remaining dusty corrosion crust. As the condition of the metal was stable, and a controlled exhibit case environment was assured, a protective coating was not needed.

Supporting material

Carbon fiber was used for in-filing missing parts of the wagon, and was chosen because it is light and strong, provides adequate support for the object, and is aesthetically pleasing. To fit the cleaned fragments together, pegs or rods made from carbon fiber were used. Examples of areas that were in-filled include the missing hind legs of one of the horses, (see Figure 11), and several areas on the two front wheels that had suffered extensive loss. In order to achieve as minimal intervention as possible, the pegs were fitted into existing holes that were drilled into the metal during the first major restoration in 1881. Araldite 2020 epoxy resin was chosen as the adhesive, with Paraloid B-72 as a separating layer between the original surface, the carbon fiber peg and the adhesive.

Figure 11. Carbon fiber rods were used to construct supports for missing areas where stability was necessary, such as for a horse's hind leg.

To reinforce the broken and fragmented base of the artifact, a carbon fiber support was created. Each surviving fragment of the base was first cast in resin, and these were assembled and embedded face down in modeling clay, with a sheet of EP stretch wrap used as a separating layer. Several sheets of carbon and glass fiber in various thicknesses were then applied with Araldite 2020. To produce a thin (1.5mm) uniform lamination free of bubbles, the entire assembly was placed under vacuum. After the laminated support had cured and was separated from the model, areas on the new carbon fiber support corresponding to areas of open-work on the original base were cut out (see Figure 12). Rods made from carbon fiber of various diameters were adhered onto the new carbon fiber support in order to connect the wheels of the wagon to the support, thus replacing the missing axles.

To ensure reversibility, the existing screw holes in the figures from the 1901-1902 restoration were re-used to attach the figures to the base and to the carbon fiber template with small stainless steel screws. Paraloid B-72 was applied as a separating layer, and Araldite 2020, with graphite for lubrication, was used to fill the screw holes. The stainless steel screws were coated with a release agent (Sika VP810), and then pressed into the fresh resin. The screws are reversible and secure the figures, the base, and the carbon fiber base support. Owing to the weight of the wagon, which is approximately 6 kg, thin (8mm), cylindrical Perspex rods underneath the axle bearings and a Perspex ring underneath the center provide extra support while the wagon is on display (see Figure 13).

Conclusion

Results from technical investigation and treatment of the ceremonial wagon of Strettweg have provided detailed information concerning the fabrication of this complex object from the early Iron Age. The examination of the wagon has revealed the use of many complex manufacturing techniques; especially impressive is the craftsmanship shown in the technique of casting-on for joining copper alloy elements on the wagon. Conservation treatment and re-assembly of the wagon was achieved using materials and methods that are fully reversible. The wagon was returned to Austria in 2009 and is prominently displayed in a new permanent exhibition at the Universalmuseum Joanneum in Graz.

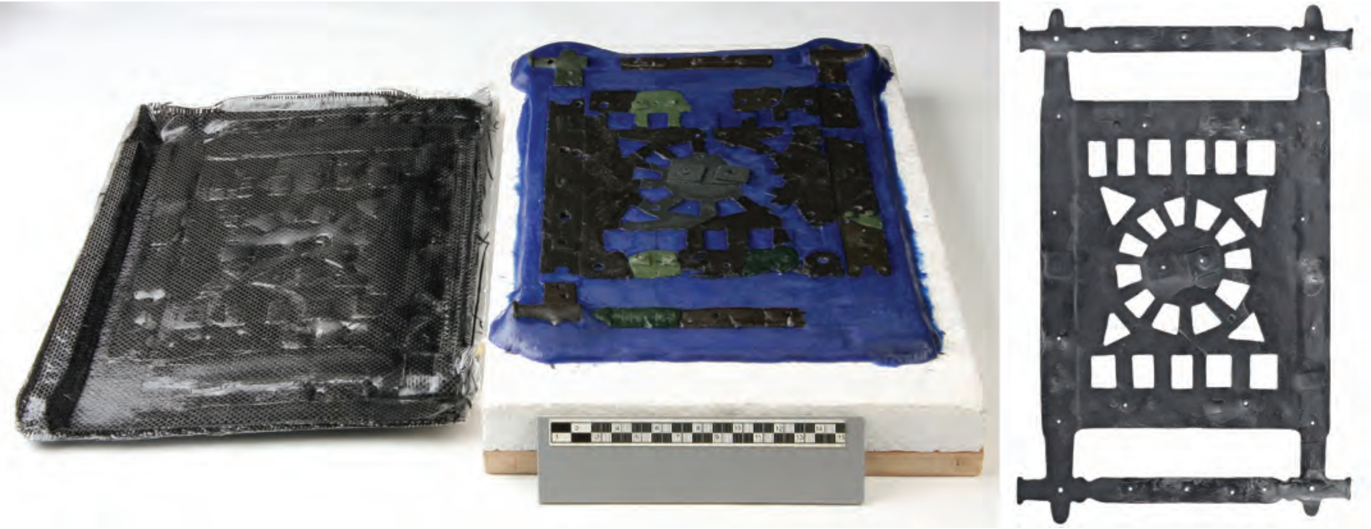

Figure 12. Carbon fiber template, used to support the broken base plate of the wagon. At the left: the carbon template after setting. In the middle: the base dummy of modeling clay and resin copy fragments. On the right: the finished support.

Figure 13. The Cult Wagon of Strettweg after conservation treatment.

Endnotes

[1] For analyzing the composition of the bronze a Micro-XRF-system by Roentgenanalytik Messtechnik GmbH (Taunusstein, Germany) was used with an analytical spot size of 0.3 mm. The system used was an 'Eagle III XXL' with an extra large sample chamber measuring 0.75 x 0.75 x 1.35 m. The device is equipped with a Rhodium tube, with the option to measure in air or in a vacuum and a nitrogen-cooled Oxford EDAX-system with a Si(Li) detector (FWHM resolution for MnKα = 146 eV). The conditions were as follows: Beam 40 kV and 355 μA, spot size 0.3 mm, forming time 35 μs, no vacuum conditions, 300 live seconds acquisition time. Quantification was performed by means of a system-integrated software package based on commercially available bronze reference materials. Detection limits for most elements are around 0.01wt.% and 0.07wt.%. For each sample three points were measured. Preparation of a small surface area of bare metal (approximately 0.5 mm^2) was necessary. Some of the damaged areas from the 1901-1902 restoration were targeted for analysis without need for further cleaning.

[2] The X-ray radiography was undertaken on a Seifert Inc. "MB 350/1-Isovolt 320/13. The machine settings were as follows: a 3min exposure time, a film focus distance of 90 cm, 0.6 Pb filter, 12 mA, on a D7Aqua film with 80 -220 kV. Approximately 3 to 4 pictures per object were captured.

Materials

Paraloid B-72 (Methyl-Methacrylate)
Kremer Pigmente, Hauptstr.41, D-88317
Aichstetten, Tel: +49 7565 91120
www.kremer-pigmente.de

Petrol Ether, Acetone, Alcohol (Spirit)
Seulberger Chem.-Grosshandlung, Fettweisstr.
2b, D-76189 Karlsruhe, Tel: +49 0721 57097

Sika VP810 (release agent)
Sika Germany GMbH, D-72574 Bad Urach,
Tel: +49 7125 9400

Araldite 2020 (Epoxy resin)
Huntsman Advanced Material (Europe) BVB A,
B-3078 Everberg,
Tel: +41 6196 61599
Huntsman AM_CSL@huntsman.com

Carbon Fabric pain weave (Carbon and Glass fiber)
R&G GmbH Composite Technology
D-71111 Waldenbuch
Tel: +49 (0) 7157 530460, info@r-g.de
www.r-g.de

EP stretch wrap 20μ
RajaPack, Postfach 1226, 75212 Birkenfeld,
Tel: +49 180 5306307
www.rajapack.de

Perspex XT rod (PMMA)(colorless)
Evonik Röhm GmbH – Werke Darmstadt, Kirschallee,
64293 Darmstadt, www.evonik.de

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Universalmuseum Joanneum, inventory of collections (185- decade certain but not year).

Author

Ulrike Lehnert is a conservator and conservation-instructor at the Römisch Germanische Zentralmuseum in Mainz, Germany, where she also received her training as a conservator from 1993-1996. She studied Art History from 1986-1989 and also trained as a watchmaker in both Germany and Switzerland. Prior to joining the staff of the Musuem in 1998, she held positions at the University of Prehistory and Early Middle Ages in Vienna, Austria, and was an intern in the metal conservation lab at the British Museum, London. She has also worked as a conservator for archaeological excavations in Syria, Sicily and Austria.

Q & A SESSION

David Watkinson: When you reused the screw holes in the reconstruction, you said you put in [Paraloid] B-72 as a release agent. Was the carbon fiber bar you used threaded?

Ulrike Lehnert: No.

David Watkinson: Ok, so the [Araldite] 2020 went into the thread, and the B-72 on the bar? Would there be any undercuts in that if you wanted to remove that in the future?

Ulrike Lehnert: Yes, but you could just drill the hole a little bit bigger in the resin and squeeze it together.

Mark Erdmann: I didn't quite catch the technique of the carbon fiber support for the base of the wagon. Could you describe that in a little further detail?

Ulrike Lehnert: We produced copies of the surviving base plate and we embedded them face down in this modeling clay because we had to have a negative from the positive. And then we put the assembly onto the base model to laminate the carbon fiber weave onto it with Araldite 2020.

DRY ICE BLASTING FOR THE CONSERVATION CLEANING OF METALS

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Abstract

This research was carried out to assess the feasibility of dry ice blasting as a replacement for solvent cleaning for the removal of organic layers from metal cultural heritage objects. The effects of dry ice blasting on test samples of aluminium, bronze and weathering steel were studied along with its effectiveness at removing organic layers from four objects. Metal surfaces were studied in detail before and after cleaning using light microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). It was possible to remove wax layers from most of the metal samples. The removal of spray paint from aluminium was very successful, however, its removal from weathering steel proved very difficult. The gradual removal of patina/corrosion from weathering steel and bronze was possible without damaging the substrate. Results indicate that dry ice blasting is a good alternative to other air abrasive methods, such as sandblasting or walnut shell blasting.

Keywords: dry ice blasting, solid carbon dioxide (CO_2), air abrasive, micro abrasive blasting, removal of organic layers, bronze, aluminium, weathering steel, Scanning Electron Microscopy (SEM)

Introduction

Dry ice, or solid carbon dioxide (CO_2), blasting for surface cleaning is used in the industry for a wide range of cleaning applications[1]. Several studies have been published on the use of dry ice blasting in the industrial world, but none of these have focused on low blasting pressures and machines suitable for use in conservation applications (Kinder 2007, Lemos 2007, Krieg 2008, Curtis 2008, Silverman 2008 Spur 2009, Brush 2010). Dry ice blasting uses dry ice pellets or particles in a pressurised airstream directed at an area to be cleaned. Dry ice blasting is known as a non-toxic, non-abrasive cleaning method with unique thermal and sublimation effects[2].

The cleaning process of dry ice blasting is thought to be based on a thermal effect, a sublimation effect, and a mechanical effect (Spur 1999). The thermal effect is caused by its low temperature (-78°C) causing the targeted layer to shrink and become brittle, which aids removal. Krieg (2008) showed that the contribution of the thermal effect towards the overall cleaning effect was 10% when blasting on an object at room temperature and 50% at an object temperature of 500°C. He also showed that the sublimation effect of dry ice blasting was negligible (Krieg 2008). It follows, therefore, that the mechanical (kinetic) effect of dry ice blasting is responsible for most of the cleaning effect at ambient and elevated temperatures, but heating the object to be cleaned can improve its performance.

Because the mechanical effect is the most significant, particle speed is the most important parameter of dry ice blasting, just as for other air abrasive blasting methods. Particle speed is mainly (but not linearly) dependent on blasting pressure, but factors such as nozzle type, particle size/shape, machine and hose dimensions have an influence. The most effective blasting angle, in general, depends on the layer to be removed — a lower angle being more effective on ductile layers (Achtsnick 2005). Several studies reported dry ice blasting at an angle of 90° to be most effective for removal of ductile coatings from metal (Spur 1999, Krieg 2008). Varying blasting distance between 5 cm and 15 cm did not influence the result (Krieg 2008). The effectiveness of a blasting medium is determined by its mass, shape and hardness. The hardness of dry ice pellets was found to be 1.5 Mohs, which is soft compared to walnut shell granules (2.5-3.5 Mohs) and sodium bicarbonate (2.5 Mohs) (Krieg 2008)[3].

This research was carried out to determine if dry ice blasting is a feasible alternative to using solvents for the removal of organic layers from metal cultural heritage. The dry ice blasting machine chosen for this study was the i^{3}Microclean (Coldjet©) because it can operate at low blasting pressures, uses small particles and was used in other conservation applications (Lemos 2007, Curtis 2008, Silverman 2008). Firstly, the effect of varying blasting pressure was tested on uncoated metal samples using parameters similar to those found in literature (Chase 1985, Lins 1989, Turner 2000). Secondly, parameters for the removal of wax and spray paint were determined on metal samples and study objects: a pewter candlestick, a bronze sculpture and a weathering steel pedestal. The parameters derived from the second test were then applied on the same uncoated metal samples as in the first test.

Materials and methods

Sample characterization and preparation

Four different types of metal samples were prepared for the tests. (Please refer to Table 1 for sample information, including the size, of the metal samples.) The alloy composition of the metals was analysed by X-ray Fluorescence (XRF) and the Vickers hardness was measured. Surfaces before and after blasting, and one polished cross section from each metal, were studied with optical microscopy as well as with Scanning Electron Microscopy (SEM), and were also photographed. Patina layers on the samples were analysed with SEM. Temperature during blasting was monitored using an Infrared (IR) camera[4].

Aluminium S1 plate (AL) was prepared for the test by degreasing with ethanol. Bronze (B) samples were prepared by cutting slices from a contemporary piece of cast bronze using a band saw, followed by degreasing. Six of these bronze samples were patinated using a copper(II) nitrate solution (BPat). A first layer was applied and heated to create a black patina and a second layer applied and heated to produce a green colour. The resulting patina was quite powdery. The black layer had a thickness of I0 microns-16 microns and the green of 35 microns-50 microns. Weathering steel (WS) (CorTenA) samples were cut from the rim of a circular tray that had been sandblasted to S2.5 industrial standard and weathered outdoors for six months. The corrosion build-up on the weathering steel was the following: a black base layer of 0-20 microns; a brown layer of 5 microns-7 microns and an orange top layer of 10 microns-25 microns.

On one sample of each metal type (AL, B, BPat, WS), eight rectangular areas of 1 cm x 2 cm were marked (sample no 1-4; area 1-8, shown in Figure 1). In each area, a circle was marked in order to be able to study the same location before and after blasting. These samples were used in test 1 and 3.

For the cleaning tests, molten black microcrystalline wax or spray paint were applied to the four types of metal samples and on study objects[5]. In the case of two patinated bronze samples, (sample no 6 and no 12), the artificially applied patina was first coated by brushing molten clear microcrystalline wax onto the surface before applying black wax or spray paint (please refer to Table 3 for all samples/objects and layers).

Machine

The i³Microclean, Coldjet© is a one hose dry ice blasting machine of table top size (56 x 41 x 51 cm) in which a block of dry ice is placed (15 x 15 x 30 cm) from which sugar grain sized particles are shaved. A rectangular so-called laval nozzle,14 cm in length with a 3 mm x 9 mm opening (G12), and the standard hose 3.7 m in length with a diameter of 9.5 mm were used. The blasting pressure of the machine can be adjusted between 0.5 bar and 8.6 bar and the mass flow can range from 0 to 0.55 kg/min.

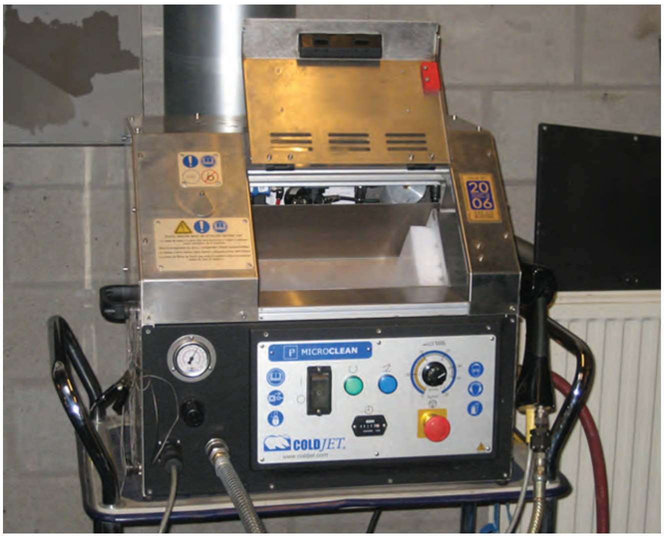

Figure 1. The i³Microclean, with a half used block of dry-ice inside.

Type	Composition (wt%)	Size (cm)	Patina thickness	Hardness (vickers 5kg)
Aluminium (AL)	Al99/Si1 traces: 0.1 Mg, 0.3 Fe	10 x 10 x 0.1	n.a.	34 HV5
Bronze (B)	Cu93/Sn5/Pb2	8 diameter x 0.5	n.a.	80 HV5
BronzePat (BPAt)	Cu93/Sn5/Pb2	8 diameter x 0.5	35-60 micron	80 HV5
Weathering Steel (WS)	Fe98/Cr0.8/Mn0.4/Cu0.3/Ni0.2	7 x 10.5 x 0.5	25-50 micron	198 HV5

Table 1. Sample 1-4 characterisation of metal samples used in dry-ice blasting tests.

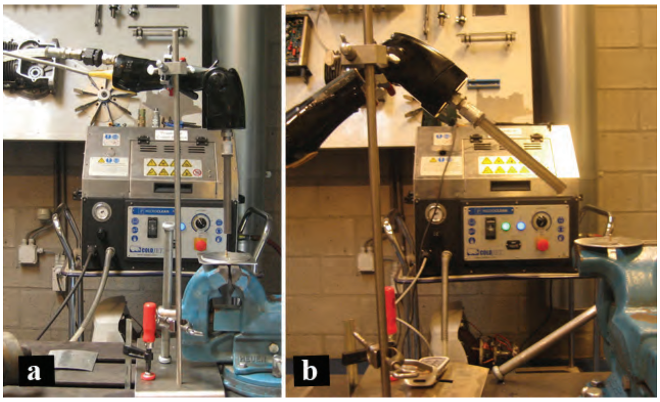

Figure 2. (a) The setup for test 1(*left*). (b)The setup for test 3 (*right*).

Experimental design

In the first test, the nozzle was fixed into place at an angle of 90° to the surface of the samples (no 1-4) and one area at a time was blasted while other areas were protected. The mass flow rate was set to half of the maximum for this machine at 0.18 kg/min, and the blasting pressure set at 1.5 bar, 4 bar and 7 bar successively (see table 2 for all parameters).

In the second test, wax and spray paint layers were removed, holding the blast applicator by hand. Discrete parts of the samples or the objects were cleaned with various settings for blasting pressure and mass flow rate, adjusted as needed. For each sample or object, the machine parameters as well as blasting angle, time, and distance were recorded. In order to compare the effectiveness of cleaning parameters, the cleaning rate was calculated in seconds per cm^2 (see Table 3).

For the third test, blasting parameters were derived from the results of test two and applied to samples without organic layers to mimic a situation where a cleaned area on an object is adjacent to an area without a coating. For this test, the blast applicator was positioned with the nozzle opening at a distance of 10 cm and at an angle of 45° to the surface of the samples (Figure 2b). The mass flow dial was set to 0 kilograms per minute, but a small non quantifiable amount of dry ice would still come out of the nozzle. The blasting pressure was set to 1.5 bar. One area at a time was blasted for 10 seconds, 30 seconds and 60 seconds successively while the other areas were protected (see Table 2 for details).

Results and discussion

Results for test 1: effect of particle speed

Visual inspection of metal surfaces showed mechanical damage of the aluminium (sample no 1) at all pressures. It showed no visual mechanical damage on the untreated bronze (no 2) and removal of corrosion from weathering steel and patinated bronze (no 3 and 4) (see Figure 1a, 1c, 1e and 1g).

Sample no.	Type	Test	Pressure (bar)	Angle (degree)	Distance (cm)	Mass flow (grams/min)	Time (sec)
1	Aluminium	1	**1.5**	90°	5	0.18	60
			1.5	90°	5	0.18	60
			4	90°	5	0.18	60
			7*	90°	5	0.18	60
		3	1.5	45°	10	0	**10**
			1.5	45°	10	0	**30**
			1.5*	45°	10	0	**60**
			2	45°	10	**0.09**	**5**
2	Bronze	1	**1.5**	90°	5	0.18	60
			4	90°	5	0.18	60
			7*	90°	5	0.18	60
		3	1.5	45°	10	0	**10**
			1.5	45°	10	0	**30**
			1.5**	45°	10	0	**60**
3	Patinated Bronze	1	**1.5**	90°	5	0.18	30
			4	90°	5	0.18	30
			7*	90°	5	0.18	30
		3	1.5	45°	10	0	**10**
			1.5**	45°	10	0	**30**
			1.5	45°	10	0	**60**
4	Weathering Steel	1	**1.5**	90°	5	0.18	60
			7*	90°	5	0.18	60
			4	90°	5	0.18	60
		3	**2**	45°	10	0	**30**
			2**	45°	10	0	**60**
			1.5	45°	10	**0.18**	**30**
			1.5	45°	10	**0.18**	**60**

Bold: variable parameters.
* Microscopical images of these areas are shown in figure 1 and SEM images of the cross sections of these areas are found in figure 4.
** Microscopical images of these surfaces are found in figure 7.

Table 2. Sample type and parameters for test 1 and 3.

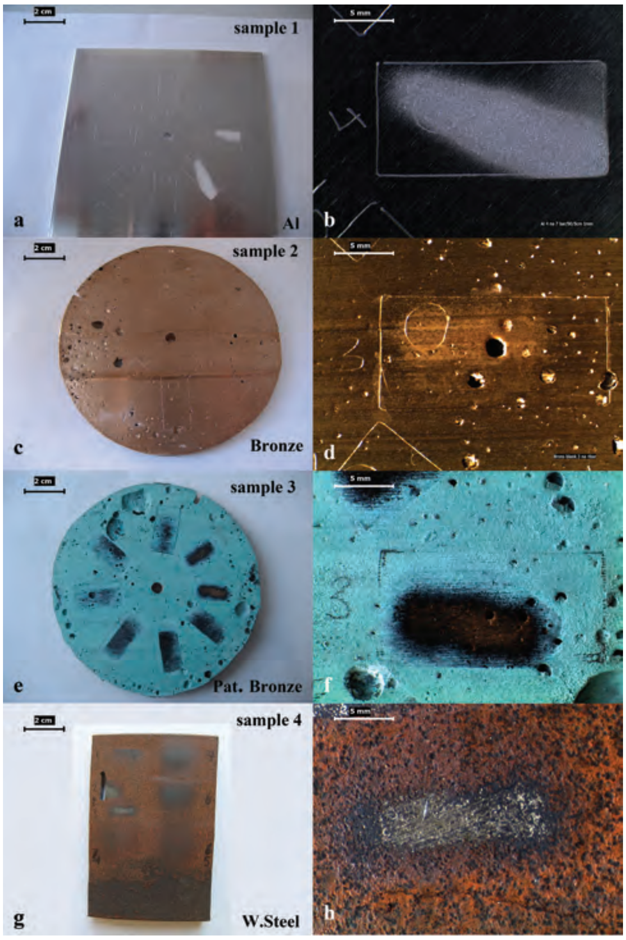

Figure 3. Samples 1-4 and microscopic images of the areas blasted at 7 bar in test 1: (a,b) aluminium, (c,d) bronze, (e,f) patinated bronze, (g,h) weathering steel.

Optical microscopy showed that impact craters could be seen on the aluminium sample (see Figure 1b). The surface of the untreated bronze sample showed very little mechanical damage; if anything, it was possibly a bit shinier. However, a white haze could be seen (see Figure 1d). This was a corrosion product that most probably formed due to condensation on the sample after the sample was left wet for a few hours. The white corrosion was studied with SEM (see Figure 8) and analysed with X-ray diffraction (XRD). The mineral was identified as lead oxide hydroxide ($Pb_5O_3(OH)_4$)[6].

Both patina layers were partly removed from the patinated bronze sample after blasting at 1.5 bar. However, using a pressure of 7 bar produced an area of bare metal in the middle of the blast area. (see Figure 1f). On the weathering steel sample, corrosion layers were removed at all blasting pressures. At 1.5 bar, only the top orange corrosion layer and part of the underlying brown corrosion layer were removed. At 7 bar, all corrosion was removed and the bare metal substrate was visible (see Figure 1h).

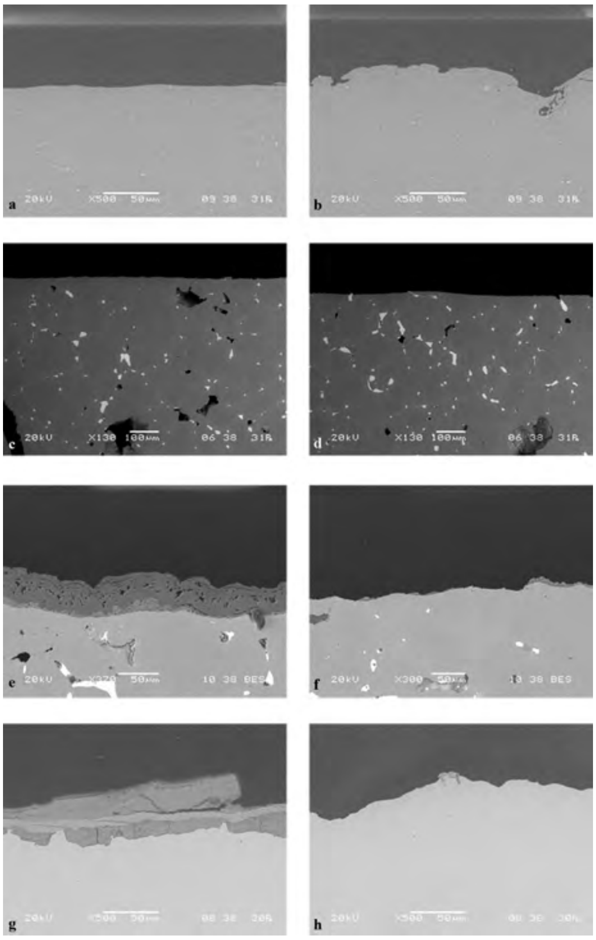

Figure 4. Backscattered electron images (BEI) of cross sections, 20 keV, 30 Pa. Test 1, blasted at 7 bar, images show areas outside and in the middle of the blasted area: (a,b) aluminium, (c,d) bronze, (e,f) patinated bronze, (g,h) weathering steel.

Examination of the surfaces using SEM showed that at a pressure of 1.5 bar the lines on the surface of the aluminium that were present before dry-ice blasting, were still visible, but at 4 bar and 7 bar a large number of deep impact craters could be seen, and these lines had disappeared. The surface of the bronze showed no impact craters (at a magnification of 1,000 times) and cut marks from sawing during sample preparation were still clearly visible. SEM examination of the polished cross sections of the area blasted at 7 bar clearly showed mechanical damage to the aluminium (see Figure 4a and 4b), and slightly rounded upper edges of the saw marks on the bronze (see Figure 4c and 4d). The patinated bronze showed isolated areas of remaining patina and no mechanical damage to the substrate (see Figure 4e and 4f). The surface of the weathering steel showed almost total removal of the corrosion layers and no mechanical damage of the substrate (see Figure 4g and 4h).

Results for test 2: removal of organic layers

During test 2, the lowest operating pressure of 0.5 bar to 1 bar was difficult to use in practice because the hose tended to clog. Intermittent blasting without dry ice at 7 bar was later found to solve this problem, but until that time, tests were carried out at 2 bar. During the cleaning tests, in general, much milder settings were used than in test 1. In general, an angle of 45°, a distance of 10 cm and a mass flow of '0' were used (see Table 3 for details).

It was possible to remove black wax from BPAt (sample no 5) without removing the black patina closest to the metal surface (see Figure 5a and 5b). Removal of black wax from the sculpture (object/ sample no 7) resulted in slight patina damage, and as the black wax had impregnated the patina, total removal was impossible (see Figure 5c and d). The temperature of the surface at the back of the sculpture (the cleaned area) dropped from 22°C to 15°C after 1.5 minutes of blasting, while the temperature of the front stayed stable.

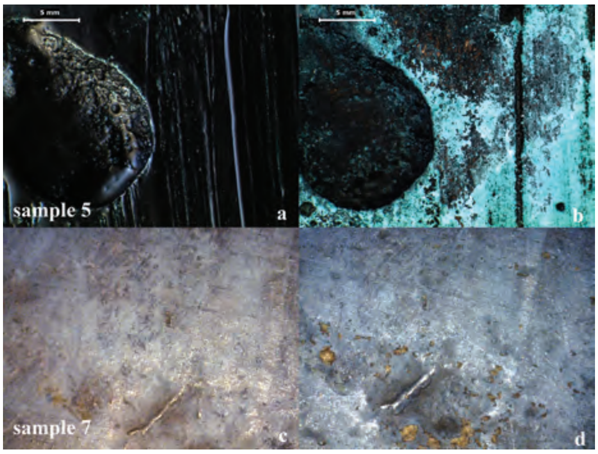

Figure 5. Removal of black wax from patinated bronze sample (*top*): (a) before cleaning (b) after cleaning. Removal of black wax from bronze sculpture (*bottom*): (c) before cleaning (d) after cleaning, showing patina damage.

Spray paint was easily removed from the aluminium sample (sample no 10) with dry ice blasting, (see Figure 6a) but it was not possible to remove spray paint from weathering steel without also removing all corrosion layers in some areas (see Figure 6c and 6d). The temperature of the WS pedestal (sample/object no 14) in the middle of the blasting area was 7°C and outside the blasting area stayed stable at 22°C after two minutes of blasting at a pressure of 3 bar, and 0.36 kg/min (see Figure 6b).

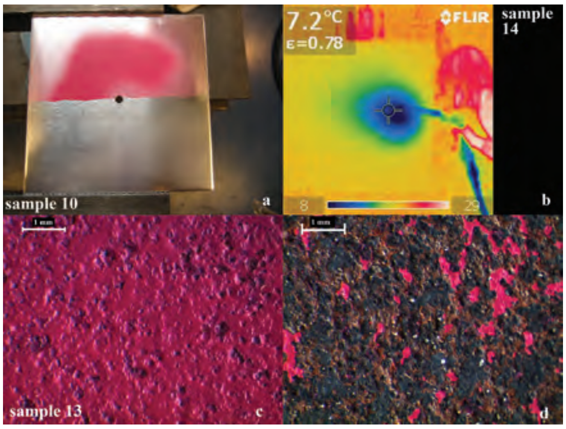

Figure 6. Removal of graffiti from aluminium and weathering steel: (a) aluminium plate half cleaned, (b) weathering steel pedestal during blasting, 7°C in middle of blasting area, 22°C on light grey/yellow area, IR image, (c) weathering steel before cleaning (d) weathering steel after cleaning.

Results for test 3: varying blasting time

The most striking result of this test was the fact that the surface damage/amount of patina removal is very small when using the parameters derived from the cleaning tests in test 2. For all samples, the difference in effect on the surface between 10 seconds and 60 seconds of blasting was slight. For aluminium (sample no 1), the surface became slightly more matte which was only visible with microscopy when the sample was lit with raking light (see Figure 7a).

For the bronze sample (sample no 2), the edge of the blasted area was just discernible with raking light after blasting for 30 sec and up (see Figure 7b). Most of the green, outer layer was removed from the patinated bronze (sample no 3) but the black layer remained (see Figure 7c). The orange and brown outer corrosion layers

no.	type	layers*	parameters**	result
5	BPat	black (mc) wax	1 bar 0,09 kg/min ± 45° ± 10 cm 12 sec/cm^2 ***	It was not possible to remove wax without removing the green top patina, but possible to keep most of black patina.
6	BPat	clear mc wax black mc wax	2 bar 0 kg/min ±10-45° ± 5-20 cm	It was possible to remove black wax without removing green layer and wax.
7	bronze sculpture	black mc wax	2.5 bar 0.18kg/min 45° ± 5-10 cm 2.3 sec/cm^2	It was possible to remove bulk of black wax, not all because no previous wax layer was present, and black wax had been embedded in the patina.
8	pewter candlestick	old candle wax	2 bar 0 kg/min ± 45° ± 10 cm	Very clean, very quick, no damage visible on visual inspection.
9a	painted iron	black mc wax	2 bar 0 kg/min ± 45° ± 5 cm	It was easy to peel of thick black wax layer only paint damage on one previously damaged location.
9b	painted iron	pink spray paint	2 bar 0 kg/min ± 45° ± 3-5 cm	Around half of the paint was removed quickly, the rest did not really want to come off. After 6 min. of blasting not all paint was cleaned off. Yet possibly the solvent of spray paint dissolved the white paint partly.
10	AL	pink spray paint	2 bar 0 kg/min ± 45° ± 10 cm 1,2 sec/cm^2	Very quick removal, same result with lower blasting pressure should be possible too.
11	BPat	pink spray paint	2 bar 0 kg/min ± 30° ± 10 cm	It was not possible to remove all graffiti without removing all green patina on those spots as well.
12	BPat	clear mc wax pink spray paint	1.5 bar 0 kg/min ± 30° ± 20 cm ± 1.5 sec/cm^2	It was not possible to remove all graffiti without removal of entire top patina layer at those spots. Most of bottom patina layer remained intact.
13	WS	pink spray paint	2 bar 0 kg/min ± 45° ± 5-10 cm	It was not possible to remove all graffiti without removing all corrosion and onto bare metal in some spots.
14	WS pedestal	black spray paint	7 bar 45-90° 0.36 kg/min	It was not possible to remove black spray paint without removing all patina/corrosion layers.

* Layers in order of application.
** Blasting parameters top to bottom: blasting pressure, mass flow rate, blasting angle, blasting distance, clean rate.
*** The cleaning was often done with several different settings on different parts which made it sometimes impossible to calculate the clean rate. Only for quite straight forward, quite succesful cleaning it was possible to calculate a clean rate.

Table 3. Details for test 2: applied layers, removal parameters and results.

were removed from the weathering steel (sample no 4) but the black base layer remained intact (see Figure 7d). Blasting with 0.18kg/min dry ice exposed bare metal in some areas.

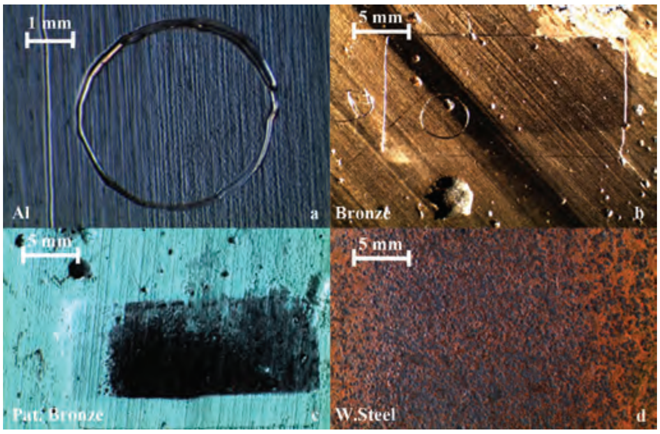

Figure 7. Microscopic images of the surface of samples 1-4 after blasting in test 3: (a) aluminium/60 sec. in raking light (b) bronze/60 sec. in raking light (c) patinated bronze/30 sec. (d) weathering steel/60 sec.

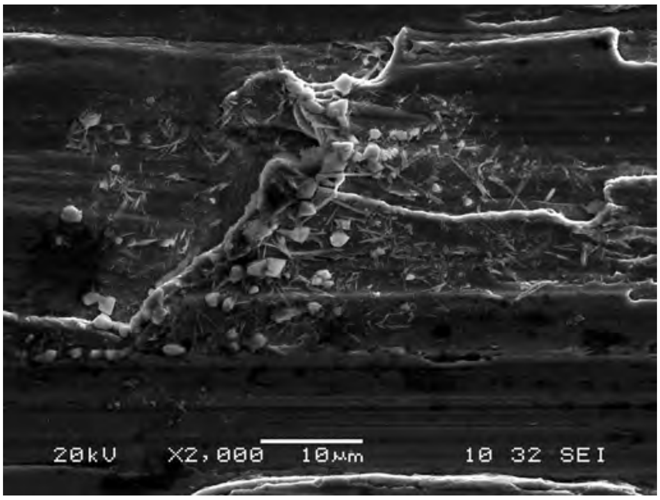

Figure 8. Secondary electron image (SEI) of corrosion on the Bronze sample.

Discussion

During blast testing, it was found that when blasting the small metal samples, they would cool down so much that condensation would form and freeze onto the surface. The larger objects did not cool down outside the immediate blast area. In practice, when blasting on larger objects, condensation is not expected to form. Warming the object or applying the method intermittently should prevent condensation. It is not expected that dry ice blasting damages the microstructure of any of the metals because the maximum temperature drop measured in this research was 15°C.

Conclusion

Dry ice blasting is very effective in the removal of organic coatings from metals as long as the coating is not absorbed into the porosity of the metal. Its use as a replacement for solvent cleaning is limited to cases where a slight abrasion of the surface is acceptable or where it can be used as a first cleaning step for removing thick layers. As a mild air abrasive method, dry ice blasting proved to be a useful addition to other cleaning methods because of the wide range of settings available that provide soft to hard cleaning. Another advantage of this technique for conservation purposes is the fact that embedding of particles into the surface of the object is prevented by the sublimation of dry ice.

Acknowledgements

The authors would like to thank Tom Diepenhorst (Coldjet Benelux), Hans vd Weijde and Peter Remijn (Corus), Suzan de Groot (ICN), Ton Lommers and Jan van der Wal (Segno d'arte) for their assistance.

Notes

[1] http://www.coldjet.com/en/industries/index.php

[2] Personal communication of representatives of five different dry ice blasting companies at the 6th Parts2Clean trade fair (28-30 October 2008, Stuttgart); MyconGmbh, ColdJet DE, ColdJet NL, IceTech DK, Kro Tech NL. Company brochures and personal communication in October 2008 with a representative of Cryotechnics NL.

[3] Nusschalengranulat by Paul Auer Gmbh and Armex © (a SodiumHydrogenCarbonate).

[4] XRF: Bruker AXS Tracer III-V, equipped with a rhodium x-ray tube operating at 40 kV and 2.2 µA, a titanium and aluminium filter and a Si-PIN detector. Vickers hardness was measured by Peter Remijn at Corus. Leica EC3 camera and LasEZ software was used, and a Dinolite Pro-AM 413 TL microscope. SEM: JEOL JSM5910LV. Infrared camera: Flir systems ThermaCam™i series.

[5] Microcrystalline wax Paramelt Microwax PW, with a melting temperature of 76-82°C, was applied hot with a brush. It was used both clear as well as mixed with carbon black pigment (Verfmolen De Kat).

[6] X-ray Diffraction: Bruker-AXS GCCS with GADDS.

Materials

i^{3}Microclean
Coldjet Europe bvba
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Belgium
Ph: 0032 (0)13 53 95 47

Dry Ice ACP Belgium N.V.
Dellestraat 55B-3550
Heusden-Zolder, Belgium
Ph: 0032 (0)13 53 03 15

Copper Nitrate powder
De Hazelaar Art Supplies
Pimpelmees 1
3766 AX Soest
Ph: 0031 (0)35 60 12 825

Paramelt Microwax PW
Paramelt B.V.
Costerstraat 18
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Ph. 0031(0)72 57 50 600

Montana gold© spray paint
L&G GmbH
Heidelberg
Germany
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Ph. 0049 (0)6221 36333 30

Tenco Ferro roestwerende ijzerspray©
Touwen en co. BV
Oostzijde 300
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Authors

Rozemarijn van der Molen studied design at the Rietveld Academy in Amsterdam, and obtained her Bachelor of Arts in 2005. She then studied conservation of historic and ancient metals at the Netherlands Institute for Cultural Heritage (ICN), graduating in 2009. She has recently graduated from the Master's programme in conservation at the University of Amsterdam, and works as a conservator in private practice.

Dr. Ineke Joosten earned a master in Geochemistry at the University of Utrecht (RUU) in 1992 and a PhD in Earth and Life Sciences at the Free University (VU) Amsterdam, the Netherlands in 2004. From 1992 she worked at the National Service for Archaeological Heritage (ROB) in the field of archaeometallurgy and conservation of archaeological metal. In 2001, she joined the staff of the Netherlands Institute for Cultural Heritage (ICN) as a research scientist. Her work involves the application of diverse analytical methods, but mainly SEM/EDS, to the study and conservation of objects such as plaster casts, dying techniques of ancient textiles and metal objects.

Tonny Beentjes was originally trained as a gold and silversmith in the Netherlands. This was followed by a degree in metal conservation in Belgium and soon after he started teaching metalwork conservation at West Dean College in England. He currently holds a position as the Programme Leader in metal conservation at the University of Amsterdam where he is also carrying out research towards a PhD in historical goldsmithing technology.

Dr. Luc Megens earned a Master in Chemistry and a Master in Classical Archaeology at the University of Nijmegen in1994, and a PhD in the characterisation of particulate organic matter in coastal waters at the University of Groningen in 2000. Since 2004 he has worked as a research scientist at the Netherlands Institute for Cultural Heritage (ICN) on inorganic analysis of cultural heritage objects, investigation of the effects of treatment methods on objects, architectural paint research and art technological studies. Current projects focus on the conservation of plaster casts, Van Gogh's studio practice and cleaning of painted surfaces.

Q & A SESSION

Lesley Frame: I was just thinking it would be interesting to see the relationship between the thermal expansion coefficient between these different layers and the effect it has on the technique – did you look at that at all?

Rozemarijn van der Molen: No I didn't. There are some papers of people who have and I have some information on that in my thesis but I didn't incorporate it - we didn't measure those, no. But in general you know that the metal would not have a very big thermal expansion coefficient and your paint would have a bigger one so you can work with that and there are lots of case studies from people that use it that actually determine what kind of layer it works best on. Of course the bigger the difference the better the thermal effect is going to work.

Alisa Vignalo: It says in your abstract you tried this on weathered steel and it was less effective, and I'm wondering if you can talk about that and whether or not you estimated the thickness of paint that could be removed as well from these metals?

Rozemarijn van der Molen: How do you mean estimate the thickness of the layers?

Alisa Vignalo: Meaning how thick was the spray paint on the aluminum and also did you try this on steel?

Rozemarijn van der Molen: Yes, I put graffiti on the weathered steel and there are images of that in the paper. It didn't work at all. Which I think is due to two reasons: the layer was really thin and it got embedded into the porous corrosion of the weathered steel and also my weathered steel had only been outside for 6 months, which is not very long. There is one paper on very successful [removal] of paint on weathered steel but I am suspecting that weathered steel has a much thicker corrosion layer, so they could remove the paint layer and little bit of the top layer of the weathered steel, which in my case wasn't possible – it just got very damaged.

Alisa Vignalo: Also I have another question: when you remove the paint, where does the paint go?

Rozemarijn van der Molen: Of course you still have your fraction that you are taking away. It just goes everywhere. There are certain nozzles that can blast and suck up the [debris] at the same time. They are actually using it for asbestos removal as well.

Ian MacLeod: Just an observation. This has potential application for removal of graffiti from rocks in terms of where vandals have gone to a rock art site and they've painted racist slogans on it. Using solvents on heavily weathered rocks doesn't work. And I think I might try it.

Rozemarijn van der Molen: Yes you should.

Molly Carlson: I wondered if you could tell me/translate 7 bar? What would that be in psi?

Audience: 125 psi.

Rozemarijn van der Molen: I know the maximum of the *Microclean* is 125 psi which would be 9 bar, so maybe 100? I mostly used 1 or 2 bars for the cleaning (15-30 psi).

Molly Carlson: We used anywhere from 50 to 75 psi I think for our tests. We also found similar concerns with condensate formation. We found that with a thermocouple attached to the backside of our sheathing samples and double checked with an Infrared thermometer, that in 60 seconds we could have a temperature drop of 147 degrees (Fahrenheit). So if you are operating in a high relative humidity, condensate would form. We had proposed to clean the *Snow Squall* in the middle of winter when you can hardly move your hand for the coldness, but it would have been good for the object (because of the low relative humidity).

Stéphane Lemoine: It is a very expensive technique, I think.

Rozemarijn van der Molen: It is a bit. The CO_2 snow machine starts up at 4000 euros, and the I3 *Microclean* equipment 4 years ago cost 16,000 euros.

Stéphane Lemoine: And I wanted to know what is the regular industrial use of this technique?

Rozemarijn van der Molen: It's extremely varied. It is all kinds of production lines, like for cars, casting, and baking factories - they would clean baking ovens, they would clean moulds for casting car parts, because there are steel parts and they don't get abraded – there are advantages of speed: before they would have had to take everything apart and now they can be cleaned all together.

Stéphane Lemoine: And the use in patrimony is the same in fact.

Andrew Lins: I might just comment that dry-ice has been used for quite a long time in the lead abatement industry in the U.S. as well.

Randall Heath: I have been doing this process for 10 years and would like to congratulate Rozemarijn for accurately portraying many of the aspects of dry-ice blasting. And putting a little bit of science to the thing, if anyone is interested in more science we this last year worked with a graduate student in Canada to characterize dry-ice dusting for cleaning smoke-damaged books. A very nice paper written on that – it has color imagery and profile measurements done before and after cleaning. And if anybody has any questions about dry-ice blasting, like I said I've been doing it for 10 years and I've done everything from rocket motors to dinosaur bones. And every project is different – I've done some things successfully and some didn't work so well. The internet is full of examples of what does work and if you want to know what doesn't work then I guess you should talk to me.

Jean-Bernard Memet: Thank you for your talk. It is a nice technique and we all know about it since Amsterdam. There were some posters in Amsterdam. We all have tried to use it but I want to point out one fact: the lifetime of the pellets – it is really inconvenient – the lifetime is from 24 to 48 hours. After that you cannot use it well – you can use it but with much less effect. After that you have much more condensation onto the substrate so it is a problem after 24 hours.

Rozemarijn van der Molen: Yes the dry ice absorbs moisture from the air and it gets softer. The producers of the dry ice always assured me that they could deliver dry ice to me in a few hours.

Jean-Bernard Memet: The good thing to do is to buy the machine and to buy out the producers of dry ice.

Rozemarijn van der Molen: To buy the dry-ice making machine yes. It is a little more expensive. I would suspect the dry-ice bricks are also affected, but not as rapidly as the pellets.

Randall Heath: I just want to say that the lifetime of the dry-ice depends on the producer, so it is extremely variable.

PRESERVING METAL ARTIFACTS IN THE FIELD: AN APPROACH TO CONSERVATION WITH LIMITED FUNDS, TIME AND SUPPLIES

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Abstract

Conservators without Borders (CWB) is an organization that provides field conservation support to archaeological sites and projects where insufficient funding or expertise prohibits on-site conservation. CWB coordinated and completed five different missions in Greece, Jordan and Peru during 2007 and 2008 with assistance from professional volunteer conservators and students. Each project also involved cooperation with archaeologists, heritage specialists and local communities. All of the projects required the assessment, stabilization and re-housing of excavated metal artifacts. CWB also conducted practical sessions with museum professionals in each country in an attempt to implement effective, yet realistic solutions. Although the focus is on preventive conservation methods, the team also explained and demonstrated basic remedial conservation techniques. This paper addresses CWB's treatment of vulnerable metal objects in the field with limited funding, time and supplies, while simultaneously promoting training and interaction with local museums.

Keywords: archaeological metals, fieldwork, preventive conservation, training, community outreach

Introduction

Conservators without Borders (CWB) is an international volunteer organization. In two years, with an overall finite budget of £12,570.00, CWB completed five projects in three countries: Greece, Jordan and Peru. CWB's aim is to lay foundations for the improved protection of a range of archaeological artifacts, including metals, by heightening awareness about conservation and actively promoting the principles of preventive care.

As post-graduate conservation students at University College London's (UCL) Institute of Archaeology, in 2006, Melina Smirniou, Christie Pohl and Dominica D'Arcangelo identified a need for increased conservation on archaeological sites. The co-founders hypothesized that conservators could help local museums and projects develop long-term strategies to care for their moveable heritage through effective two-way communication. CWB's strategy is to build collaborative relationships through training and conservation education while understanding practical limitations and the risks to local collections. CWB's experience to date suggests that there are real benefits to this kind of collaboration and the work is fulfilling a need.

UCL Futures is a grant making body, composed of alumni, staff and friends that awards funds to members of the UCL community for academic initiatives and innovative projects. UCL Futures awarded CWB with a grant in the spring of 2007 that allowed the founding members to test their objectives by initiating several international projects during 2007 and 2008. Through professional affiliations and contacts, CWB learned of several projects that could benefit from conservation assistance. Discussions with these project directors and Departments of Antiquities ensued and collaborative work was arranged. CWB worked for two summers on the Greek island of Kythera, hosted by the Kythera Island Project (KIP) in Mitata. The Jordanian Department of Antiquities hosted CWB for two three-week seasons to work on six different museum collections throughout the country. In 2008, CWB worked at two different sites in northern Peru: San José de Moro and Magdalena de Cao Viejo. This paper will detail CWB's fieldwork in Peru and the work completed at the Jordan Archaeology Museum in 2008.

Each CWB project has involved the assessment, stabilization and re-housing of excavated metal artifacts. This paper will contextualize CWB's approach to conserving metal objects in the field through a discussion of the various practical limitations: funding, time and supplies. It will also describe CWB's training strategy whereby an emphasis is placed on communicating the principles of preventive conservation and working with local participants in hands-on training sessions. Two case studies provide examples of CWB's approach towards preserving vulnerable metal artifacts. However, without long term funding, CWB is unable to make long-term project commitments, and therefore, the overall effects of the program are limited.

Conservation Challenges Encountered

Limited Funds

CWB's funds covered travel expenses, insurance, accommodation (when necessary), equipment and conservation supplies. The total amounts spent on each of the five projects ranged from £1,150 - £3,450. Many of the hosts were very generous with providing some on-site accommodation and subsistence for the CWB team members. This allowed CWB to purchase useful field equipment such as a microscope.

Limited Time

Due to the founding members' availability outside of their full-time jobs, each project lasted between two and three weeks. Between two and four professional conservators and/or students were present and staggered during each project, not including museum employees and other local participants. Several of the field school students at the San José de Moro excavation in Peru assisted with some of the conservation work, both in the lab and on-site.

Balancing the extensive conservation needs and the desire to spend ample time on the training and interaction with local participants proved to be challenging. Each project required working within fixed times, typically 4-5 hours each day. The conservators were often asked to assess storage facilities and museum displays; this was an important component for understanding the larger issues and conservation challenges faced at each site. The CWB teams also created a written set of guidelines (Pohl et al 2007), tailored for each project, which provided details about documentation, handling, treatment and storage of archaeological materials.

Limited Supplies

One of the criteria for selecting CWB initiatives are those projects with limited or no resources for acquiring conservation supplies. These materials are expensive and conservation-grade supplies are often very difficult to acquire or not available at all in-country. As a result, the CWB team brought as much conservation-grade equipment and supplies with them as possible. Some supplementary supplies that were inexpensive and readily available were purchased locally, such as Tupperware® containers for packing and storage. Although some of the conservation materials used in North America and Europe are not readily available in Peru and Jordan, it was important to explain why and how they are used. Samples were provided to in-country trainees who were interested in investigating local alternatives. Two of the CWB founding members are planning a future research project to investigate and identify suitable, yet economic, storage options for archaeological materials in developing countries.

Emphasis on Preventive Conservation

CWB experienced a variety of conservation-related challenges and obstacles throughout the five projects completed during 2007 and 2008. However, the most common, and detrimental, problems were inadequate storage and fluctuating temperatures and relative humidity (RH) levels due to uncontrolled environments. The preventive conservation approach serves as a realistic way of training local people in a limited amount of time and instills practices that can continue after CWB's visit. The methods covered, such as choosing suitable packaging materials and creating a controlled microenvironment, could usually be implemented and maintained by different members of staff with varying levels of experience, provided they first received training. Basic remedial treatments were completed on unstable metals (see Figure 1) through mechanical cleaning with a scalpel or glass bristle brush and the aid of a microscope. This process was followed by coating with a protective layer of 10% w/v Paraloid® B72 in acetone. Since the identification of active versus inactive corrosion can be problematic, CWB prepared a PowerPoint® slideshow presentation that showed examples of active corrosion and stable patinas on different types of metal.

Figure 1. CWB and museum employees treating metal objects from Jarash, Jordan.

More complex treatments requiring chemicals or other toxic substances were avoided for health and safety reasons and the inability to transport and properly dispose of these chemicals. Re-housing stabilized metals to withstand fluctuating environmental conditions proved to be a very effective solution.

Hands-on Training and Demonstration Sessions

For each project, CWB conducted training sessions with museum curators and employees, those responsible for artifact stores, archaeologists, students (both field school and conservation) and other interested local participants. Topics included safe object handling, an overview of conservation materials, before and after treatment photography, condition reporting, packaging and storage techniques, appropriate environmental conditions for different types of archaeological materials, mechanical cleaning and coating of metals and ways of improving the conditions and longevity of objects inside of museum cases. After the demonstrations, the participants had the opportunity to try the technique themselves. These sessions were very successful in terms of exposing the participants to a range of practical conservation strategies (see Figure 2). CWB is aware that in many locations certain equipment, such as a microscope, is simply not available; however, the team felt it was valuable for the participants to view and understand how one can be used, even in field environments. Other simple and less expensive forms of magnification, such as magnifying glasses and Optivisors, were also introduced and discussed.

An overall interest in conservation was often noted, even by participants who had no prior conservation knowledge or experience. CWB did interact with individuals who are responsible for conservation-related activities and treatments in-country. In Kythera, the team trained a local museum employee to clean and reconstruct fragmentary ceramic objects. In Jordan, CWB interacted with several people who routinely work on packing, storing and maintaining archaeological collections. During the 2008 season, CWB worked with two recently hired Jordanian conservators who will be working in a new museum in Amman. In Peru, the team worked each day alongside the on-site laboratory manager who regularly performs conservation-related tasks such as environmental monitoring and packing objects for storage.

Figure 2. CWB giving a demonstration at the Department of Antiquities in Amman, Jordan.

CWB fully acknowledges that training non-conservators in remedial techniques is problematic. The reality is that there is a shortage of conservation expertise in the developing world and in many cases heritage professionals do treat objects even without formal training. The goal was to give the trainees an overview of various remedial conservation treatments and demonstrate the hand skills required, while emphasizing that these treatments should not be performed without formal conservation training or supervision by a trained conservator.

Case Study 1: Metal Artifacts from Magdalena de Cao Viejo, Peru 2008

The site of Magdalena de Cao Viejo in Northern Peru is an early Colonial town and church, established in the mid-1500's by Dominican friars. CWB worked on a variety of materials from the site for 10 days during July 2008. Most of the metal finds were small, fragmentary and made from iron or copper alloy; almost all of the metal objects from Magdalena de Cao Viejo are European imports or made in European style (Quilter 2008). The metals that CWB examined had been stored in brown paper envelopes or plastic bags inside cardboard boxes in an unregulated storage environment (see Figure 3). The climate in this part of Northern Peru is very dry and quite favorable for metals.

Figure 3. Metal finds from Magdalena de Cao Viejo before treatment.

Fortunately, the CWB team observed only minimal amounts of active corrosion on the copper alloy objects in storage at the site. All of the metal finds from the Colonial site were photographed (before and after treatment), mechanically cleaned (where necessary) with a scalpel and/or a glass bristle brush and enclosed in a polyethylene bag, backed with Tyvek®. The corners of the bags were cut-off to prevent condensation. A few of the well preserved finds were selected for display in a new museum on-site. These were cleaned and repacked in custom-made Heritage corrugated board boxes with an Ethafoam® support or cavity, lined with Tyvek®. The metal finds were labeled and packed together in a sealed polyethylene box with silica gel and a humidity indicator card (see Figure 4). CWB creates a written record of all

Figure 4. Metal finds from Magdalena de Cao Viejo after treatment and re-housing.

conservation treatments that are completed; this is included in a final report for each project, which details the team's activities and recommends ways to improve the condition of objects and storage facilities. The reports become part of the archived documentation for each project. CWB also suggests that conditions be checked regularly and any changes noted.

Adjacent to the Colonial site is the El Brujo archaeological complex, a Moche period site where an important female ruler was buried in the 4th century BC. The mummified remains of Senora de Cao were accompanied by a large hoard of metal objects, including 18 necklaces of gold, silver, lapis lazuli, quartz and turquoise; 30 gold nose ornaments and silver diadems; and crowns of copper and gold (Gammara 2008). Although CWB did not treat any of the finds from the Moche site, the team was asked to advise on storage conditions and long-term preservation of the metal objects from the burial (see Figure 5).

Figure 5. The CWB team working with employees from the El Brujo Archaeological Complex in the laboratory at Magdalena de Cao Viejo, Peru.

The temperature and RH levels in the shared on-site store for the El Brujo archaeological complex and Magdalena de Cao Viejo are not controlled, although readings of both are taken on a regular basis by laboratory technicians. CWB did not have access to the environmental data but the store felt humid during a visit. CWB emphasized the importance of using a desiccant such as silica gel for the storage of metal objects in uncontrolled environments with high levels of RH. The importance of monitoring and re-conditioning the gel once it has absorbed a significant amount of moisture was also explained. The desiccant is very expensive in Peru and difficult to acquire. CWB left some loose silica gel at the site and demonstrated how to create packets using a breathable material such as nylon tulle.

The team recommended re-housing the smaller metal finds inside polyethylene bags placed inside Tupperware® containers with lids. The danger of storing metals in acidic brown envelopes was explained and the team left samples of more appropriate padding materials, such as acid-free tissue. CWB also suggested that the collection be checked on a regular basis for signs of active corrosion. A new museum is now open at the site, and the collections have been transferred to a more appropriate long-term storage space with improved environmental control.

Case Study 2: Metal Artifacts from the Jordan Archaeological Museum in Amman, Jordan 2008

CWB travelled to the Jordan Archaeological Museum in Amman in November 2008. The objective of the team's visit was to examine some of the objects on display and advise on preventive measures and possible future treatments. CWB also carried out remedial treatment on several objects that were assessed to be unstable or actively deteriorating.

Several problematic issues were observed in relation to the deterioration of the metal artifacts on display in the museum. There is no environmental control within the building or display cases. In addition, the textile lining inside the cases may be emitting acidic gases that could be encouraging the corrosion of the displayed metal objects. Some of the glass display cases are constructed with a copper alloy frame and portions of the frame are actively deteriorating. Powdery corrosion products from the frame were observed inside the cases (see Figure 6).

In Jordan, conservation expertise is limited due to a lack of training and resources. CWB conforms to contemporary conservation practices by aiming for minimal intervention on all treatments that are undertaken. The difference between active and stable corrosion products on copper alloys and iron, and how to determine these visually, were important points covered while CWB worked with museum employees in Amman. The team mechanically cleaned only the active corrosion products on copper alloy objects from the museum, leaving the stable patina in place.

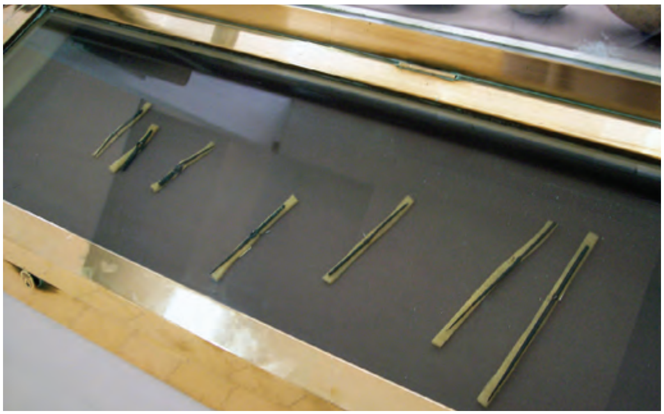

Figure 6. One of the display cases at the Jordan Archaeological Museum in Amman, Jordan.

One object that the CWB team treated in 2008 was a thin copper alloy belt, excavated in northern Jordan, dating from the Late Roman period. It was displayed inside a glass case, mounted on a strip of fabric secured to a curved plaster support, and showed several small areas of active corrosion (see Figure 7). CWB treated the object by first degreasing it with acetone. It was then mechanically cleaned using a scalpel under a microscope and then coated with 10% w/v Paraloid® B72 in acetone. Loose joins and fragments were reconstructed using 40% w/v Paraloid® B72 in acetone. After a discussion with the curator, the belt was remounted on a custom-made Plastazote® support and placed back on display (see Figure 8).

Conclusion

Each project undertaken by CWB was unique and provided conservation challenges. The co-directors have evaluated the organization's strengths and the areas where the program could be improved. Part of CWB's overall assessment involved feedback from the project directors and students who worked with the teams. The feedback from stakeholders was very positive and many expressed a desire to continue working with CWB and considered it a valuable experience for those in training. Although CWB faced constraints in terms of funding, time and supplies, with careful planning and multi-disciplinary collaboration CWB was able to add value to all of the projects and assist with the long-term preservation of several collections. In many cases, routine checks of the condition of artifacts in storage and reconditioning of silica gel have continued after CWB's departure. Since CWB's involvement, portions of the funds from the existing projects' budgets in Kythera and Magdalena de Cao Viejo have been allocated towards proper storage regimes. CWB has simultaneously raised the profile of each project through several publications and conference papers (Pohl and Smirniou 2008, D'Arcangelo et al 2009). By advocating consistent communication with stakeholders and by taking into consideration specific local needs and circumstances, it is feasible to formulate solutions and implement successful conservation practices. CWB is seeking additional funding to build upon the work completed in Greece, Jordan and Peru, and aims to develop new projects. In the meantime, the directors are available via email or phone to provide advice or have on-going dialogues with project leaders and museum specialists.

Acknowledgements

The authors would first like to thank University College London Futures for awarding CWB with a grant and making the five projects possible. Many thanks to Cyprian Broodbank and Evangelia Kyriatzi, the Kythera Island Project Directors, for hosting and working with CWB for two seasons. The authors are very grateful to Dr. Fawwaz Al-Khraysheh, Maysoon Qaterneh and May Shaer of Jordan's Department of Antiquities, as well as all of the museum employees, students and archaeologists that worked with CWB on museum collections from Amman, Umm Qais, Irbid, Karak, Petra and Jarash. Thank you to Jeffrey Quilter, Director of the Magdalena de Cao Viejo project, and Luis Jaime Castillo Butters, Director of the San José de Moro Archaeological Project, for their willingness to cooperate with CWB in Peru. The hard work and dedication of the following volunteer conservators is very much appreciated: Saray Naidorf, Amy Drago, Jackie Chapman, Judy Jungels, Diana Medellin and Margrethe Felter. The CWB Directors would also like to acknowledge the support of their respective employers who have granted leave requests, allowing the coordination of all of CWB's projects: the Smithsonian's Museum Conservation Institute, The Peabody Museum, The British Museum and the Institute of Archaeology, University College London.

Materials

Acid-free tissue
Shepherd's Bookbinders Ltd. (formerly Falkiner's
Fine Papers)
76 Southhampton Row
London WCB1 4AR

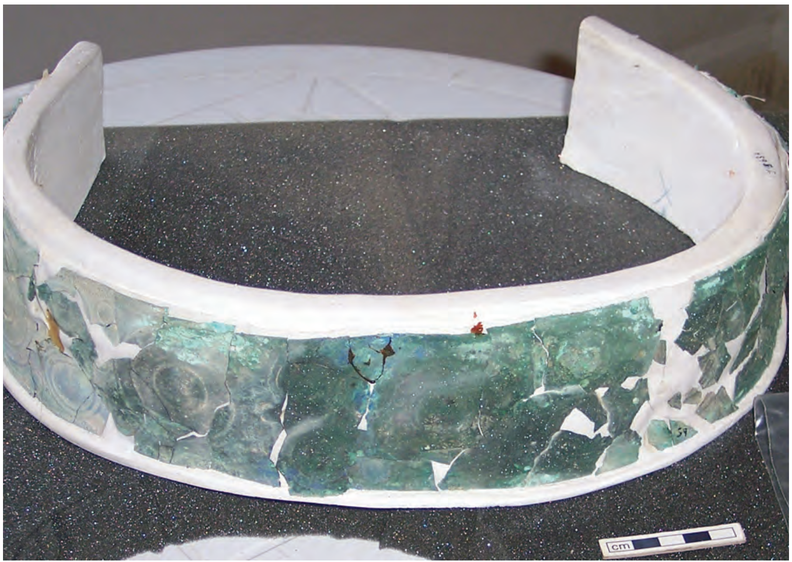

Figure 7. The copper alloy belt on its plaster support before treatment.

Figure 8. CWB conservator Magrethe Felter placing the belt on its new mount after treatment.

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Heritage corrugated board; Tyvek®
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Brooklyn, NY 11211, USA Phone: (212) 219-0770 Fax: (212) 219-0735
Website: www.talasonline.com

Nylon tulle
Jo-Ann Fabrics and Crafts
43 Middlesex Turnpike
Burlington, MA 01803, USA
Phone: (781) 272-9727
Website: www.joann.com

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Q & A SESSION

Paper Not Presented

PANEL DISCUSSION

Case Studies

Chair: Andrew Lins
Panelists: Emma Schmuecker, Ulrike Lehnert, Rozemarijn van der Molen

Claudia Chemello: Ulrike I really loved your paper and we really loved reading it during the editing process because it was so interesting. I found that it was like an excavation, a mini excavation again, and it just reminded me of how important documentation is in our field, and you did refer to records, can you just talk a little bit about that, were there hand-written records? Can you also tell us the size of the piece? Because it looked from that photo…but it is not actually that big. Is that correct?

Ulrike Lehnert: You mean the small male figures or the….it's about 34 cm high.

Claudia Chemello: So the old photograph was not to scale, because it looked giant [in the black and white photo in your presentation].

Ulrike Lehnert: We always wondered about the old photograph, but I think that the photographer might have taken a different angle, I don't know what he did. We always wondered about that.

Claudia Chemello: And so tell us about the records, because I know that you referred a lot to unpublished records, and that was very interesting, because I work on a lot of material that has had previous restoration and I don't now what they did, and it is really just a bit of an excavation, a mini-excavation again. So I thought that was interesting.

Ulrike Lehnert: Well, I am afraid that I can't really tell you anything about the records because I never saw them, I have to rely to the stuff that my Director told me because he saw those documents and he was in the depot and looked for them in Graz, and he had to dig very deep into it I can tell you. And he told me that he just found them by chance, there were not really fully there, it was a lot work, but he told me that he was surprised that he also found a bill about the screws that were used or were bought, so we have a variety of records but not all of them. And they were all handwritten, yes, right.

David Hallam: A common theme that comes out of two of your papers is the use of curators and curatorial records and how that can influence the conservation of an object. So, Emma, would you like to comment on that and start a discussion in that area?

Emma Schmuecker: I shall try. Well I thought that mine and Ulrike's papers were both very interesting, because we both had objects that had gone for restoration in the past. I think your object probably had more documentation on its restoration do you feel? No, not sure? Mine certainly did not have any documentation on its restoration, and really the only documentation I had was on its exhibition history in the UK, so I thought it was very interesting in my paper, not so much in my talk as I didn't have quite enough time, I just really did the very basic conservation practice to make it stable. I didn't want to remove any of these restoration areas as I felt that they were very important to the physical documentation of the object, but obviously you felt more confident removing the restoration and sort of displaying it more aesthetically.

Ulrike Lehnert: It was not because of the records that I felt more confidence at removing old restorations attempts, it was just that we wanted to get this wagon back to its original state, so just remove everything which didn't belong to it. So, we didn't really have to have those records because it was obvious what happened to the wagon. But it was quite nice to have them because it is a historical document.

Paul Mardikian: What I like about your paper Ulrike is that basically you are giving a final chance to put that documentation together, your conservation expertise and the archives, and you are creating a paper, and this paper is adding [to the information about the object], and it is not like having those archives available somewhere, you put them together and put them into an intelligible way so people can find those records and the fact that the paper is published now gives some kind of guarantee that this information is going to stay because we know how difficult it is to keep the conservation documentation. So, one way to do that is to publish. And like Claudia was saying it is a mini-excavation, and you're excavating a conservation project that has been going on for so many years, and you've been only part of the final years of that artifact, but you've tried to reconstruct the history of it, and I think that is just one way to say that we need to publish and case studies are extremely important, and publications might sound a little bit ideal compared to what we have to go through with artifacts, and we don't say everything, but still, this is I think an effort to compile the information and create something intelligible.

COATINGS AND CORROSION INHIBITION

Session Chair: David Thickett

AN INVESTIGATION OF GLYCOL BASED CORROSION INHIBITORS IN MUSEUM COLLECTION VEHICLE BRAKING SYSTEMS

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Abstract

An investigation into a variety of commercial glycol-based inhibited brake fluids was conducted to assess their suitability for use in maintenance regimens for museum collection vehicles. Testing of fluids incorporated weight loss, accelerated weight loss and potentiodynamic electrochemical analytical techniques. All of the glycol-based fluids tested performed significantly better than the uninhibited control fluid. A number of the U.S. Department of Transport (DOT), DOT 3 classified fluids generally performed well inhibiting corrosion on steel, aluminium alloy and brass with addition of 0-5 wt.% water and one DOT 4 fluid performed exceptionally well. The DOT 4 fluid has been selected in consultation with our engineers for use in National Museum of Australia collection vehicles. Addition of dodecanedioic acid to the control fluid was shown to increase performance and reduce corrosion rate two orders of magnitude. Further testing in glycol based brake fluids is recommended to determine efficacy in scheduled maintenance programs. Overall we can conclude that the museum's current regime of changing fluid at intervals of approximately two years will provide sufficient protection of all the systems surfaces and could be extended to between three and four years.

Keywords: Aluminium alloy, brass, steel, corrosion, glycol, Dodecanedioic acid, Brake fluid, Electrochemical testing

Introduction

This work is part of the National Museum of Australia's (NMA) use of risk and significance assessments to determine the treatment of objects (Russell and Winkworth 2009). Corrosion in braking systems was identified as a problem through our collection surveys. Understanding deterioration processes before selecting a product that minimises deterioration and enables maintenance was critical to reducing the risk of deterioration in brake system storage.

Vehicle braking and hydraulic systems are composite structures made from rubber, steel, aluminium alloy, copper, natural and synthetic textiles and are filled with a variety of fluids. Their function is to transmit force around a machine (see Figure 1).

A literature review revealed that non-commercial literature relating directly to corrosion in brake fluid is limited. The majority of relevant information comes from regulating bodies and manufacturer's claims (Wheeler 2006, Jackson et al. 1997). No specific conservation literature related to the conservation of car braking systems in museums was identified. The nearest related work was by Argyropoulos et al. (1999), who conducted a series of studies involving corrosion inhibitors in a polyethylene glycol fluid.

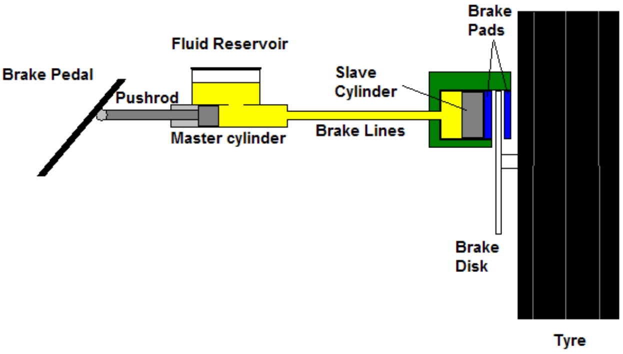

Figure 1. Simplified diagram of braking system showing fluid interaction.

Traditionally in technology museums, braking systems are either maintained or simply drained and ignored (Brunott 2009). Oxygen and water enter the brake system through sealing components resulting in varying degrees of corrosion activity on internal surfaces. The brake system of a vehicle that is operated regularly will have a periodic fluid circulation with sweeping and replenishment of an inhibitor on areas exposed to the environment. Under normal operating conditions, it is rare that the brake systems would fail due to corrosion.

The purpose of the brake fluid is to transmit and multiply the force from the master cylinder through brake lines before imparting force onto a secondary slave cylinder that causes contact between a stationary pad or shoe, with a rotating surface thus inducing friction. This actuation facilitates the transformation of the vehicle's kinetic energy into heat at the braking surface. The brake fluid must lubricate moving parts and provide corrosion protection.

Brake fluids

There is a vast array of brake fluids available, each with its own characteristics, composition and specific use. For this study, the United States classification system used for brake fluids is sourced from Standard 116 of the Federal Motor Vehicle Safety Standards (FMVSS) section of the National Highway Traffic Safety Administration Chapter of the Code of Federal Regulations (49 CFR 571.116). This standard is a measure of three performance levels (DOT 3, DOT 4 and DOT 5) of fluids and not of specific fluid chemistry or range of compositions. Fluids of these classifications have to meet with the same corrosion and elastomer compatibility requirements. The differences in classifications are determined by physical attributes, including corrosion resistance, boiling points and viscosities (Ricker et al. 1998).

PROPERTY	DOT 3	DOT 4	DOT 5	DOT 5.1
Dry Boil Point (ERBP*)	205°C	230°C	260°C	260°C
Wet Boil Point (Wet ERBP*)	140°C	155°C	180°C	180°C
Chemical Composition	Glycol	Glycol	Silicone	Glycol
Viscosity (-40°C) mm2/s max	1500	1800	900	900

**ERBP = Equilibrium Reflux Boiling Point*

Table 1. Requirements for brake fluid classification according to DOT standards.

DOT 3, 4 and 5.1 fluids are current and are based on polyethylene glycol-based fluid with additives. Glycol fluids are hygroscopic in nature, which can result in poor performance and decreased corrosion resistance.

DOT 5 fluids, including DOT 5.1, are silicon based and primarily used by the U.S. military, U.S. postal service and motorcycle manufacturer Harley Davidson (Rudnick and Shubkin 1999). These fluids have a boiling point comparable to glycol without the hygroscopic nature, potentially leading to longer service intervals. However, silicon reintroduces the problem of rubber compatibility and the new problem of the brake fluid and water existing as separate phases. When this occurs, water has a tendency to accumulate in the lowest points of the system resulting in severe pitting corrosion at this point.

Materials Selection

Selection of appropriate DOT brake fluids for museum vehicles is predicated on reduction of corrosion deterioration to minimal levels and maximizing maintenance interval periods. Mineral or silicon-based fluids require a complete overhaul of the vehicle's brake system. Dot 5.1 fluids, for instance, are for race applications and are not suitable. Dot 4 fluids are acceptable, however, added borates interact with absorbed water in the system through hydrolysis and can result in a build-up of boric acid that will increase corrosion rates (Anon 1999). Therefore DOT 3 and DOT 4 fluids were selected for investigation.

Inhibitors

All modern brake fluids employ some form of corrosion inhibitor, commonly in the form of amines. Amines serve as a pH buffer to neutralise the deleterious effects of acidic breakdown products from the fluid and to protect some of the metal by adsorption to the surface (Jackson et al. 1997). After 40 months of service, nearly all of these inhibitors are deactivated by thermal reactions that turn them into non-inhibiting chemicals. Buffer capacity and inhibitor concentration is also greatly reduced (Jackson et al. 1997).

The main reason for decay is the constant thermal cycling of the system during normal operation. However, in infrequently used systems, increasing water concentration will dilute these inhibitors and any corrosion will deactivate a portion of the active inhibitors (Hamner 1973). Inhibitors are most effective when there is good circulation of the fluid and consistent inhibitor concentration (Jones 1992).

The policy of the NMA is to operate collection vehicles once every six to 24 months. It was hypothesized that at such an intermittent use, the propagation of corrosion in the braking systems would be significantly reduced. However, this was found not to be the case as some braking systems were seizing within six months of going into storage or display. Corrosion was observed mainly in the areas of the wheel cylinders at the interface with the environment.

Figure 2. Corrosion and failed slave cylinder from a 1962 Mini Minor Car.

It seemed that, due to the hydroscopic nature of polyethylene glycol-based fluids, water concentration dictated the service life of the brake fluid in the system.

Investigations

The overall objective of this study was to establish a viable methodology to maintain functionality in selected brake systems of collection vehicles. Laboratory experiments were conducted on readily available DOT 3 and DOT 4 glycol-based brake fluids for effectiveness. The experiments allowed observation of the impact of water concentrations on corrosion rates. Brake fluid performance was assessed by electrochemical potentiodynamic polarization, American Standard Testing Materials (ASTM), weight loss techniques and Federal Motor Vehicle Safety Standards (FMVSS) elevated temperature weight loss techniques. The testing enabled comparison of corrosion protection offered by commercial brake fluids with an uninhibited base fluid.

Brake fluids were tested with the addition of de-ionized water in 10 wt.% increments for the weight loss experiments, and 0-5 wt.% increments for electrochemical potentiodynamic polarization experiments.

Room temperature weight loss

Weight loss testing ASTM G31-72 (2003) was undertaken to determine sample performance in the brake fluid solutions. Mild steel nails were selected as the test material as it is representative of the chemical composition of the steel commonly found in brake cylinders. The mild steel nails were each placed in 50 ml test tubes and immersed in 40 ml of the brake fluid solutions. The test tubes were placed in a laboratory with an average ambient temperature of 25°C + 1°C for a period of 105 days. Three replicates were used for each solution.

Once removed from the solution, the samples were stripped, dried and weighed. Weight loss in grams was calculated for each coupon. Visual observations of coupon corrosion were recorded over the duration of the experiment.

Elevated temperature weight loss

A modified laboratory test TP-116-04 for FMVSS 116 Motor Vehicle Brake Fluids (Department of Transportation 2005) was applied to a series of copper, mild steel and aluminium alloy coupons (25 x 60 mm) that were prepared to ASTM G 1-90 Standards (ASM International 1992) (see Figure 3). The test assembly was placed in a screw-top glass jar and immersed in 200 ml of the brake fluid solutions (see Figure 4). The test assemblies were then placed in an oven at 100ºC. After three months, the test assemblies were removed and disassembled. Each coupon was cooled, cleaned, dried and weighed to determine relative weight loss. Visual observations of coupon corrosion were recorded over the duration of the experiment.

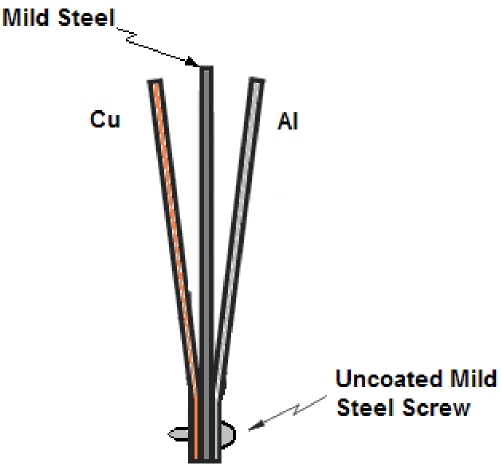

Figure 3. Elevated temperature test strip assembly.

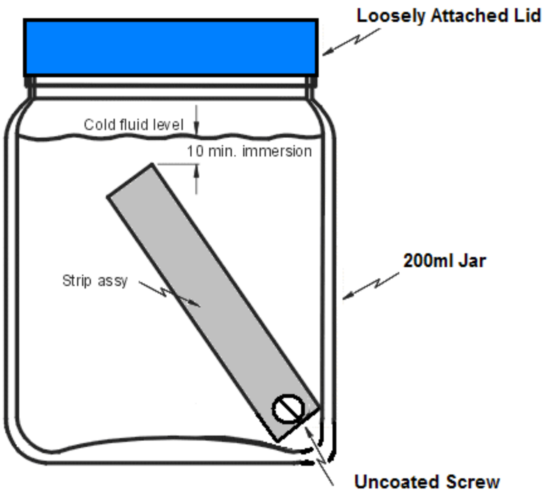

Figure 4. Elevated temperature experimental set up.

Electrochemical potentiodynamic polarization analysis

Non-aqueous electrochemistry is a well established branch of electrochemistry. In the case of the brake fluids we are not looking at a 'non-aqueous' environment, but rather a semi-aqueous high resistance environment where the standard electrochemical rules still apply or give a good approximation of relative corrosion rates. Electrochemical potentiodynamic polarization techniques were conducted on mild steel, brass, and aluminium alloy electrodes, as they are commonly found in components of brake systems, to determine:

- The effect of water concentration on corrosion resistance of various commercial brake fluids
- The efficiency of their inhibitors.
- The effect of addition of 0.05 M dodecanedioic acid.

The sample was slotted into a basic electrochemical cell (100 ml) fitted with a silver/silver chloride reference electrode and two platinum counter electrodes (see Figure 5). The cell was connected to a Parstat 2263 Princeton potentiostat (Applied Research Advanced Electrochemical System). Tafel plot data was obtained with Electrochemistry Software — Powersuite Version 2.55 Advanced.

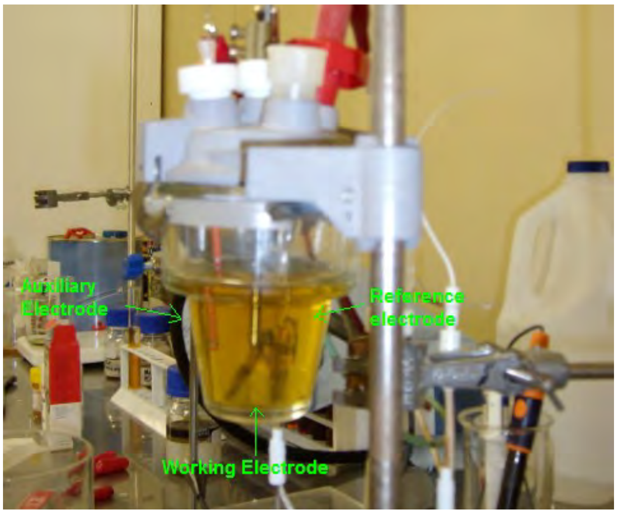

Figure 5. Electrochemical cell set up.

Results and Discussion

Water Concentration

Room temperature weight loss tests demonstrated that corrosion forms earlier and in greater quantities as water concentration increased. At the conclusion of this experiment, corrosion was observed in water concentrations as low as 30 wt.% (see Figure 6). The available data (see Figure 7) indicates an exponential relationship between water concentration and corrosion rate.

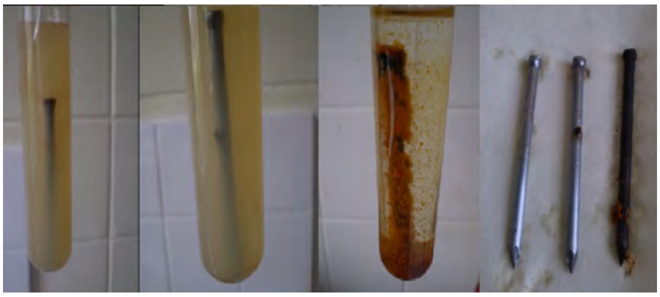

Figure 6. From left to right: 70% water in solution (particulate corrosion), 80% water in solution (localised corrosion), 100% water control (significant uniform corrosion), and nails after removal 70%, 80% and control.

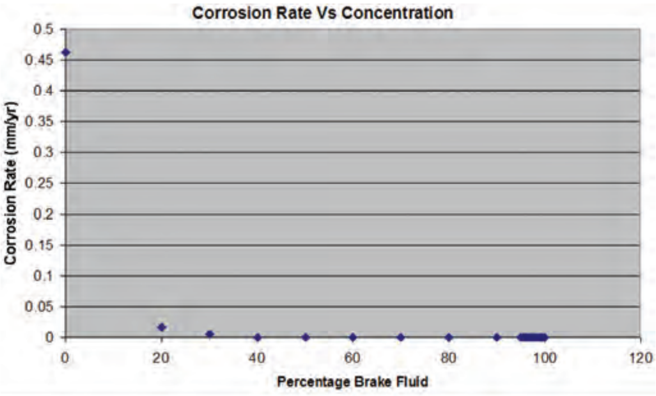

Figure 7. Corrosion rate versus concentration calculated from un-accelerated test over a period of 105 days.

Tafel Data

Tafel data of brake fluid in varying water concentrations using a mild steel electrode resulted in a clear indication that corrosion rate increases exponentially with higher water concentration (see Figure 8). This data confirms the significant effect that ingress of water will have in the corrosion of vehicle brake systems.

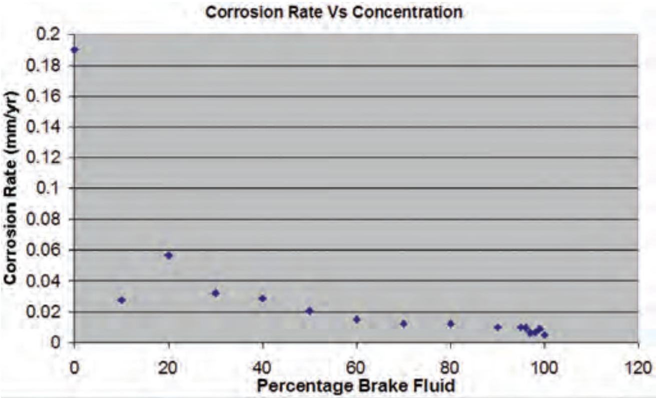

Figure 8. Corrosion rate versus water concentration. Tafel data using mild steel electrode.

Tafel data using a mild steel electrode of the corrosion rates in the standard working range of brake fluid at 0-5 wt.% water indicates a doubling of the corrosion rate from pure brake fluid to a 5 wt.% inclusion (see Figure 9). This result is significant however it falls within a minimal corrosion rate of 0.02mm/yr that is suitable for museum maintenance programs.

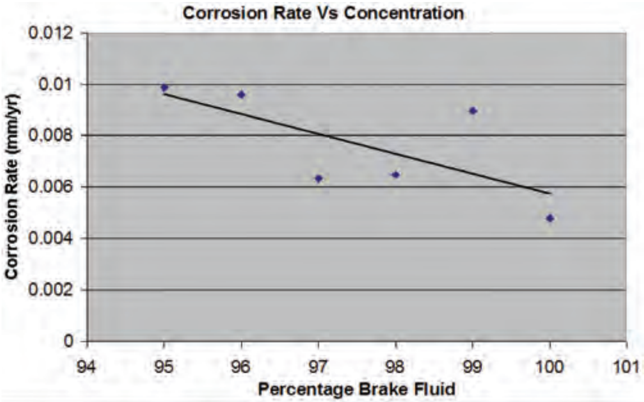

Figure 9. Corrosion rates in the standard working range of brake fluid, which is 0-5 wt.% water.

Comparison of Fluids

A variety of DOT 3 and DOT 4 brake fluids were tested using mild steel, brass and aluminium electrodes in order to determine which fluid offered the best corrosion resistance. An inhibitor free polyethylene glycol-base fluid was used as a control. The uninhibited control was found to have a corrosion rate an order of magnitude greater than some of the inhibited brake fluids (see Figure 10).

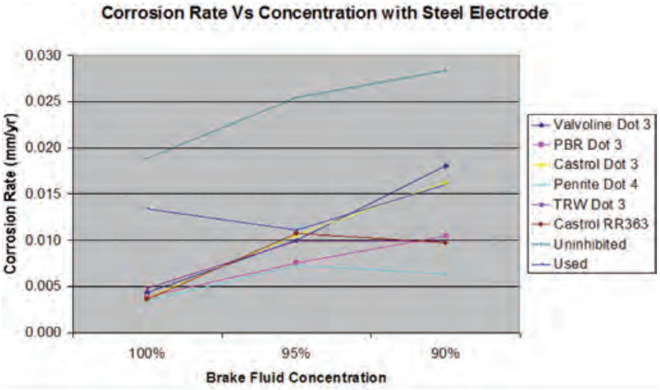

Figure 10. Comparison of corrosion protection offered by various fluids with steel electrode.

In pure form, all the new and commercially available brake fluids provide very similar levels of protection. However, protection levels begin to differ as the water concentration increased. PBR super DOT 3 and Penrite DOT 4 offer better protection at the 5 wt.% water concentration. At the 10 wt.% water level Penrite DOT 4 clearly offers the best protection. Protection offered to the aluminium electrode proved erratic (see Figure 12).

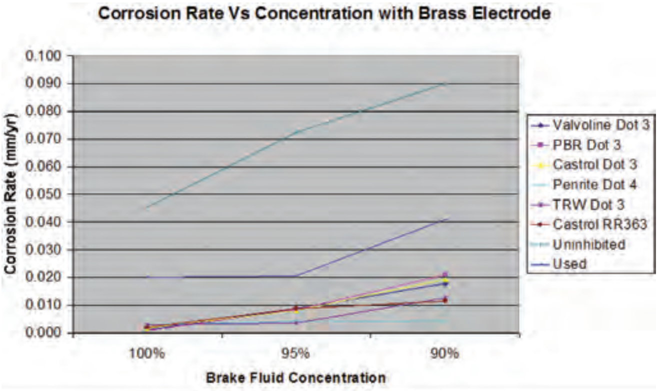

Figure 11. Comparison of corrosion protection offered by various brake fluids with brass electrode.

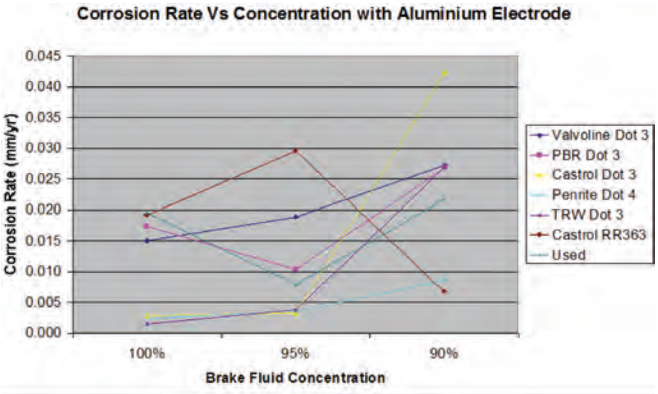

Figure 12. Comparison of corrosion protection offered by various fluids with aluminium electrode.

Effects of Inhibitor

With all tested brake fluids it was determined that the inhibitors, both included by manufacturers and added, were primarily influencing the anodic process. Dodecanedioic acid 0.05 mol/L was added to the uninhibited base fluid as this concentration has proven to be effective (Rocca et al. 2007). The test was run after a 48-hour settling period and data produced indicated a reduced corrosion rate of almost two orders of magnitude, and continued to reduce over six days in a stable manner (see Figure 13).

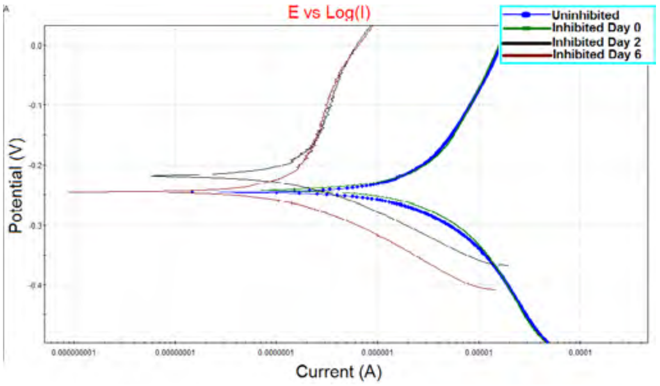

Figure 13. Addition of Dodecanedioic acid 0.05 m/L to uninhibited base fluid with 10 wt.% water inclusion over 6 days.

Application to current maintenance practice

Prior to this work, brake system integrity could not be guaranteed for longer than six months, and the authors expected to have to carry out major work on brake systems after each prolonged session of display.

Currently, the maintenance regimes for storage and display are:

- Back off drum brakes from drum, if fitted.
- Exercise brakes every six months.
- Sample and Monitor fluid at master and slave cylinders at least every 12 months.
- Renew fluid if Fe or Cu levels rise significantly in slave cylinders.
- Completely change fluids at two years.

As a result of this work, in some instances we are extending the fluid change interval to three to four years and employing corrosion inhibitors for interfacial areas of the brake systems.

Conclusions

The tests undertaken in this study indicate that fluids in brake systems of museum collection vehicles should be regularly monitored to determine performance and potential corrosion rates within the system. The data presented clearly demonstrates that corrosion rates will increase exponentially with water concentration. All of the glycol-based fluids tested performed significantly better than the control fluid. A number of the DOT 3 classified fluids generally performed well at inhibiting all metal types tested with the addition of 0-5 wt.% water, and one DOT 4 fluid performed exceptionally well. The DOT 4 fluid has been selected in consultation with our engineers for use in our collection vehicles.

The addition of Dodecanedioic acid to the control fluid has proven to increase performance and reduce the corrosion rate by two orders of magnitude. Further testing in glycol-based brake fluids is recommended to determine efficacy in scheduled maintenance programs.

Overall, we can conclude that the museum's current regime of changing fluid at intervals of approximately two years will provide sufficient protection of all the systems surfaces. Further, the experimental data in conjunction with the findings of Wheeler (2006) indicate that extension of monitored fluid service intervals to a period of three-and-a-half years is achievable in our dry storage environment.

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Col Ogilvie and Ian Stewart for their unwavering contribution to valuable discussions and engineering guidance. The Australian National University, School of Engineering and Computer Science and the National Museum of Australia for supporting this work.

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Q & A SESSION

Molly Carlson: What kind of metal is the slave cylinder made out of?

David Hallam: It depends on the vehicle. But normally cast iron. The pistons in the cylinders in this particular case, which was a prototype Holden, it was made of aluminium.

Molly Carlson: So the fluid touches both the iron and the aluminum.

David Hallam: Yes.

Molly Carlson: How did you come to choose that particular inhibitor? Does that have properties for both those metals? Have you thought about, and I don't know its effect on aluminum, but Hostacor IT?

David Hallam: Yes. I'm more tempted to look more solidly. With this we just wanted to say 'does it make a difference?'. With what inhibitor we add to it, I am far more tempted to go towards something like the Cortec products. Because we know that commercially they are used for mothballing of vehicles. So that is the next step of the process. And rather than looking at what we would call conservation inhibitors I'd much rather go the commercial way.

Molly Carlson: Thank you that was interesting.

Paul Mardikian: By looking at what you found – the more water you have, the more corrosion, which seems intuitively right – what about using 100% solutions? 100% brake fluids.

David Hallam: You never end up with 100% because it is hygroscopic – it will always be about 2% water. So it absorbs moisture from the atmosphere – that's the critical thing. So what we were interested in there was how much difference does that make and it makes quite a bit of difference to the corrosion rate. And what we actually think is happening at the interfaces is we are getting very thin layers of glycol and much higher concentrations of water in that area.

Eric Schindelholz: When you did your polarization tests did you carry them out under de-aerated conditions?

David Hallam: No, just natural.

Eric Schindelholz: Is your brake cylinder sealed? I mean as far as oxygen exchange in you fluid?

David Hallam: No, oxygen can go straight through the rubber seals.

Eric Schindelholz: I would think that some of the corrosion that you are showing may be a little lower inside your cylinder because you have an oxygen diffusion controlled reaction there.

David Hallam: No, the oxygen will go straight through the rubber.

Ian MacLeod: We have a motor vehicle collection which is prone to similar problems, but I was wondering – given that your two points of leakage of air into the system are at opposite ends: one with the reservoir and the other with the pads and the seals, have you looked at spraying on or coating the rubber seals with polyvinyl butyral solutions which do stop penetration of water quite effectively. And whether or not it's worthwhile or whether it is interfering too much with the potential operational use of the vehicle. And the second question: how do you balance out the extra care you have got to put in trying to stop moisture getting in with being able to run the car as a useful vehicle?

David Hallam: We have certainly played around with methods of trying to reduce the water and oxygen ingress through the rubber seals. So far we haven't really been successful. The problem is the interactions that they have with the rubber seals and causing them to swell and not function. We have also worked out methods where we – what we call is 'back-off' the cylinders, so the seals move further into the cylinder. And that seems to work. The other thing that we know works, is periodically – this is every 3 months – someone goes in and puts their foot on the brake. And it's really a very simple thing and what that does is it renews the glycol at that interface and renews the corrosion inhibitors in that area. Because what we think is happening is we get a depletion of corrosion inhibitors at the interface, which is why we also use the Senson VCI (Vapor Corrosion Inhibitor).

Eric Nordgren: I think maybe that last method or driving the vehicle sounds the best but I was wondering if you'd considered the silicon or other types (of hydraulic fluid) – I know they were not original to the vehicle and you might have to change the seals. I was just wondering if you had thought about that.

David Hallam: Yes we have. And the problem with silicon is that if you want to use silicon and not get some really quite amazing corrosion problems you need to totally change all of the hardware in the braking system. The glycol gets into everything and you can never completely remove it. So we just view that intervention as being far too great. On that, we do have in our collection a vehicle on which the original owner did that. And that vehicle still has the same brake fluid that it had in 15 years ago. So yes it does work but we feel the intervention is too great.

David Watkinson: Just wondering what the protocol was for when you were checking for concentrations of ferrous ions and copper ions – do you bleed the brakes and get samples from there and check in the master cylinder as well?

David Hallam: Yes, we bleed some out of either end and we basically do an XRF on what we remove. And we just use a handheld XRF – it's quite simple.

DEVELOPMENT OF NEW ENVIRONMENTALLY SAFE PROTECTION SYSTEMS FOR THE CONSERVATION OF IRON ARTEFACTS

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Abstract

In the framework of safeguarding iron artefacts belonging to museum collections, the anti-corrosion performances of two new non-toxic corrosion inhibitors, based on carboxylic acids extracted from vegetable oil, were evaluated. Electrochemical measurements, accelerated and natural ageing tests have demonstrated the efficiency of these inhibitors as temporary treatments. Surface analysis experiments undertaken with field emission gun scanning electron microscopy (FEG-SEM) and Raman spectroscopy, have revealed that their anti-corrosion properties are correlated to the precipitation of an iron carboxylate protective layer at the metal surface. Evaluation of their potential application for preservation of cultural heritage is addressed.

Keywords: atmospheric corrosion, cultural heritage, protection, iron carboxylate, corrosion inhibitor

Introduction

Atmospheric corrosion is a major problem for metallic collections stored in uncontrolled environmental conditions within museums. To avoid corrosion, barrier coatings must be employed. Many different barrier coatings have been developed for use in conservation, but most do not fulfil the basic ethical requirements of being easy to remove, causing no change in visual appearance to the surface of the object. Moreover, their impact on the environment must be reduced as far as possible. Among the protection systems tested by conservation scientists on real artefacts (Rocca 2007), it appears that some corrosion inhibitors could meet these basic ethical requirements while offering significant measurable protection for metallic artefacts.

Since the 1980's, the number of papers related to the study of new inhibitor compounds for artefact protection has increased (Rocca 2007). Unfortunately, many of the products tested are hazardous to human health, especially for copper alloy artefacts (Merck 1981, Faltermeier 1998, Dermaj 2005). Relatively few studies are directed towards the investigation of non-toxic organic compounds. A survey conducted during the PROMET (Innovative Conservation Approaches for Monitoring and Protecting Ancient and Historic Metals Collections from the Mediterranean Basin) project (Argyropoulos 2008) identified benzotriazole and tannic acid as the most commonly used inhibitors for corrosion control of historic iron within the Mediterranean Basin (Argyropoulos 2007). PROMET was a research project funded by the 6th Framework Program of the European Union, with the participation of 21 partners from 11 countries from the Mediterranean Basin, with the aim of developing new techniques and materials to improve the conservation of metallic cultural heritage. Within the framework of PROMET, the authors have studied and developed new safe corrosion inhibitor solutions for iron-based artefacts (Hollner 2007 a and b).

Inhibitor systems based on linear saturated long chain carboxylic acids have been studied for more than 10 years (see Table 1). These compounds, of general formulae $CH_3(CH_2)_nCOOH$, abbreviated to HC_n, are generally used under the form of sodium carboxylates, abbreviated to NaC_n. They are environmentally friendly compounds extracted from vegetable oils (sunflower, colza, palm), easy to remove, and inexpensive. Their anti corrosion properties were successfully investigated for copper, zinc, lead, and magnesium; see previous publications cited in Table1).

The performances of these new inhibitors have shown promising results when applied to clean metal surfaces (Hollner 2007a). As demonstrated by characterisation of the protective layer by scanning electron microscopy (SEM) and in-situ synchrotron radiation experiments, the protection mechanism is attributed to the presence of a thin metallic soap film made of iron decanoate (Mirambet 2010).

Surface tested	Treatments tested	Reference
Copper	Sodium carboxylates NaC_n with n=6 to11	Rapin 1998
Magnesium	Sodium carboxylates NaC_n with n=6 to11	Daloz 1998
Lead	Sodium carboxylates NaC_n with n=6 to12	Rocca 2001
Zinc	Carboxylatation treatments HC_7 and HC_{10}	Peultier 2003
Lead	Sodium carboxylates NaC_7 NaC_{10}	Rocca 2004

Table 1. Publications citing treatments performed with HC_n and NaC_n on different metallic surfaces.

In the case of scientific and historic iron artefacts, surfaces can be covered by thin corrosion products, corrosion layers and/or rust pits. To investigate the effectiveness of these new environmental friendly inhibitors on such surfaces, the authors tested them on pre-corroded samples of iron whose surfaces are similar to historic cultural iron objects (Hollner 2007b, Argyropoulos 2008). Results from this previous research, which tested inhibitors of several chain lengths and concentrations, demonstrated the effectiveness and the suitability for application on objects from museum collections of two specific inhibitors (NaC_{10} and HC_{10}). In this paper we propose to compare their performances by electrochemical measurements and climatic chamber tests. This paper also discusses their respective field of application for the preservation of iron objects.

Experimental

Experiments were carried out on iron coupons, called “PROMET coupons” (low carbon steel 0.14wt % C), produced to simulate iron objects. These coupons have been pre-corroded after exposure in a humidity chamber (24h at 30°C /100% relative humidity (RH) + 24h at 25°C /50-60% RH + 24h at 30°C /100% RH) with no addition of specific corrosion accelerants (Argyropoulos 2008). The artificially aged coupons were mechanically cleaned to remove corrosion, mirroring how corroded historic iron might be dealt with in a conservation laboratory prior to adding a protective coating. Linear sodium decanoate solution ($0.1 mol.L^{-1}$, hereafter cited as NaC_{10}), was prepared through neutralisation of decanoïc acid by sodium hydroxide. A carboxylatation solution, hereafter cited as HC_{10}, was prepared by mixing in an hydro-organic medium, decanoïc acid HC_{10} at $30g.L^{-1}$, with an oxidant agent, hydrogen peroxide H_2O_2 (pH=3.5, at $0.1 mol.l^{-1}$).

Electrochemical tests were performed in a three-electrode electrochemical cell connected to a Gamry PCI4/300 potentiostat. A circular and horizontal working electrode ($3.14 cm^2$) was placed at the bottom of the cell under a Pt-disk electrode. The reference electrode was a KCl-saturated calomel electrode (Hg/Hg_2Cl_2, E=+0.242 V /SHE). The corrosive medium simulating the atmospheric corrosion was the ASTM D1384-87 standard (hereafter cited as ASTM water), which has the following composition: 148 mg/L Na_2SO_4, 138 mg/L $NaHCO_3$, 165 mg/L NaCl.

The polarisation resistance (R_p) measurements were carried out with a scan rate of 125 mV/s for a range of 20 mV (E_{corr} +/- 10mV). Measurements of the electrochemical impedance spectrum were performed from 0.01 to 10^5 Hz with amplitude of 10mV.

For the assessment of the NaC_{10} solution, the EIS experiments were performed on a PROMET coupon immersed in a medium containing the ASTM water with 0.1M of NaC_{10}. For the carboxylatation treatment, the PROMET coupon was treated for four hours in the HC_{10} solution then immersed in the ASTM water. Solid iron decanoate powder was synthesised by mixing an iron nitrate aqueous solution with a NaC_{10} solution.

Surface characterization was carried out with an FEG-SEM (Hitachi S4800) and by Raman spectroscopy on a Jobin Yvon LabRam Infinity spectrometer, with a Nd:YAG laser emitting at 532 nm coupled to an Olympus microscope, allowing micrometric observation and analysis of the sample.

Climatic chamber tests were undertaken in a LIEBISCH - KSE 300 chamber. The treated samples were exposed to the following test cycle (DIN 50017 standard): eight hours at 100% humidity, using twice-distilled water heated to 40°C, then 16 hours at room temperature and humidity (T between 18°C and 22°C and RH around 40%).

The protection system was also applied to a real artefact, a torpedo from the National Maritime Museum located in the Romainville fortress near Paris. Before application of the inhibitor, the surface of the torpedo was partially cleaned by application of a nitric acid solution to remove the non-adherent corrosion products. This step was only carried out to allow a clear evaluation of the effectiveness of the carboxylatation treatment during the ageing process. Each month, the treated surface of the torpedo was recorded with in-situ macroscopic digital images collected with a standard photographic camera in order to evaluate the efficiency of the protection system.

Results

Figure 1 shows the corrosion potential evolution of treated PROMET coupons with immersion time in the ASTM corrosive medium. For the non-treated coupon and the NaC_{10} treated coupon, the corrosion potential rapidly decreases to the –0.7V value after two hours. In comparison, the E_{corr} of the treated coupon in the HC_{10} solution decreases more slowly and remains at higher values.

The polarisation resistance of treated PROMET coupons in the ASTM corrosive water was measured as a function of the immersion time as shown in Figure 1. During all experiments, the polarization resistance values recorded for the coupon treated in the NaC_{10} solution remain very close to the values obtained with the non-treated coupon ($1\text{-}2 kOhms.cm^2$). In contrast, polarization resistance for the HC_{10} treatment at the beginning of the test is almost one order of magnitude higher than the values measured for the untreated iron plate. A slow decrease of the Rp value of HC_{10} occurs with increasing immersion time, the polarization resistance remains above that recorded with the NaC_{10} solution at the end of the test. The best improvement in anti corrosion performance is obtained with the HC_{10} carboxylatation treatment.

In order to better characterise the electrochemical behaviour of iron during the treatments, electrochemical impedance spectroscopy (EIS) measurements were

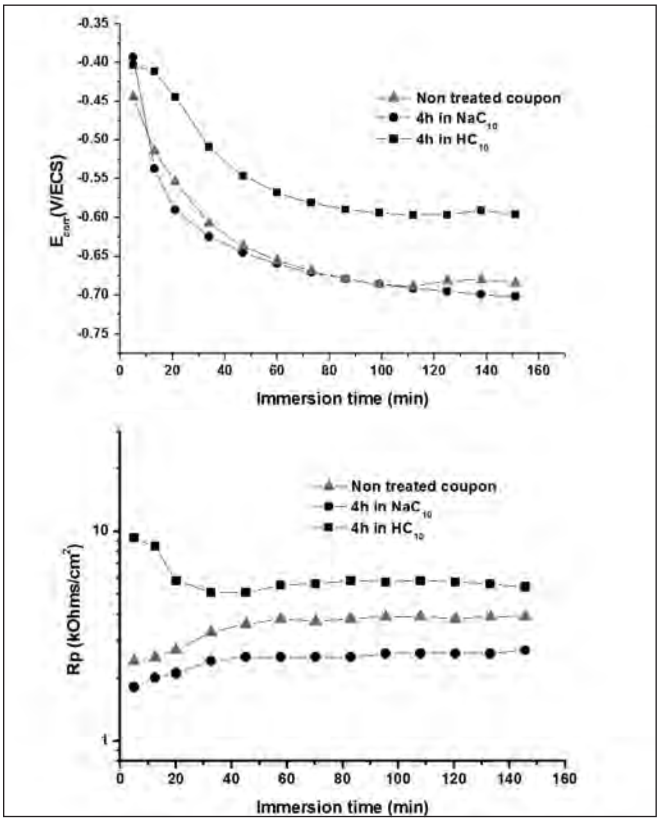

Figure 1. Influence of the immersion duration on the corrosion potential *(top)*. Influence of the immersion on the Rp values of PROMET coupons *(bottom)*.

performed. Figure 2 shows the impedance Nyquist plot of a PROMET coupon measured at open circuit potential after seven hours of immersion in ASTM water, with and without the addition of 0.1M of NaC_{10}. The addition of NaC_{10} to the corrosive medium leads to an increase of the capacitive loop of the impedance spectra. The EIS measurements performed for a PROMET coupon previously treated in HC_{10} for 4h then immersed in the ASTM water for 1h are presented in Figure 3. The impedance modulus recorded at low frequency is above the one detected with the ASTM water. For this specific treatment a second time constant appears at high frequencies (10^3-10^4 Hz), which can certainly be associated with the formation of a protective film at the metal surface.

Finally, the electrochemical experiments and particularly the impedance data from the surface of the PROMET coupon in contact with HC_{10}, highlight a much more capacitive and resistive behavior than with NaC_{10}.

The surface of the PROMET samples after 24h of immersion in a 0.1M NaC_{10} solution and 30min in a HC_{10} solution (Hollner 2007b), was observed by SEM. Figure 4 shows that the surface of the coupon treated in HC_{10} is well covered by a layer of a crystallized compound. As displayed in figure 5, Raman spectrum of the passive layer formed after treatment in a HC_{10} solution shows several characteristic vibration bands of a synthetic iron decanoate, especially around 2800-3000 cm^{-1} (CH_3 groups) and 1500 cm^{-1} (COO^- groups). On the contrary, even after 24h of immersion in NaC_{10}, no similar layer can be observed with SEM. These results show that as with clean iron and copper surfaces (Rocca 2001, Mirambet 2010) the inhibition effect of sodium carboxylate on the PROMET coupon is correlated to the formation of a very thin layer of a metallic soap, since only very weak bands around 2800-3000 cm^{-1} were detected by Raman spectroscopy (see Figure 5).

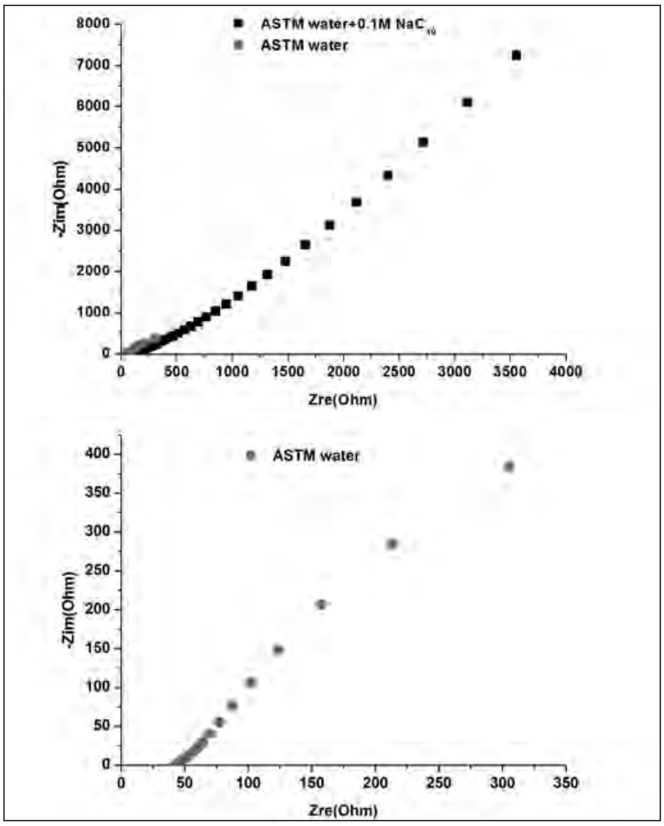

Figure 2. Nyquist plot for PROMET coupons after 7h of immersion in ASTM water with or without a 0.1M NaC_{10} solution *(top)*. Detail of the Nyquist plot recorded for iron in ASTM water *(bottom)*.

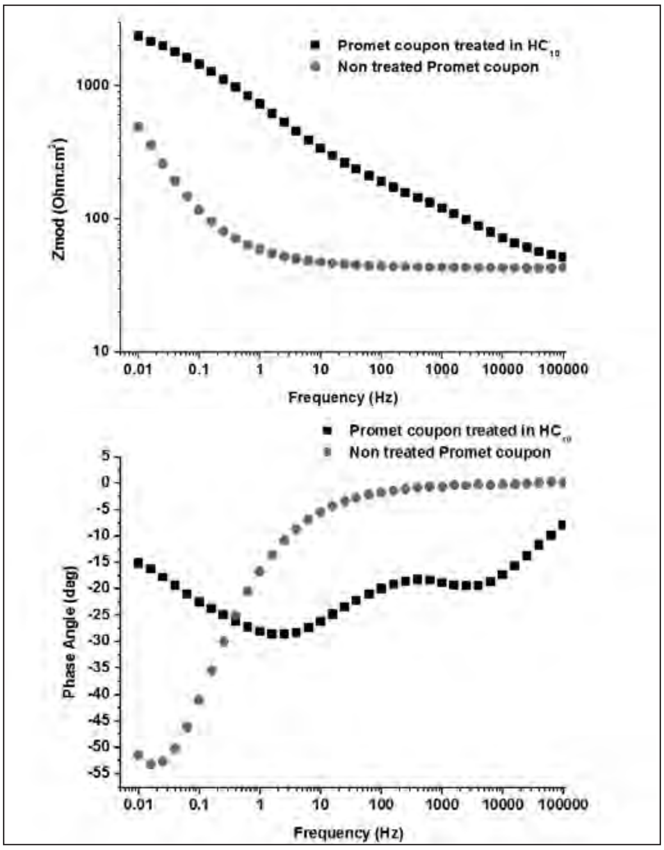

Figure 3. Impedance Bode plots for PROMET coupons treated with or without HC_{10} after 1h of immersion in ASTM water: Impedance modulus Bode plot *(top)*. Phase Bode plot *(bottom)*.

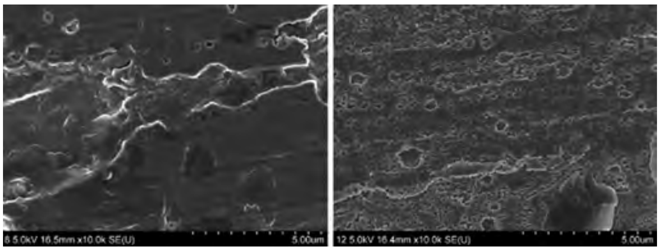

Figure 4. FEG-SEM images of the surface of PROMET coupons treated in NaC_{10} *(left)*, HC_{10} *(right)*.

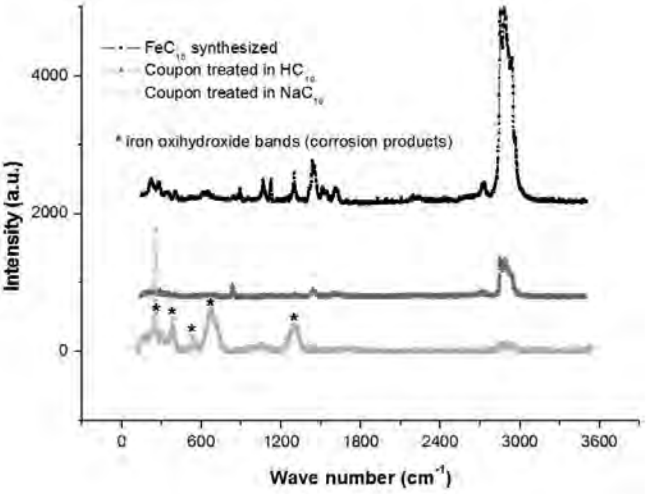

Figure 5. Raman spectra of the synthetic iron decanoate and of a PROMET coupon treated in HC_{10} and NaC_{10}.

The assessment of the efficiency of the sodium decanoate and carboxylatation solutions was carried out in a climatic chamber. Figure 6 shows the different coupons after several days in the climatic chamber. In the case of the HC_{10} treatment, a very soft red-orange coloration of the surface, characteristic of the precipitation of a thick iron carboxylate protective layer can be seen. This may be ethically unacceptable in conservation contexts. However, the objective was to evaluate coating performance and not the appearance of the surface for this specific test. However, the authors note that surface appearance may be an important factor to consider before using the treatment. Nevertheless, this point was taken into account in the following tests especially for application on real artefacts.

For the untreated sample, pitting phenomenon was clearly observed after only three days in the climatic chamber. In the case of the coupon treated in the NaC_{10} solution, only a few rust pits were visible after three days. At the end of the experiment, a large part of the surface of the NaC_{10} coupon remained uncorroded in comparison with the non-treated sample. This result confirms that the treatment in sodium decanoate slows down the development of rust at the metal surface. The best performance was obtained with the HC_{10} carboxylatation solution, since only a few spots of corrosion were observed after 22 cycles.

The final test was carried out on a torpedo belonging to the National Maritime Museum of Paris, which is stored in a boathouse in an uncontrolled environment. Considering that HC_{10} treatment provided the best performance during the accelerated ageing test, only this treatment was tested in real conditions. For comparative purposes, only half the surface previously cleaned with nitric acid was treated by brush (two coats) with the carboxylatation solution (see Figure 7). The carboxylatation treatment did not modify the appearance of the surface on the torpedo. This test ascertains that surface appearance can be controlled by brush application of the carboxylatation treatment unlike what was observed with the coupons treated by immersion during the accelerated ageing test. Should there be a color change, the iron carboxylate layers can easily be removed with a solvent like ethanol, allowing complete reversibility of the treatment. After three months exposure in very bad conditions (fluctuations of RH% and T°C during the test: RH between 90% and 30% and T between 2°C and 30°C), only the untreated part of the torpedo was covered with rusts pits. At the end of the 17-month test, the treated surface remained uncorroded, thereby confirming the efficiency of the HC_{10} treatment in real storage conditions.

Discussion

This study demonstrates that the NaC_{10} solution and the HC_{10} treatment are effective corrosion inhibitors for iron in a corrosive medium simulating atmospheric corrosion, but that HC_{10} is potentially a better performing inhibitor. Surface analysis demonstrated that the protection of the PROMET coupon is based on the formation of a protective layer, which has already been observed for other metallic surfaces, made of iron carboxylate whose thickness is very dependant of the applied treatment (Peultier 2003).

For sodium decanoate solutions only a very thin protective layer has precipitated at the metal surface (Mirambet 2010). The joint effect of the carboxylic acid and the oxidizing agent enhances the release of iron cations leading to the precipitation of thicker iron carboxylate layers, which improves the anti-corrosion performance (Peultier 2003, Hollner 2007b). This result was clearly demonstrated by the SEM and EIS experiments and by the surface appearance of the PROMET coupon treated for accelerated ageing tests.

Based on the results obtained in this study, the sodium decanoate solution and the HC_{10} carboxylatation treatment can be considered as low maintenance protection systems for slightly corroded iron surfaces (like the ones observed on the PROMET coupons) encountered in historic, industrial and technical collections. As the NaC_{10} treatment delivered the least effective performance in terms of inhibition, its application must be limited to the protection of objects for short-term exposure (less than one year). On the contrary, the effectiveness of the HC_{10} treatment, demonstrated over a period of almost two years, seems to prove its ability to protect iron surfaces for a much longer duration. Application of this inhibitor could be combined with a preliminary study of the storage conditions to determine the aggressiveness of the environment and to obtain some information about the corrosion rate. The data collected (RH% and T variations) will determine the duration between each treatment application. The main field of application for this new family of non-toxic corrosion inhibitors would be for large collections

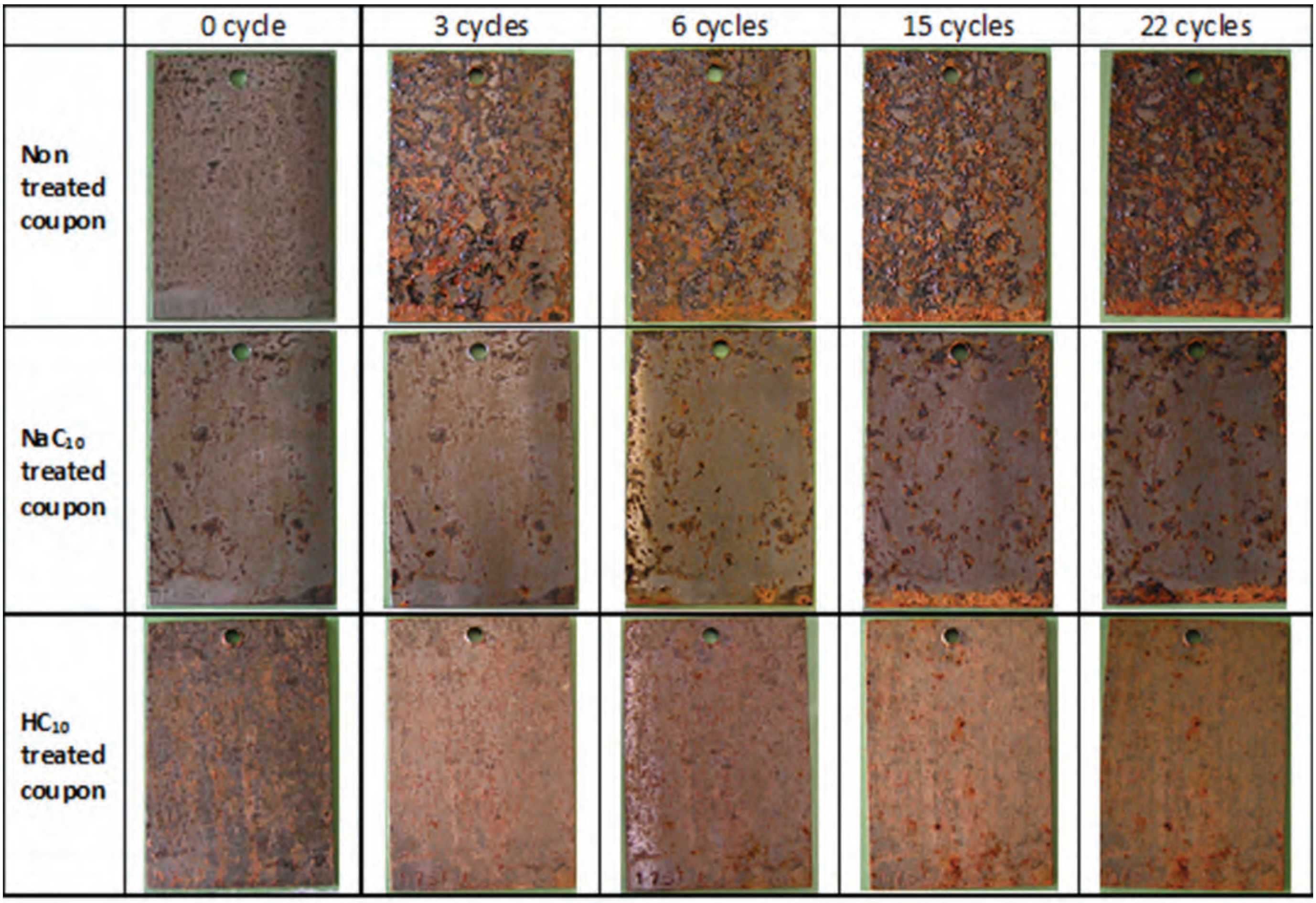

Figure 6. Treated (4h in NaC_{10} or HC_{10} solutions) and non-treated PROMET coupons during artificial ageing.

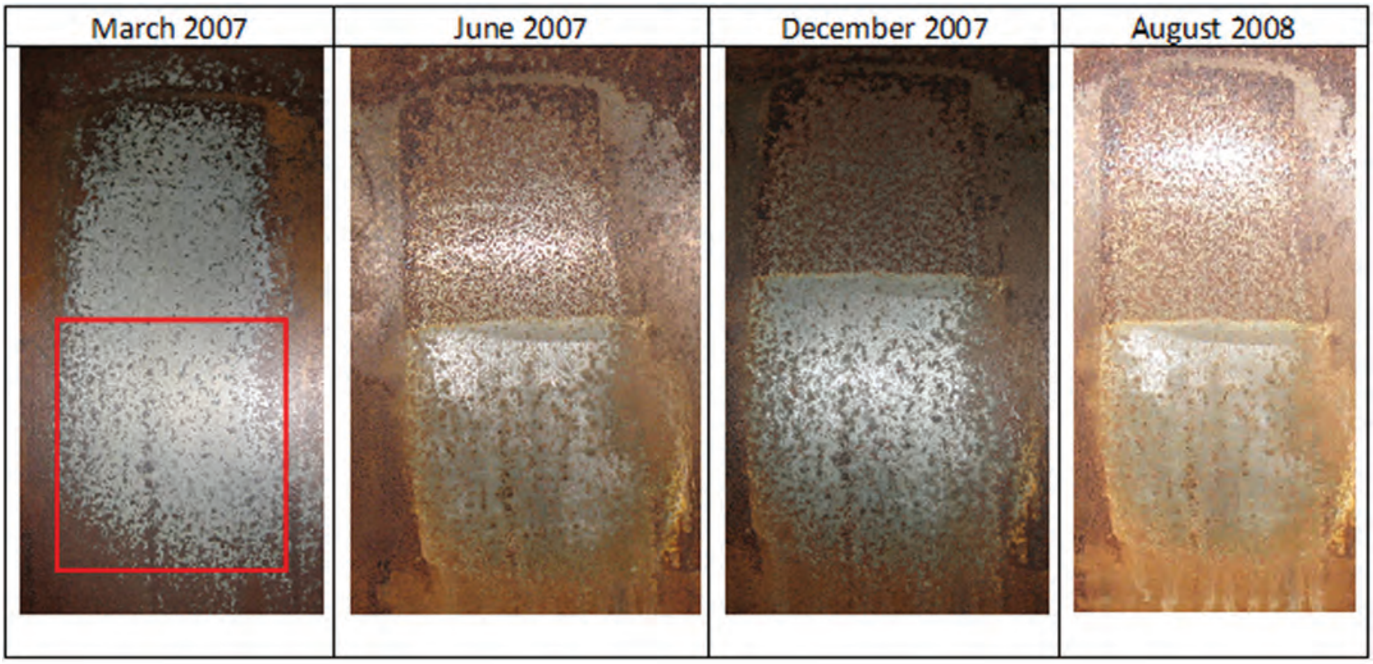

Figure 7. Evaluation of the performance of the HC_{10} solution by natural ageing. Examination of the torpedo surface after different periods of time; the treated surface is visible in the red square.

sheltered from the rain, but stored in uncontrolled conditions. These treatments can be prepared and applied very easily and safely, and can be used as temporary treatments. Reapplication can be carried out by brush or spray, and, depending on the aggressiveness of the environment, without a preliminary cleaning of the surface. This potentially reduces maintenance time for large collections.

Conclusion

This study reveals the promise of sodium decanoate solution and carboxylatation treatment for temporary anti-corrosion protection. These new formulations of corrosion inhibitors could be used as temporary treatments to reduce the corrosion rate of iron objects that cannot be immediately fully conserved.

A comparison of their respective anti-corrosion performances clearly reveals that the HC_{10} treatment is more effective at preventing corrosion. These inhibitors are cheap to use and offer an easy way to control the corrosion of large collections of iron alloys exposed to uncontrolled environmentals. In this context, these corrosion inhibitors are currently being tested on metallic objects from various collections in the POINT project (Protection temporaire d'Objets métalliques base fer et cuivre à l'aide d'Inhibiteurs de corrosion Non Toxiques) funded by the Haute Ecole Spécialisée de Suisse Occidentale (HES-SO), in close collaboration with several museums in France.

Acknowledgements

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Q & A SESSION

Paper Not Presented

BETTER THAN PARALOID B-72? TESTING POLIGEN® WAXES AS COATINGS FOR METAL OBJECTS

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Abstract

This paper presents results from a comparative test of six products for coating metal objects. Poligen® ES 91009, Poligen® ES 91012, and Poligen® ES 91018 were tested and compared to Paraloid® B-72, Paraloid® B-44 and Cosmoloid® H80. Tests were undertaken on copper alloy and ferrous coupons, and ferrous nails, which were coated by brushing, immersion or impregnation. The coupons and objects were subjected to natural and accelerated aging under different climatic conditions (humidity and polluted atmospheres) and within museum galleries. Corrosion monitoring, as well as computer-assisted optical inspection techniques, were used to evaluate coating qualities. Results to date indicate that Poligen® ES 91009, Poligen® ES 91012, Paraloid® B-72 and Paraloid® B-44 offer comparable surface protection when applied to different ferrous metals, whereas Poligen® ES 91018 and Cosmoloid® H80 are inferior. On copper alloys, Paraloid® B-72, Paraloid® B-44 and Cosmoloid® H80 show better results than Poligen® ES 91018.

Keywords: protective coatings, iron, copper alloys, Poligen®, Paraloid®, Cosmoloid®

Introduction

The research project PROMET ('Protection of Metals', 2004-2008) tested different coating materials to find the best product for historical iron and copper alloy objects in museums around the Mediterranean. Seven promising coatings were tested on bare and corroded ferrous and copper alloy coupons, and on real objects (Argyropoulos et al 2007, Cano et al 2007, Siatou et al 2007, Argyropoulos 2008, Degrigny 2008). It was concluded that the recently developed polyethylene wax Poligen® ES 91009 is more suitable for protecting iron than traditional Paraloid® B-72.

The research project discussed in this paper was initiated to verify results from PROMET, and began in 2008. The study is a joint project between the State Academy of Art and Design in Stuttgart, Germany, and the Deutsches Bergbau-Museum Bochum in Bochum. Poligen® ES products from BASF are recently developed water dispersed polyethylene coating products for industrial application on metal, based on the copolymer wax BASF Luwax® EAS 5 (2004). Poligen® ES 91009 has caused a lot of interest in the conservation community because it is solvent-free and can be used without health risks. To confirm its suitability as a coating, Poligen® ES 91009 was tested with a different methodology to that used in the PROMET project (see Table 2, 3 and 4).

Other interesting products, Poligen® ES 91012 and Poligen® ES 91018, were included in this study, and compared to Paraloid® B72, Paraloid® B-44 and Cosmoloid® H80, commonly used in conservation. All coatings, besides Poligen® ES 91009 and Poligen® ES 91012, which cannot be used for copper alloys because of their ingredients, were tested on iron and copper alloy coupons and archaeological iron nails by accelerated aging.

In addition to testing the protective capabilities of these coatings, further technical information on the Poligen® ES products, including constituents, pH, volatile emissions and reversibility, are presented. This information is collected from technical data or is the result of analysis by FTIR, pH-test, Oddy-test or personal experience of the authors.

Coating materials

Poligen® ES

Polyethylene waxes are co-polymerized from polyethylene and methacrylic acid. According to the BASF data and the acid number, the ratio between methacrylic acid and polyethylene is 1: 8-9 (BASF

Luwax® EAS 5 2004, Csihony 2009). Water dispersibility is achieved by neutralizing the acid group with either an organic amine (Poligen® ES 91009), ammonia (Poligen® ES 91012) or potassium hydroxide (Poligen® ES 91018) (Schmidt 2007). The commercially available Poligen® products contain approximately 20%-25% copolymer and have a pH of approximately 8.5-9.5. These products can be diluted with water unless the pH drops below 8.5, in which case they will segregate. The minimum temperature at which film formation occurs is 10°C. Drying time at room temperature is over 24 hours, however, at 60°C products dry in one hour (BASF Lugalvan® FDC 2007).

Fourier transform infrared spectroscopy (FTIR) was carried out to analyze the ingredients of the Poligen® ES products to verify the composition. A variety of techniques were applied to ensure accuracy. Attenuated total reflectance (ATR) was performed in-situ on clean steel coupons (“DC04B”), coated with the products described. Further analysis was undertaken with FTIR in transmission mode; a) with pellets of a mixture of potassium bromide (KBr) and dried Poligen® ES, and b) on a Poligen® ES film (for methodology see Günzler and Böck 1983, Gottwald and Wachter 1997). All spectra established the presence of a polyethylene/methacrylic acid copolymer (see Figure 1). The neutralizing compounds could not be identified.

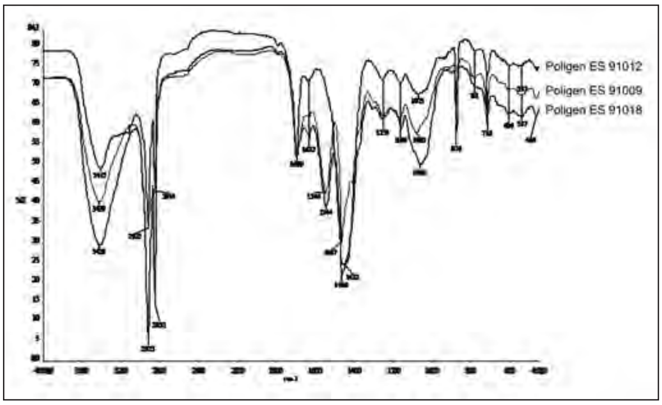

Figure 1. Poligen® IR spectra in transmission with KBr pellet.

The pH of all Poligen® ES films, measured according to the methodology of Down et al (1996), stayed slightly alkaline during testing for 74 days with only slight variation. The Oddy-test, performed according to the methodology described in Lee and Thickett (1996), showed reactions for volatile emissions from Poligen® ES 91009 with copper and from Poligen® ES 91018 with lead. With regard to reversibility, the coatings are only soluble in aqueous sodium hydroxide (20% w/w, pH 14, BASF Lugalvan® FDC 2007). The greatest solubility is given for Poligen® ES 91018 and the least for Poligen® ES 91012 (Csihony 2009).

The application of Poligen® ES coatings is often difficult as films tend to crack during drying if they are applied too thickly. For brush application, the quantity of material applied is easily controlled, but it is important to use a very fine synthetic brush, otherwise bubbles appear on the surface that do not disappear during drying. For application to rough surfaces, like archaeological iron, an application using small dabs of the brush is best.

For application by immersion, all Poligen® ES coatings must be diluted in water to a concentration of 75% (w/w), otherwise layers are too thick and cracks appear. Even then, when applied to rough surfaces, excess coating must be removed with a brush or swiped with a tissue paper after immersion to avoid a thick coating.

Other coating materials

Paraloid® B-72, Paraloid® B-44, and Cosmoloid® H80 are well described in the literature (Johnson 1984, Down et al 1996, Horie 2002, CAMEO 2009). For testing purposes, these Paraloid® formulations were applied as a 10% solution in ethyl acetate (w/w). In the PROMET study, these products were diluted to a 15% solution in acetone (w/v), but the authors observed that both Paraloids dried too fast and produced streaky coatings. Cosmoloid® H80 was used as a 10% dispersion (w/w) in the mineral spirit Shellsol® T, which is free of aromatic compounds but highly flammable above 60°C.

Testing Methodology

Specimens

For the aging tests, three coupons of each metal, coating material and application method were assessed. The coupons consisted of ferrous metal and copper alloys. The ferrous metals selected for the study were: uncorroded, low alloyed steel coupons 10 x 5 cm in size (“DC04B” with 0.08% carbon, 0.03%, phosphorus, 0.03% sulfur, 0.40% manganese); artificially corroded iron coupons 10 x 5 cm in size (“DC04B”, prepared by defined accelerated weathering until the surface was completely covered with thick brown and orange corrosion layers); historic iron specimens from the preindustrial period before 1850, 3.5 x 3.5 cm in size with less than 0.5% carbon and a clean surface free of corrosion[1]; and Roman iron nails approximately 3-10 cm long with an iron core, one group desalinated in sodium hydroxide, the other group desalinated in alkaline sulphite. Copper coupons for the study consisted of un-corroded bronze 4 x 9 cm in size (8% tin,); brass 4 x 9 cm in size (20% zinc); and gunmetal 4.5 x 10.5 cm in size (7% tin, 4% zinc, and 7% lead). The number of specimens that could be included in this study was limited due to the size of the testing chambers.

Before coating, the artificially corroded iron coupons were sandblasted with aluminium oxide to remove loose corrosion layers, then all metal coupons were cleaned and degreased in acetone and mineral spirits in an ultrasonic bath, dried at 105°C and stored in a dessicator. The coupons were handled with latex or nitrile gloves at all times.

Coating techniques

Ferrous coupons were coated with each protective material described previously. The copper alloys coupons were only coated with Poligen® ES 91018, Paraloid® B-72, Paraloid® B-44 and Cosmoloid® H80 due to corrosion of copper with amine and ammonia, which are present in Poligen® ES 91009 and Poligen® ES 91012. All coupons were coated by brushing or immersed in baths. The archaeological nails were impregnated under vacuum. The nails desalinated in sodium hydroxide were only tested with the Poligen® ES products.

Film thickness measurements

For evaluation of the average film thickness, each coupon was weighed before and after coating. Thickness was roughly calculated by the given density of the products. To obtain more precise results, additional tests were carried out. Because of low film thickness of 1-2 µm, most methods for calculating thickness are too imprecise (as can be seen from DIN EN ISO 2808). Tests with a magnetic inductive system and tactile measurements failed; only microscopic analysis and reflection measurements showed precise results. As an example, Table 1 compares the average film thickness of coatings applied to new steel and bronze coupons, obtained from weight measurements, microscopic analysis and reflection measurements. To measure the average film thickness, three coupons were weighed. For the microscopic analysis, only four coupons could be measured, and for the reflection measurement, the wax Cosmoloid® H80 could not be evaluated because of its soft wax constitution. All results vary considerably. However, a thickness of 1-2 µm is an average thickness achieved for these films.

	Average mass difference (µm)		**Microscopic analysis (Confocal-Microscope)** (µm)		**Reflection measurement** (µm)
Material	**steel**	**bronze**	**steel**	**bronze**	**steel**
Po09	1.9	-	3	0.8	2.1
Po12	0.9	-	-	-	1.2
Po18	2.1	1.2	-	-	2.4
PB72	1.3	1.2	3	0.6	1
PB44	2.9	3.2	-	-	1.3
CH80	0.6	0.3	-	-	-

Table 1. Film thickness in µm of brushed coatings on bare metal coupons. (**Po09** = Poligen® ES 91009; **Po12** = Poligen® ES 91012; **Po18** = Poligen® ES 91018; **PB72** = Paraloid® B72; **PB44** = Paraloid® B44; **CH80** = Cosmoloid® H80)

Testing the coatings

The coupons were subjected to accelerated and natural aging in three different climatic chambers and in two different environments in the Deutsches Bergbau-Museum Bochum; (a) an exhibition hall, and b) an underground mine that is part of the museum. The terms of the tests are reported in Table 3. Accelerated aging was performed in chambers that simulated different environmental conditions: a) condensation effects: relative humidity (RH) ranging from > 100% RH (condensation period) to 35% RH (drying period); b) high humidity effects: relative humidity cycling between 95% RH and 35% RH, and c) a chamber that simulated an industrial environment with high levels of sulphur dioxide (SO_2). Chamber

Aging tests	**Tested specimens**
Alternating condensation atmosphere (16hrs. @ 35 °C, 90% RH +8hrs. @ 23 °C, 55% RH)	steel artificial corroded steel natural corroded steel copper gunmetal artificial corroded red brass natural corroded red brass
Museum gallery	natural corroded steel natural corroded red brass historical iron objects

Table 2. PROMET aging tests of the coatings (Siatou et al 2007: 3, Degriny et al 2007: 34, Degriny 2008: 182).

Aging tests	**Tested specimens**
Alternating condensation - dry atmosphere (8hrs. @ 40°C, 100% RH + 16hrs. @ 20 °C, 35%RH) (DIN 50017: 1982)	bare steel, corroded steel historic iron bare bronze and brass (brushed and immersed)
Varying humidity atmosphere (8hrs. @ 40°C, 95% RH + 16hrs. @ 20 °C, 35% RH)	bare steel corroded steel archaeological nails bare gunmetal (brushed and immersed)
SO_2-climate (acid rain simulation) (4 min. wetting/ 1 min. stop/ 3 min. wetting/ 12 min. SO_2-exposure (4 mg/m^3)/ 15 min. of warming till 60 °C/ 30 min. cooling till 20 °C)	corroded steel (brushed and immersed)
Museum gallery with 22-27 °C and 30-60 % RH	bare steel and corroded steel (brushed only)
Mining gallery with 13-14 °C and 60-100 % RH	bare steel and corroded steel, (brushed only)
Airproof chamber with silica gel	Each coating and metal with 1 specimen

Table 3. Authors' aging tests of the coatings.

parameters and aging conditions were adopted from several former research studies dealing with the efficacy of transparent coating materials[2].

Two uncoated specimens of each metal were kept as a reference in the aging tests. Furthermore, one coated and uncoated specimen for each metal and type of coating was stored in a desiccator (room temperature and under 30% RH). Tests with cycling condensation humidity and temperature ran for 77 days, and the SO_2 test for approximately 68 days (1500 cycles of 65 min each). Natural aging was performed for 12 months and was continued after a first inspection, because the coatings did not show enough differences. This test is still ongoing at the time of writing.

For documentation purposes, all coupons were scanned by a flat bed scanner with high definition[3] before, during and after the aging tests. The archaeological nails were photographed and all specimens were documented in writing.

Evaluation of results

Three different methodologies were applied to evaluate the results of the aging tests.

The appearance of corrosion products over time was monitored as an indicator of layer protectiveness. The length of time that elapsed until the surface of the iron or copper alloy coupon was corroded was recorded. This point was defined as having been reached when approximately 90% of the surface was covered by corrosion products. In some cases, a coupon was entirely corroded after 20 days, while others showed little corrosion over the same time period, and were still not fully corroded after 40 days.

Computer-assisted visual evaluation of data was carried out with the application of an image analysis system[4]. Freshly formed corrosion was defined by its particular color on images of scanned coupons, and the image analysis system was then used to calculate the percentage of fresh corrosion on the surface. Finally, visual monitoring (performed by one person to ensure consistency) was carried out for all samples. All these evaluations were then rated according to their performance (see Table 4 and 5). SEM did not provide applicable results, because the coating was not visible.

Results

Good surface protection was achieved for brush application of Poligen® ES 91009, Poligen® ES 91012, Paraloid® B-72 and Paraloid® B-44 onto a ferrous surface (see Table 5 and Figure 2 and 3) with a few exceptions. One specimen of corroded steel coated with Poligen® ES 91009 failed in the SO_2 test due to intensive formation of new corrosion products, and one specimen of bare steel coated with Paraloid® B-44 failed in the condensation test. Poligen® ES 91018 and Cosmoloid® H80 failed twice and Cosmoloid® H80 performed well only once (see Table 5). Uncoated reference specimens performed better than expected, because not much more corrosion formed on the reference coupons than on the coated specimens.

If applied by immersion, the ferrous coupons with Poligen® ES 91009 and Poligen® ES 91012 performed quite well, while those immersed in Paraloid® B-72

PROMET evaluation methods	**Authors' methods**	**Advantage / Disadvantage**
Visual inspection, macro and micro	Same	Recording and rating effects / subjective
Weight change	Only for measuring the film thickness before aging	Reason for weight change during aging still not finally clarified (preliminary interpretation: weight loss because of loss of corrosion products, weight increase because of water absorption by the coating; both effects will appear at the same time)
Film thickness measurements	-	Imprecise, coatings too thin to measure correctly with applied techniques
Colorimeter	-	Can show changes within the coating / influence on protection abilities?
SEM	Same	Details like cracks in coating, filiform corrosion, etc. observable / coating not visible
Electrochemical with polarisationresistance (Rp) and Impedancespectroscopy (EIS)	-	Results difficult to interpret
-	Time monitoring of corrosion	Which coating does fail first, which last / quite rough results
-	Image analysis	Percentage of new corrosion can be determined / on precorroded surface difficult because of similar corrosion colors

Table 4 . Evaluations methods used by PROMET (Siatou et al 2007: 3 f., Degriny et al 2007: 34, Argyropoulos et al 2007: 11 f., Cano et al 2007: 122) compared to the authors' methods.

and Paraloid® B-44 showed good or satisfactory results (see Table 5 and Figure 4). Poligen® ES 91018 and Cosmoloid® H80 performed satisfactory but failed on bare steel. Cosmoloid® H80 gave a very good result when it was applied to corroded steel in the humidity test (see Table 5).

The archaeological iron nails desalinated with sodium hydroxide showed the best results when coated with Poligen® ES 91009. Those desalinated with alkaline-sulphite had good results with Paraloid® B72, and satisfactory with all other coatings besides Poligen® ES 91018 and Cosmoloid® H80 (see Table 5).

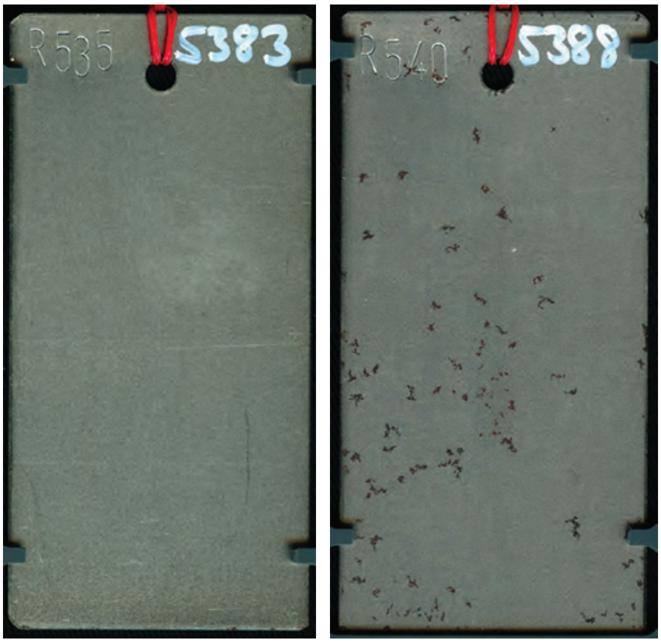

Figure 2. Bare steel coupons with coatings applied by brush; Coupon A, coated with Poligen ES® 91009, shows less corrosion (*left*); Coupon B, coated with Poligen ES® 91018, shows much more corrosion (*right*).

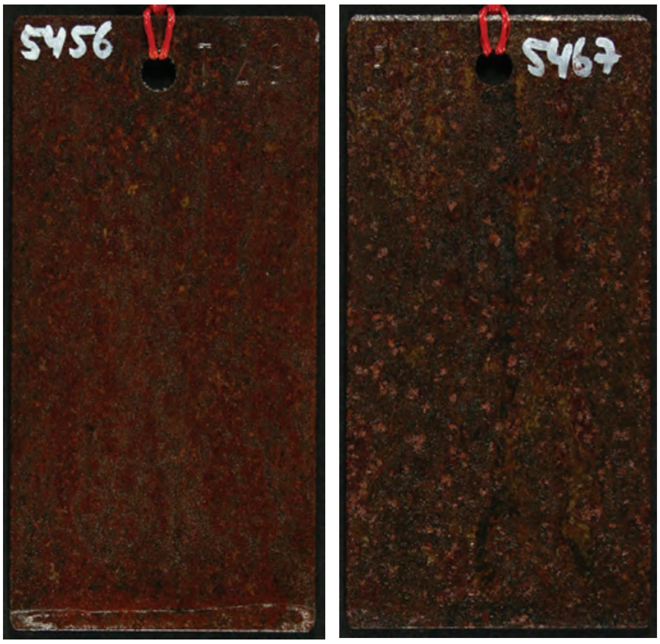

Figure 3. Corroded steel coupons with coatings applied by immersion: Coupon A, coated with Poligen ES® 91012, shows less corrosion (*left*); Coupon B, coated with Paraloid® B-44, shows much more corrosion (*right*).

Suitability	**Bare steel** (humid-test)	**Bare steel** (condensation-test)	**Corroded steel** (humid-test)	**Corroded steel** (so$_2$-test)	**Corroded steel** (condensation-test)	**Historic Iron** (condensation-test)	**Arch. Nails** (humid-test)
Brushed							**NaOH**
Very good						Po09	
Good	PB72, Po09, Po12, PB44	Po 12, PB 72	Po12, CH80, Po09, PB72		Po 09, Po 12	Po12, PB44, PB72	Po09
Satisfactory	without coating	Po 09, CH 80	PB44, Po18, without coating	Po12, Po18, PB72, PB44, CH80	Po 18, PB 72, PB 44, without coating	CH80, without coating	Po12, Po18
Failed	Po18, CH80	Po 18, PB 44, without coating		Po09, without coating	CH 80	Po18	without coating
Immersed							**Alkali-Sulphite**
Very good			Po09, Po12, CH80	Po09			
Good	Po09, PB72, PB44, Po12		PB44	Po12, Po18			PB72
Satisfactory	CH80		PB72, Po18	PB72, PB44			Po09, Po12, PB44, without coating
Failed	Po18			CH80, without coating			Po18, CH80

Table 5: Evaluation of the protectiveness of coatings on ferrous materials.

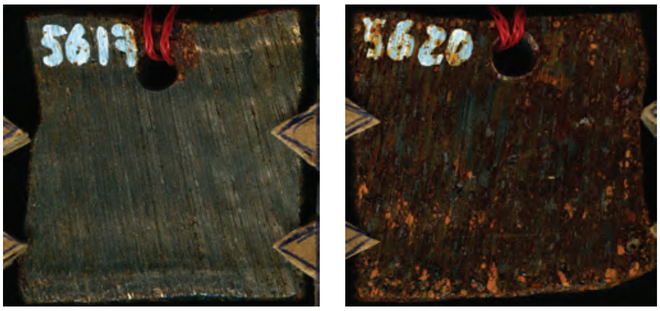

Figure 4. Historic iron coupons with coatings applied by brush; Coupon A, coated with Poligen® ES 91012, shows less corrosion (*left*); Coupon B, coated with Poligen ES® 91018, shows much more corrosion (*right*).

Suitability	**Bronze** (condensation -test)	**Brass** (condensation -test)	**Gunmetal** (humid-test)
Brushed			
Very good	PB44	PB44, PB72	CH80, without coating
Good	PB72, Po18	Po18	PB72, PB44
Satisfactory	CH80, without coating	CH80, without coating	
Failed			Po18
Immersed			
Very good			
Good	PB44	PB72	PB44, PB72, CH80
Satisfactory	CH80, PB72	CH80, PB44	
Failed	Po18	Po18	Po18

Table 6. Evaluation of the protectiveness of coatings on copper alloys.

Figure 5. Brass coupons coated by immersion: Coupon A, coated with Paraloid® B-72, shows less corrosion (*left*); Coupon B, coated with Poligen ES® 91018, shows much more corrosion (*right*).

On copper alloys, Paraloid® B-72 and Paraloid® B-44 performed comparatively well (see Table 6 and Figure 5). Poligen® ES 91018 behaved fairly well when brushed on bronze and brass, but otherwise it failed. The results of Cosmoloid® H80 were mostly just ‘satisfactory’.

Conclusion

In this study, Poligen® ES 91009, Poligen® ES 91012, Paraloid® B-72 and Paraloid® B-44 applied to different ferrous metal coupons offered good protection of the metal surface during the accelerated aging tests. Poligen® ES 91018 and Cosmoloid® H80 displayed less ability to protect iron. On copper alloys, Poligen® ES is not suitable because of its basic ingredients of amine and ammonia, which corrode copper and its lack of reversibility. The coatings were soluble in sodium hydroxide, however, sodium hydroxide is corrosive to copper. Paraloid® B-72 and Paraloid® B-44 both performed well, however, Cosmoloid® H80 only performed satisfactorily.

For iron coupons, results indicate that both Poligen® ES 91009 and Paraloid® B-72 offer comparably good protection of iron. This result is in contrast to that determined in the PROMET project, which found that Poligen® ES 91009 provided better protection of iron than Paraloid® B-72. The result obtained here would seem to suggest there is no need to replace Paraloid® B-72 as a coating for iron objects, especially with regard to its well-proven reversibility and familiarity as a conservation material. At the time of writing, the long-term tests in the galleries of the Deutsches Bergbau-Museum Bochum are ongoing and results are not yet available. Results from PROMET’s long-term testing of coatings on historic metal objects housed in museum conditions showed similar results for Poligen ES® 91009 and Paraloid® B-72 in Athens, Greece, whereas in Malta with abundant salt aerosols, Poligen ES® 91009 performed better than Paraloid® B-72. The comparison between the long-term effectiveness of Poligen® ES and Paraloid® B-72 is still to be determined and requires further testing.

Further research on the reversibility of Poligen® ES products is needed before these products can be recommended for routine application. Based on the results of this study, Poligen® ES 91009 and Poligen® ES 91012 should only be recommended for non-composite ferrous objects, that is, those with no organic or copper alloy component. Archaeological iron, which still contains chloride, will corrode during the application of Poligen® ES because of its water content, so it is not suitable for iron objects that have not been desalinated. A further disadvantage of Poligen® ES is the difficulties of handling during application, which can cause the appearance of bubbles and cracks in the coating.

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Endnotes

[1] The historic iron was from square bar steel, taken from an historic Gate. For the test it was cut into small slices where the bare cut side was the tested area.

[2] See for example, a German project financed by the Deutsche Bundesstiftung Umwelt 'Transparenter Korrosionsschutz für Industriedenkmaeler aus Eisen und Stahl' and the European project 'Comparison of conservation materials and strategies for sustainable exploitation of immovable industrial heritage made of iron and steel (CONSIST)'

[3] 48 Bit HDR colour, 1200 dpi, tif-data

[4] Picture software from Olympus, usually used for microscopic picture evaluation.

Materials

Poligen® ES 91009, Poligen® ES 91012
and Poligen® ES 91018:
BTC Speciality Chemical Distribution GmbH (BASF)
Maarweg 163 / 165
D-50825 Köln, Germany
Tel: ++49-221-954640

Paraloid® B-72, Paraloid® B-44, and Cosmoloid® H80;
acetone, ethyl acetate, Shellsol® T, mineral spirits:
Kremer Pigmente GmbH & Co. KG
Hauptstr. 41 – 47
D-88317 Aichstetten, Germany
Tel: ++49-7565-91120

Sodium hydroxide:
Carl Roth GmbH + Co. KG
Schoemperlenstr. 3-5
D-76185 Karlsruhe, Germany
Tel: ++49-721-56060

DC 04 B steel coupons:
Franz Krüppel GmbH & Co.KG
Höffgashofweg 17-19
D-47607 Krefeld, Germany
Tel: ++49-2151-316070

Historic iron:
Schloss Borbeck, Essen
Michael Stratmann
Nierenhofer Str. 10 a
D-45257 Essen, Germany
Tel: ++49-201-8486173

Archaeological nails:
Regierungspräsidium Stuttgart, Landesamt für Denkmalpflege
Berliner Str. 12
D-73728 Esslingen a.N.
Tel: ++49-711-90445109

Bronze and brass:
Wieland Werke
Graf-Arco-Str. 36
D-89079 Ulm, Germany
Tel: ++49-731-9440

Gunmetal:
ALLMESON GmbH
Ottostr. 9-11
D-63150 Heusenstamm, Germany
Tel: ++49-6104-405980

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Q & A SESSION

Robert van Langh: Thank you for your talk – it is really interesting. Immediately I have a question for us as a field: as to where do we stand when one result comes up from one research and it is not reproducible apparently by another field. That's more of an ethical question I guess – not for you directly to answer. I have a series of questions so this is more of a remark than a question. Secondly, I saw more of the iron and the steel that you were producing that none of them were very good. All of them were good at producing results – where do you put the difference between very good and good?

Johanna Wolfram: Very good was no corrosion at all while good was small bits of corrosion.

Robert van Langh: And if I understand correctly – of course I know about the PROMET research that they've done but I don't know if they've made recommendations as to using these materials. Did they actually say these are the materials that you should use or not?

Johanna Wolfram: No. I understood they presented their results that Poligen® was comparable with Paraloid B-72 and a possible alternative. But of course I want to talk to Bessie [Vasilike Argyropoulos] about the application of Poligen as everybody has different climates for their objects so some like it, some don't like it – so just try it and see how you get along with it.

Robert van Langh: And I was thinking because the PROMET project was specifically for countries around the Mediterranean, right?

Vasilike Argyropoulos: I was the coordinator of the PROMET project and I found your research to be very interesting and I think what it shows is how do we choose coatings, using what standards exist in conservation. When we started to do the PROMET project we had all these experts in coating evaluation and we had a big discussion about what standards to use and what was suitable. We had people from the Czech Republic who have done a lot of coating testing and so we decided on the types of tests that we would use. But there are no standards for conservation of cultural heritage and that is something we need. You decided to use the DIN method, which is fine but I'm surprised about accelerated aging results because we saw filiform corrosion with the Paraloid B-72 after the accelerated aging tests. This is something noted at Heritage Malta at the Royal Armory collection where they have salt aerosols and they were finding filiform corrosion as well on their iron armor forming with Paraloid B-72 after a long period of time. So the coating was failing and we saw that as well with our accelerated aging tests. So the question I have is about the thickness of the coating that is being applied, that is a major issue.

I've used Paraloid in the Criminal Museum (in Greece) and I saw it failing and having pin-point rusting and it was because I wasn't applying thick enough coatings or the concentration wasn't good enough. We are doing this through trial and error without knowing exactly what we should be using on the material. So this is a major issue – the thickness of the coating. The second issue is: we found the same results long-term. We applied it to the iron knives at the Criminal Museum and we still cannot see any differences between the Paraloid B-72 and the Poligen – it looks the same. I don't necessarily know if it is the same though. Christian's group and the Royal Armory Collection where they had the salt aerosols found that the Poligen was better than the Paraloid, but again it wasn't conclusive enough. So for me the jury is still out as to which is a better coating. I think that your point about the application is an important one and of course the reversibility.

What we tried to do with PROMET is look at alternatives because everybody across the region, I think maybe even in Europe and across the States, they love the Paraloid products and yet these products were not good enough in some cases and we needed to start looking at alternatives, whatever they are. We do not represent these companies, we don't care personally what they are. So that was the point I wanted to make. There are going to be a lot of presentations on carboxylates and the use of carboxylic acids as coatings and inhibitors and although I'm not sure that the failure of the copper coating has to do with the bases – it has to do with the carboxylic acid that is forming a coordination complex that leads to the creation of that white film or what is appearing in terms of corrosion may have to do with the carboxylic acid. This is the topic of another paper and we can discuss it later. That is all I wanted to say.

David Thickett: Bessie, while you're at the microphone, can I just ask you one further question? What did you apply your Paraloid in for PROMET?

Vasilike Argyropoulos: Acetone. And there was a reason for this, because I pounded it into everybody, that we didn't want to use things like toluene, we wanted to use things that were commonly used, that were not as toxic – although acetone is not the best product either, but it was better than toluene so we were looking for things that were not toxic which is why we went with these products – it's the only reason.

David Thickett: Because this was applied in ethyl acetate, and that's another thing, another difference.

Vasilike Argyropoulos: Yes.

Joe Sembrat: You jumped exactly on my question about reproducibility within the coupon samples about application coating thickness – and the integrity of the application. (It is all about) meaning measurements to determine how thick (the coating) is and whether it is a continuous coating. Because the coupons have the appearance as if the failure was related somehow to the brush application – and I'm just curious as to whether there was any reproducible technique that was used for each?

Johanna Wolfram: All the brushed coatings were brushed the same way.

Joe Sembrat: So I would imagine there was a specified film thickness that the manufacturer has for each of these products? So I'm just wondering if those were followed in reproducing the application?

Johanna Wolfram: Yes. We measured the film thickness, but all the coatings were under one micrometer and most of the measurements failed at that low area so we couldn't really measure it. We had some examples where we measured it but we couldn't do it for all the coupons, because after 2 micrometers you have a failure rate of 1 micrometer.

Joe Sembrat: So the measurements were done during application and then again after the final results?

Johanna Wolfram: No. Because the failure rate was too high, you couldn't have evaluated the results of the thickness. So we just tried to figure out how thick all of them are and we noticed they are all too thin to measure.

Joe Sembrat: I had one additional question: I'm assuming that these are all meant for indoor applications? Is that why there is no UV variable?

Johanna Wolfram: Well at the German Mining Museum they are also doing outdoor tests – that is why we also used the acid rain tests and the condensation atmosphere. But my aim was to find an indoor coating.

Joe Sembrat: Thank you, I enjoyed it.

Karen Stemann Peterson: It is very interesting the tests of coatings because they are so important. I wonder if you have thought about – when you say that a product is good when you see corrosion actually appearing and a lot of us would say, if it is corroding then it is not protecting. I just wanted to draw the attention to the paper that is going to be published in '*Big Stuff*'. Some of my colleagues are testing several products – a lot of industrial products. Of course this is not a complete survey but it also helps because the acrylic types, the Paraloids, are often known to be easy to penetrate (so we need something by way of comparison) but you also of course had the wax to compare with. Thank you very much.

Johanna Wolfram: Thank you.

Nestor Gonzalez: I have a very practical question: You mentioned that you quantified the presence of new rust on the coupons using digital image processing software. Is that correct? My question is, what system did you use and how do you quantify that?

Johanna Wolfram: With the image analysis system we could count the percentage of new corrosion. I rated it in 30, 50, 70 per cent steps or I saw how much corrosion the coupons had and then I rated it in different groups.

Nestor Gonzalez: What was the software you used?

Johanna Wolfram: It is from the Olympus Microscope Camera, and it is called Image Analysis System. I could use it because we had an Olympus Microscope Camera but when I tried to get the software for my thesis for private use and the software would be 50 euros per week, so I didn't manage to get the software itself, since I could use the camera for less money.

Nestor Gonzalez: Thank you very much.

Stefan Brueggerhoff: I just wanted to make a comment with regard to the standardization of these tests. I discussed at '*Big Stuff*' with Yvonne the fact that there is really a need to look for standards doing these tests. Johanna, you can really explain that it is very difficult to keep in a standard when applying samples even when considering which kinds of samples are really suited for this – so I think it is really necessary to look for a European or ISO standard for conservation purposes and using standard materials for accelerated tests to have real results which are comparable to all the world.

David Thickett: Just to add to that the European standardization project TC346 has a working group for testing materials against which your tests on those coupons could be compared…

Vasilike Argyropoulos: How were your sample surfaces prepared before or after the application of the various coatings?

Johanna Wolfram: Good question. That is described in the paper as well. The bare coupons were degreased in acetone and mineral spirits and an ultrasonic bath then dried in an oven at 100˚C and then just touched with gloved hands and stored in an ideal climate – so that is very dry – at room temperature in a desiccator. The artificially corroded steel coupons were cleaned with the air abrasive with walnut shell and afterwards the same procedure.

Stéphanie Cretté: I was wondering – it might be just air drying but – how did you cure your coating and also if you checked for the cure – if it was completely cured when you did your testing? I realized that when you were giving your talk, you said when you were brushing it you got a lot of bubbles. So if you have bubbles, you probably have pin holes in your coating and so your film or your coating is not continuous.

Johanna Wolfram: Yes. With the Poligen products you have to use a very fine thin brush. We first tried others, and it was just a bubbling surface…

Stéphanie Cretté: Did you check them under the microscope to maybe see if you had pin holes?

Johanna Wolfram: You could see by the naked eye if we had – because they were big enough to see so we didn't use coupons with bubbles on the surface.

Stéphanie Cretté: And for the curing? It was air dried?

Johanna Wolfram: Yes.

Stéphanie Cretté: Did you check if they were fully cured?

Johanna Wolfram: No but they were so thin and they stayed for 24 hours in the room and then they were kept in the desiccator for another few days before they got to the climate chamber so we were pretty sure they were dry. But we didn’t check.

Stéphanie Cretté: Ok, thank you.

THE CORROSIVE INFLUENCE OF ACETIC ACID EMISSIONS ON BRONZE AND THE EFFICACY OF TWO PROTECTIVE COATINGS

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Abstract

Acetate corrosion has been found predominantly on archaeological copper alloys that have been commonly stored in wooden cabinets. The purpose of this study is to assess the protective qualities of two coatings on two copper alloys exposed to the corrosive action of acetic acid vapor by simulating storage environments under accelerated conditions. The test coupons consisted of a copper tin alloy (ASTM B584) and a leaded copper tin alloy (ASTM B505). Two protective coatings were tested: Incralac® (acrylic copolymer with benzotriazole) and Poligen® ES 91009 (ethylene copolymer emulsion). The test coupons were exposed to acetic acid vapor of 4 ppm concentration in a relative humidity of 86% at 30°C for eight weeks. The efficiency of the protective coatings was assessed according to ASTM D1654-05, Standard Method of Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments.

Keywords: copper alloy, archaeology, acetic acid, corrosion, preventive conservation, coatings, Incralac®, Poligen®

Introduction

The aim of the corrosion test on bronze was to determine the protective qualities of two coatings against the aggressive nature of volatile emissions of acetic acid in high levels of relative humidity. The experimental conditions were chosen to simulate storage of bronze in wooden cupboards under accelerated corrosive conditions (Paterakis 2003). The acceleration is required in order to produce results within the time frame of the test.

Selection of Coatings Used in Testing

The acrylic copolymer, Incralac®, and the ethylene copolymer (polyethylene) wax emulsion, Poligen® ES 91009, were chosen to test their protective qualities on copper alloys (see Table 1). Both products were used as supplied by the manufacturer (Incralac® was a 15% solution).

Originally developed by the International Copper Research Association as a protective coating for new

Table 1: Characteristics of Coatings used in Corrosion Testing

Properties	Incralac®[1]	Poligen® ES 91009[2]
Chemical nature	ethyl methacrylate-butyl acrylate copolymer (Paraloid® B44) in toluene (40.1 wt.%), xylene (40.9 wt.%), methyl ethyl ketone (4 wt.%) with benzotriazole as corrosion inhibitor/UV protector	polyethylene wax emulsion
Color	Transparent	Transparent
Solids content (%)	15%	20-22
Tg	60˚ C (Paraloid® B44)	NA
pH	NA	8-9.5
Refractive Index	1.89 (Paraloid® B44)	NA
Viscosity (ISO 2431 cup 4 mm, 23˚ C)	NA	15-150 s
Flow time	NA	25-100 s (23˚ C)
LD-Wert/LT-value (%)(= lichtdurchlässigkeit/translucence)	NA	80-95
Freezing point (capillary tube method)	NA	0˚ C
Freeze-thaw stability	NA	Protect from frost
Average particle size	NA	NA
Density (g/cm^3) (23˚ C)	NA	0.98 - 1.0
Boiling Point	NA	100˚ C
Flash point	NA	> 100˚ C
Applications	Protective coatings for metals	1)Additive for coatings e.g. metal, glass; 2) additive for water-based adhesives; 3) resistance to corrosion: e.g. on metal
Boiling point/range	82-115˚ C	100˚ C
Vapor density	Heavier than air	NA
Evaporation rate	Slower than butyl acetate	NA
VOC content (wt.)	83.2 %	NA

NA = not available from the manufacturer; [1] MSDS, Cameo , [2] BASF 2005,2006 copper outdoors, Incralac® contains an acrylic-based polymer that has been used on copper and copper alloys to protect against corrosion from handling and bronze disease since the 1960s. Incralac® was chosen since it has been used for decades by conservators for decorative and archaeological bronze, both indoors and outdoors, and continues to be used today (Brostoff et al. 2000, Ellingson et al. 2004). The formulation of Incralac® appears to have changed over time. In 2007, it was reported to be an ethyl methacrylate-butyl acrylate copolymer (Paraloid® B44) plus benzotriazole (BTA) as corrosion inhibitor and/or UV protector (Rocca et al. 2007). The BTA in Incralac® is a chelating agent that functions both as a corrosion inhibitor and protects the Incralac® from deterioration caused by the diffusion of copper ions into the lacquer (Erhardt et al. 1984).

The second polymer, Poligen® ES 91009, has undergone accelerated aging testing as a protective coating on metal coupons, but has not yet been adopted as a standard conservation material for metals by conservators (Cano et al. 2010). Poligen® ES 91009 was selected as a new polymer coating material for testing by the European consortium, PROMET (Innovative Conservation Approaches for Monitoring and Protecting Ancient and Historic Metals Collections from the Mediterranean Basin), from 2004 to 2007. PROMET was a research project funded by the 6th Framework Program of the European Union, with the participation of 21 partners from 11 countries around the Mediterranean Basin, with the aim of developing new techniques and materials to improve the conservation of the metallic cultural heritage. Poligen® is a polyethylene wax in emulsion form. An emulsion is described as 'a stable mixture of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers (Hawley 1981)'. Poligen® ES 91009 is manufactured by BASF as a coating for metal. It is reported by the manufacturer to be free of catalyst residues, transparent, self emulsifying, micronized, and surfactant-free (BASF 2005, 2006).

Experimental

Preparation of test coupons

Twenty-four coupons, 12 unleaded bronze and 12 leaded bronze, were cut from bars of ASTM metal with an electric saw and then wet-sanded with different grades of abrasive silicon carbide paper from grit size 240 down to 600, according to ASTM G1-03. The maximum dimensions were approximately 2 cm by 1.5 cm and 3 mm in thickness. They were very similar in shape and size, and therefore surface area, thereby rendering them suitable for direct comparison (ASTM G54-84). They were degreased with acetone prior to coating application (ASTM G1-03).

Application of coating

Six leaded bronze coupons and six unleaded bronze coupons were coated with Incralac®, equal numbers of both alloys were coated with Poligen® ES 91009. The coatings as supplied by the manufacture were applied with a natural bristle brush to replicate a common mode of conservation application. One coat only was applied to the central area of each test coupon avoiding the edges and was allowed to dry in average museum conditions (±55% RH, 21ºC). Approximately 0.25 ml of each coating material was applied to a surface area of approximately 0.5 x 0.5 cm.

Masking areas of exposed metal

Approximately eight weeks after application of the coatings all areas of exposed metal were masked with an epoxy resin according to ASTM G78-01. The purpose of this was to avoid edge effects that can influence the performance of the coating by preferential attack during corrosion testing as specified in ASTM D1654-05, ASTM D2803-03, and ASTM G54-84. Basic No-Blush transparent epoxy resin from the Progressive Epoxy Polymers Inc. was used for this purpose. The epoxy component consists of bisphenol-A-epichlorohydrin and benzyl alcohol. The hardener contains amine adduct, polyglycol diamine, and nonyl phenol (Material Safety Data Sheet). Full curing was achieved in seven days.

Scribing of coatings

A test standard that involves scribing the coating, ASTM D1654-05, *Standard Method of Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments*, was followed. This standard is used to evaluate coated test coupons in accelerated atmospheric exposure tests with respect to corrosion, blistering associated with corrosion, loss of adhesion at the scribe mark, and other film failure. It provides a means of comparing and evaluating the substrate and coating after exposure to corrosive environments. The coating on each test coupon was scribed with a scribing tool as described under Apparatus in D1654 after the epoxy masking resin was applied. The conservation coatings had a total of 20 weeks to set before being scribed and were kept in low light levels during this time. The coupons were placed on Plexiglas racks during the exposure tests at an angle of 30 degrees from the vertical so that the scratch was positioned vertically following ASTM B117-09 (see Figure 1). This allows moisture droplets to run down along the length of the scribe during the test (ASTM D1654-05).

Figure 1. Coupons positioned in test chamber

Corrosion Testing

Half of the coupons were exposed to the corrosive conditions of acetic acid vapor in high humidity (see Figure 2) and the other half were controls, exposed to high humidity without acid. The corrosive testing was carried out in the Centro Nacional de Investigaciones Metalúrgicas (CENIM), CSIC, in Madrid, Spain. The test coupons were exposed to acetic acid vapor concentration of 4 ppm and 86% RH (±2%) at 30ºC (±1º) for the duration of eight weeks. The control tests were carried out at the Getty Conservation Institute in Los Angeles in 86% RH for eight weeks. Triplicate coupons were used in accordance with ASTM G54-84.

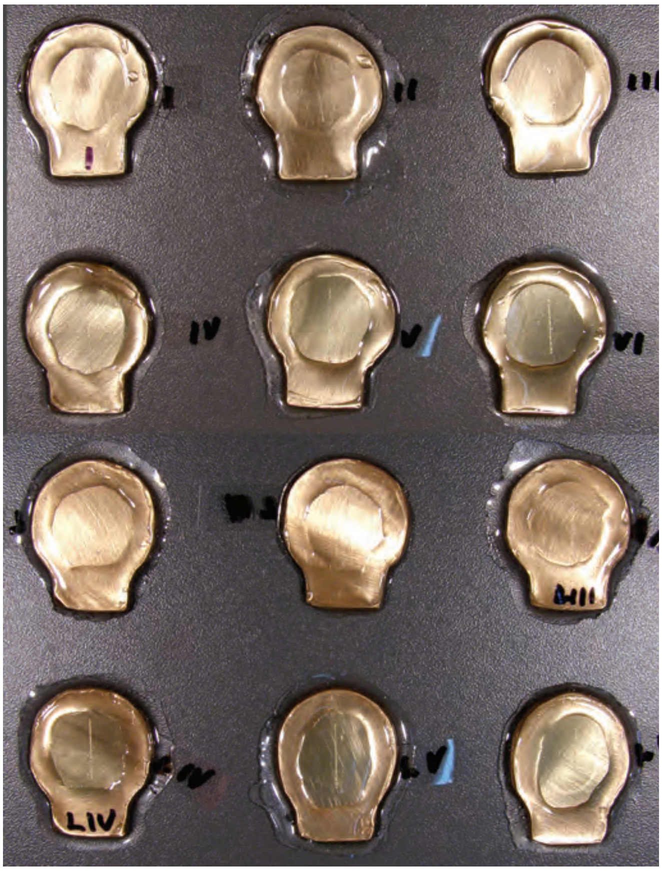

Figure 2 Coated and scribed coupons prior to testing in acetic acid vapor. Top row: Unleaded with Incralac® U I, U II, U III; 2nd Row: Unleaded with Poligen®, U IV, U V, U VI; 3rd row: Leaded with Incralac®, L I, L II, L III; Bottom row: Leaded with Poligen®, L IV, L V, L VI

Selection of acetic acid vapor and relative humidity levels

Similar corrosion tests in 0.4, 4, and 40 ppm acetic acid vapor concentration were carried out on uncoated coupons of the same two copper alloys at the Getty Conservation Institute in Los Angeles in 2004 (Paterakis 2007, Paterakis 2010). 4 ppm acetic acid concentration and 86% RH were chosen for the current test on coated coupons to facilitate comparability and interpretation of the corrosion results with those from 2004. The acetic acid concentration of 4 ppm represents approximately 10 times that measured in museum storage on average (0.4 ppm) thereby establishing accelerated aging conditions for the eight-week test (Paterakis 2003). The high level of RH used in the current corrosion tests replicates the conditions found in collections lacking environmental control in wet climates.

Test chamber

The test chamber is pictured in Figure 1. Compressed air (generated by an oil-free compressor) is passed through several particle filters, activated carbon filter and an air dryer/purifier (Peak Scientific AD70L-40). The flow is controlled using a mass flow controller (Aalborg GFC17). The airflow is then divided into three channels, 'humid', 'polluted', and 'dry', and each is equipped with a flow meter and valve. The 'humid' flow passes through a heated bubbler filled with distilled water; the 'polluted' flow goes to the emission chamber where an emission tube (glass tube filled with acetic acid) releases acetic acid vapor; and the 'dry' flow goes directly to the mixing chamber where it is mixed again with the other two channels. Air combined from the three channels passes into the exposure chamber and out through a psychrometer that measures and controls the relative humidity (Cano 2009).

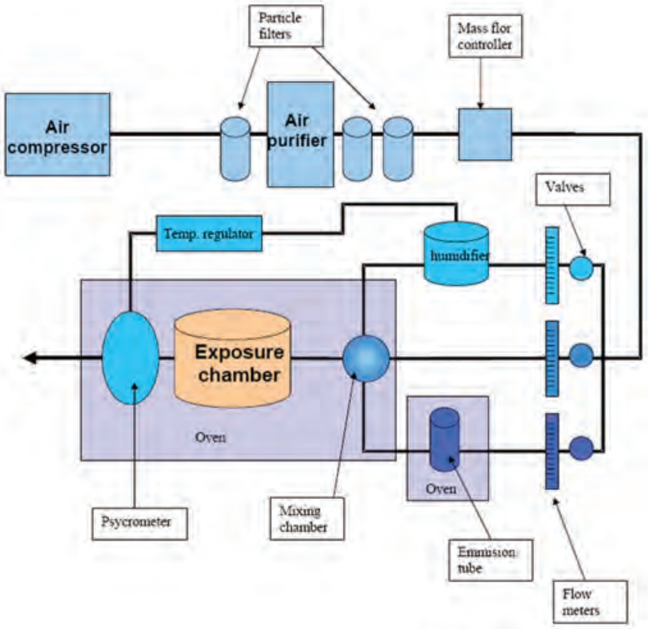

Figure 3. Test chamber diagram.

The conditions were very uniform in the test chamber since the ratio of volume to exposed surface area of the test coupons was very high, and because the test coupons were positioned away from the gas inlet and outlet (Cano 2009).The controls were run in a glass bell jar at room temperature using a saturated salt solution to maintain a RH of 86%. The bell jar remained unopened for the duration of the test.

Controlling and monitoring acidic concentration and relative humidity during testing

The emission rate of acetic acid was controlled by regulating the opening of the emission tube and the temperature of the emission chamber. The tube was weighed weekly, and the concentration was calculated using the weight loss and total air flow (Cano 2009). The psychrometer was a Pt100 temperature probe covered with a cotton wick. The RH was measured comparing the temperature of this wet-bulb temperature with the dry-bulb temperature (i.e. the temperature of the exposure chamber). When the RH falls below the desired RH, the wet-bulb temperature decreases and a temperature controller is used to heat the bubbler, increasing the total amount of water added to the system, and in turn increasing the RH of the chamber. This system allows for a real time sensible control of the RH, with standard RH variation of ±2%.

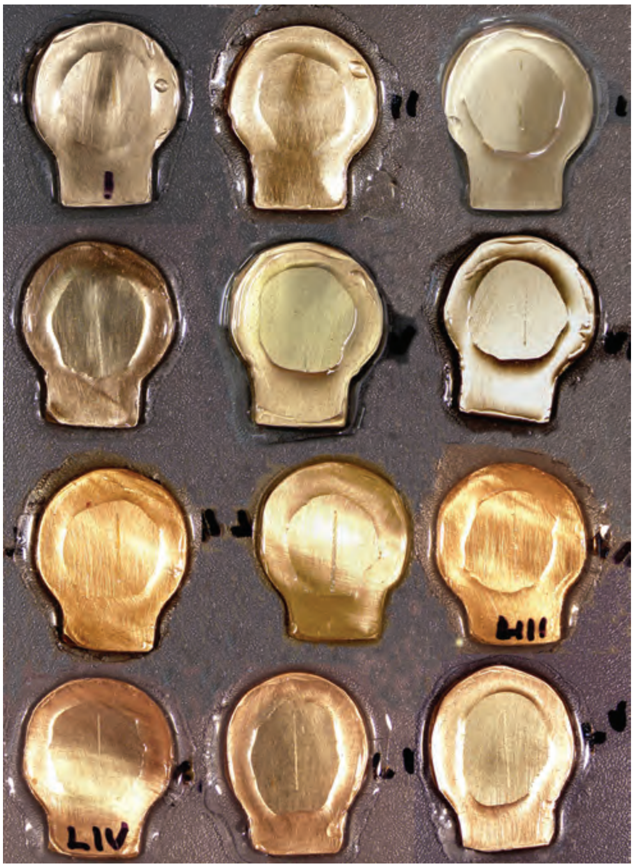

Figure 4. Coated and scribed coupons after testing in acetic acid vapor. Top row: Unleaded with Incralac® U I, U II, U III; 2nd Row: Unleaded with Poligen®, U IV, U V, U VI; 3rd row: Leaded with Incralac®, L I, L II, L III; Bottom row: Leaded with Poligen®, L IV, L V, L VI

Results

Both coatings remained intact, well adhered to the metal substrate and prevented corrosion of the underlying metal (see Figure 4). Bulky, white corrosion formed on the exposed metal in the scribe of the leaded bronze coupons (see Figures 5-6). X-ray Diffraction (XRD) of the corrosion from the corresponding tests on uncoated coupons at the Getty Conservation Institute in 2004 revealed hydrocerrusite as the white corrosion on the same leaded bronze in similar test conditions. For this reason, the white corrosion in the scribed areas of the leaded coupons may be presumed to be hydrocerrusite (Paterakis 2010).

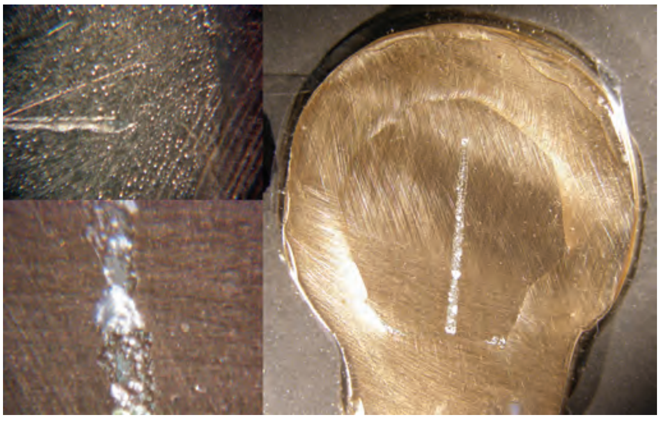

Figure 5. Pb-rich white corrosion in scribes of leaded coupons after corrosion testing: photo lower left and right is leaded coupon LII with Incralac®; photo upper left is leaded coupon LIV coated with Poligen® (air bubbles in Poligen® evident); epoxy resin masking agent visible encircling Incralac® on leaded coupon LII (right)

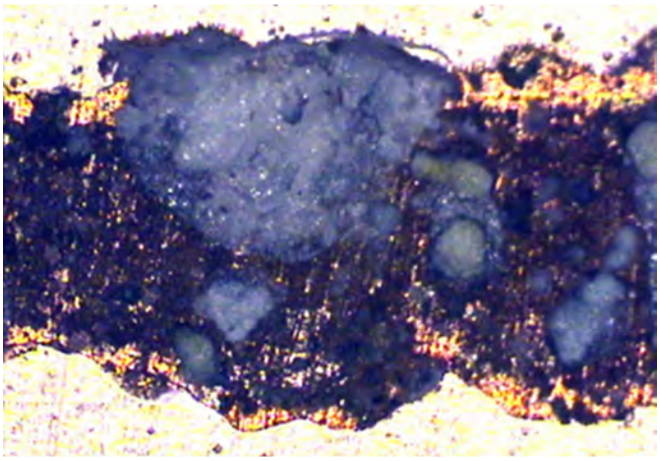

Figure 6. Detail of the scribe running horizontally, viewed from above, in leaded coupon LII coated with Incralac® after corrosion testing detailing Pb-rich white corrosion in top center of scribed groove (detail of righthand photo in Fig. 5). Upper and lower light colored horizontal borders are the unscribed, coated metal coupon surface (5X mag)

The evaluation of the scribed area of the test coupons was carried out according to Procedure A, 7.1 (Method 1, Air Blow-Off) of ASTM D1654-05. Within 15 minutes of removing the test coupons from the test chamber they were rinsed with water. The scribed area was blasted with an airgun at a 45 degree angle with a pressure of 550 kPa (80 psi) to test the cohesion/adhesion of the film to the metal surface. The evaluation resulted in a rating of 10 (zero creepage from the scribe) for all scribed coupons (ASTM D1654-05). An adjacent, unscribed area on each coated coupon was evaluated according to Procedure B of D1654-05 ASTM. This procedure checks for 'corrosion spots, blisters, and other types of failure'. The evaluation resulted in a rating of 10 (no failure) for all test pieces (ASTM D1654-05).

Optical microscopy was used to examine the condition of the films in the scribed areas before and after corrosion testing. Breaking and flaking of the Incralac® film (see Figure 7) and deformation of the Poligen® film (see Figure 8) were visible before the corrosion tests. These two morphologies were caused by the mechanical action of the scribe at the time of scribing and elucidate the difference in hardness between Poligen® ES 91009 and Incralac®. Numerous microscopic air bubbles are visible in the Poligen® film that formed during application by brushing (see Figure 5 and Figure 8).

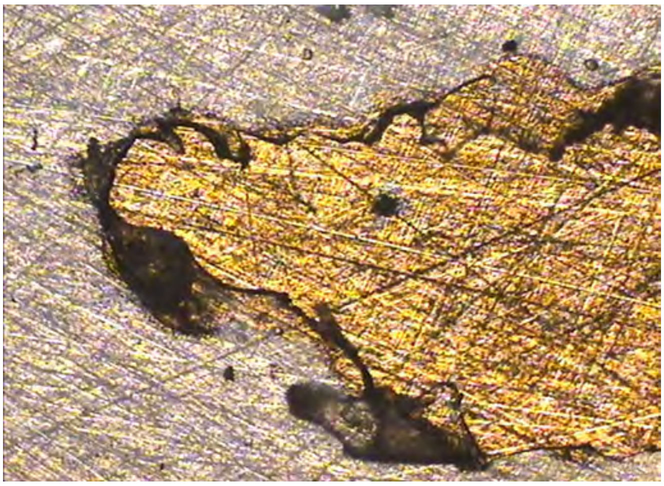

Figure 7. Incralac® coating chipped from scribing on unleaded coupon UI before corrosion testing, yellow area is uncoated metal coupon, scratching is below coating layer from coupon preparation (5X mag)

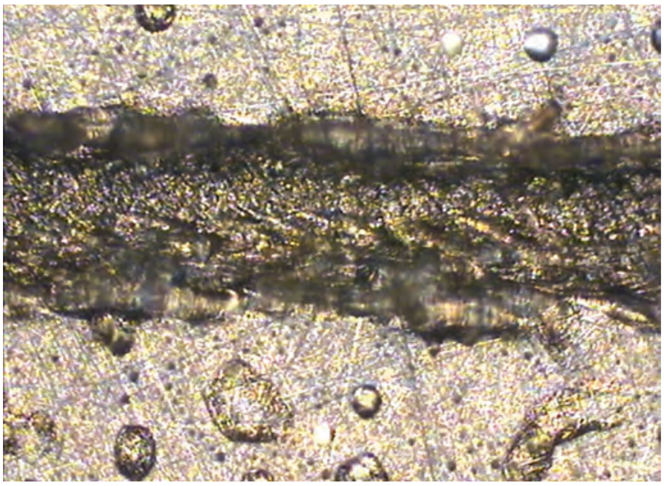

Figure 8. Scribe in Poligen® coating on unleaded coupon UIV before corrosion testing showing deformation of polymer layer at edges of scribed groove; air bubbles in the Poligen® coating are evident (5X mag)

These results compare favorably with three studies in which Poligen® ES 91009 was found to protect copper, brass, and steel in various corrosive conditions (Siatou et al. 2007, Cano et al. 2007, Cano et al. 2010). Incralac® provided equally successful results as a protective coating, in spite of the fact that Paraloid® B44 in Incralac® is reported to be permeable to water and water vapor (Rocca et al. 2007).

Conclusion

In the case of atmospheric corrosion, as was simulated in this accelerated aging test, ionic conduction through an electrolyte is the corrosive mechanism (Koehler 1981). The levels of 4 ppm acetic acid concentration and 86% RH are considered elevated, thereby exposing the test coupons to accelerated corrosive conditions during the eight-week test period. The two coatings performed efficiently by protecting the underlying metal from corrosion. A single application by brushing of Incralac® and Poligen® ES 91009 provided an adequate seal from moisture and acetic acid vapors during the eight-week exposure. The solubility of Incralac® is known to decrease upon aging, whereas the solubility behavior of Poligen® ES 91009 has yet to be determined. Solubility information for Poligen® ES 91009 is not provided by the manufacturer. For this reason Poligen® ES 91009 is considered an experimental polymer in the conservation field undergoing evaluation for its applicability as a conservation material. The determination of the means for its removal, whether mechanical, chemical, or both, will in large part influence the decision regarding its adoption as a conservation material. Conservators emphasize the reversibility of treatments and favor materials of low toxicity for reasons of health and safety.

Materials

Basic No-Blush transparent epoxy resin:
Progressive Epoxy Polymers, Inc.
48 Wildwood Dr., Pittsfield, NH 03263

Incralac® (15% solution in solvents):
Conservation Support Systems
P.O. Box 91746, Santa Barbara, CA 93190-1746

Poligen® ES91009 (emulsion):
BASF Corporation
100 Campus Drive, Florham Park, NJ 07932.
USA website: www.performance.basf-corp.com

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ASTM G1-03, *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*

ASTM G54-84, *Standard Practice for Simple Static Oxidation Testing*

ASTM G78-01, *Standard Practice for Conducting Moist* SO_2 *Tests*

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Q & A SESSION

Stéphane Lemoine: I have noticed in many cases acetic acid and organic [acids] are in the objects themselves – inside the objects. The burial context seems very important. I have noticed this in objects from the Nile Valley and the Mesopotamian regions and deteriorating contexts full of organic compounds present this type of alteration. (It is more prevalent in) bronzes than hammered brass because bronzes very often retain the clay core inside which acts like a sponge retaining organic pollutants.

Alice Paterakis: I would love to talk to you more during the break. Thank you. So I was very interested to learn about the air bubbles – I really appreciated the previous paper for explaining to us why we had air bubbles in our Poligen. That was very helpful, thank you.

Ian MacLeod: Alice, I was wondering, can you give a bit more of an explanation as to how you think the role of sodium is critical? Is it because of the inherent hygroscopicity of the sodium acetate?

Alice Paterakis: Sodium (ions are significant) even before it becomes an acetate, for example if it's sodium of sodium chloride in the object even the hygroscopic properties of that will attract water to the surface which will then encourage attack by acetic acid. (These are my thoughts) as far as I can guess.

Gerhard Eggert: Alice thank you very much for this. I think the 'take home message' is "test your corrosion products". You said there are so many unidentified corrosion products. Corrosion products are like a dosimeter, they tell you about conditions, so you will know if you will have problems with acetate if you have analyzed your corrosion products. Just one comment and one question: So I found that the source of sodium in some cases could even be corroding glass. So when you have corroding glass together with and in direct contact with copper alloys you will also get this sodium copper formate acetate. In the mean time, I found a lot of examples of that, but you can only find it when you measure and when you analyze. Just one question: I never thought that EDTA could be a source of acetic acid. As a chemist I always thought it was tightly bound. Is there any evidence, or has anyone tested if the acetic acid could come out? That would be highly interesting.

Alice Paterakis: I actually know of a case in which acetic acid was used to clean ceramics and the ceramics later developed calcacite which contains acetate. We are associating the acetate with the EDTA.

Valentin Boissonnas: I've treated brass pieces from furniture with EDTA – cleaned them – but some of them were hollow and rinsing obviously was not enough and after a couple of years I did have green corrosion coming out. I didn't test it but I think after EDTA we can have this kind of problem.

Paul Mardikian: So, for us conservators, we treat artifacts, we try to rinse them the best we can but what is again the recommendation here for getting rid of all those by-products of the treatments we use?

Alice Paterakis: As part of my dissertation I did a few cleaning tests – very preliminary cleaning tests – on two of these acetate corrosion products. Depending on the corrosion product, they are all different in their degrees of solubility in water. Some of them were soluble, some were partial and some not at all. The two I tried removing with cotton swabs and I tested different solvents with, were the sodium copper carbonate acetate and copper sodium formate acetate. I was actually able to remove the first one with a cotton swab and just with deionized water. It was a partial solubility reaction, but it was also mechanical and I realized you need both because it is only partially soluble in water. Whereas I found the copper sodium formate acetate much easier to remove with the cotton swab and water, but I think it may have just been because the surface happened to be very smooth underneath in that particular area. This is an area that needs a lot more work on how to remove these corrosion products.

David Thickett: And before you scrap all of your EDTA it is worth bearing in mind that a lot of acetic acid forms in wooden storage containers and shelving, but we certainly need to look into how stable or unstable EDTA may be.

Paul Mardikian: But for us there is so much room for misinterpretation for what we see. We look at those corrosion products and we jump to conclusions thinking that it is a chloride problem. Which may not be the case.

Alice Paterakis: Yes you don't know what you have unless you analyze it. There is no guesswork. You cannot guess. With all the experience I have of sampling these things and looking at them – I've made mistakes – I thought something was – I've even mistaken paratacamite for some of these carbonyl compounds. The colors can vary so widely that you can't guess.

Paul Mardikian: And can you just readdress the way you were able to analyze those corrosion products? Was Raman spectroscopy useful?

Alice Paterakis: I didn't use Raman. The only thing I used was XRD, which was very limiting. Raman could be very useful.

Paul Mardikian: Ok, I know that David (Thickett) you have used it. We have Raman at the lab but we haven't investigated too much the analysis of copper alloy corrosion products.

David Thickett: One thing with these (corrosion products) is that they are often very intimately mixed – you get 2 or 3 things together and the fact that with the Raman you can focus on individual crystals means you can say this one is sodium and this one is something else. It just makes interpretation a lot easier than getting an overall picture.

Peter Northover: Just a general comment on organic sources of corrosion. I generally don't analyze corrosion products – I'm usually being asked to analyze the metal for all sorts of reasons so one prefers to do it before the object has been conserved because you don't know what treatments you're necessarily going to do that ultimately protect the bronze. Just of late I've had to do a number of bronze daggers from early Bronze Age graves and bodies are the worst environment for bronze imaginable. The bodies completely disappeared from this grave, where's everything gone? Well, what I'm going to say is it's eaten the bronze. It is the most difficult object I've ever had to sample. In fact there were two bronze blades and one was just beyond redemption. So organic corrosion is as important as inorganic.

THE APPLICATION OF NON-TOXIC CORROSION INHIBITORS FOR THE TEMPORARY PROTECTION OF IRON AND COPPER ALLOY IN UNCONTROLLED ENVIRONMENTS

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Abstract

Two non-toxic corrosion inhibitors in a solution elaborated from a carboxylic acid were tested for the temporary protection of iron and copper alloy objects in the collections of the Historical Swiss Army Material Foundation (HSAM Foundation). These objects are stored in an uncontrolled environmental in storage facilities in or near Thun and Burgdorf, Switzerland. Application procedures were optimized during testing of the inhibitors on two groups of metal coupons and objects from the HSAM collection. The goal of the study is to field-test the efficiency of the carboxylate-based corrosion inhibitors over time while ensuring that the treatment is reversible. To achieve this, optical microscopy and X-ray microdiffraction (µXRD) were used. This study, named the POINT (Protection temporaire d'Objets métalliques base fer et cuivre à l'aide d'Inhibiteurs de corrosion Non-Toxiques) research project is ongoing at the time of writing and should be concluded by the end of 2010.

Keywords: temporary protection, preventive conservation, scientific and industrial objects, military heritage, copper and iron alloys, corrosion inhibitors, carboxylates

Introduction

The use of protective coatings, such as paint or varnish, in the conservation of metal objects of any scale from the industrial period exposed to uncontrolled environments is often unsuccessful since these coatings are intended for the protection of non-corroded surfaces. In order to prevent corrosion, protective coatings require excellent surface preparation (for example, by chemical etching or sandblasting), and ideal environmental conditions for their application. This is usually problematic in the case of cultural objects, since cleaning down to bare metal would create irreversible damage and loss of the original surface. In addition, large scale or heavy objects can be difficult to move into a laboratory for treatment, and storage conditions can be unsuitable for the application of protective coatings, not only because of their technical requirements, but also because of safety, health or environmental constraints.

Guidelines given by the HSAM Foundation state that protection systems applied on metal surfaces should be transparent and compatible with surviving evidence of the original surface treatment (for example, an original paint layer). If corrosion inhibitors are applied as temporary protection, they should ensure middle-term (months) to long-term (years) protection in the current storage facilities that were initially planned for military purposes, not for heritage preservation. Chemicals used should be non-toxic and the protection systems should remain reversible for possible future conservation treatment, or inhibitor re-application after its period of effectiveness has expired.

The POINT research project was initiated in 2009 in order to further test two of the non-toxic corrosion inhibitors whose efficiency was demonstrated in the context of the European project PROMET ("PRotection Of METals") (Argyropoulos 2008). These compounds (carboxylates) mainly derive from fatty acids extracted from vegetable oil (colza, sunflower and palm (Hollner 2009). Following the 2008 PROMET research project, many questions remained. These included: the type of surface preparation required for successful application; the correct environmental conditions required prior to, and after, application of the inhibitors; the number of layers necessary for adequate protection; the potential effect of alloying elements or surface treatments such as an original paint layer; the long-term efficiency of the compounds; their potential reversibility; and the potential for re-treatment of objects previously treated with carboxylic inhibitors. Our goal was to answer some of these questions.

Methodology of the POINT project

The methodology adopted for the POINT project is similar to that used in the PROMET project. Two successive steps were planned:

- Step 1: Study in a research laboratory the optimal conditions for the application of the selected corrosion inhibitors, on a first group of metal coupons simulating the composition and surface appearance of real objects, by means of accelerated ageing and destructive investigation.
- Step 2: Implement testing of the best-rated inhibitors (from step 1) on a second group of coupons, with inhibitors applied in a conservation laboratory and to real objects on site. Both the coupons and the objects will be tested next to one another in the storage facilities. The evolution of the surfaces will be monitored by photographic documentation every three months over a one-year period, under standard laboratory conditions, and between these periods on site.

Selection of Materials

The selection of metal objects for this study was made after a comprehensive overview of the HSAM collections, but also in the wider context of industrial heritage preservation. As a result, the objects chosen were one military carriage (early 20th century, see Figure 1) that represents large scale low-alloyed ferrous objects, and four brass artillery shells representative of bare copper alloy objects (see Figure 2).

The early 20th century military carriages, previously stored at several military sites in Switzerland, are currently stored at the Burgdorf storage facility of HSAM. Paint layers that originally covered the metal surfaces have partialy disappeared due to past poor environmental conditions.

Metallographic examination of embedded iron samples from the military carriage revealed a composition of 0.02 to 0.1% carbon by weight (low carbon steel). The environment in which the carriage is currently stored is partialy underground, and is therefore relatively stable, with a temperature fluctuating between 0°C and 15°C, and a relative humidity between 40% and 70%. These conditions are not ideal for the long-term storage of iron objects that are preferably stored at very low RH, as low as 15% (Turgoose 1982), but they offer a compromise with wood, the other main component of the carriage, which should be stored at around 55% RH. The site has been chosen for testing of protection systems on reactive materials such as iron alloys.

Figure 1. Early 20th century tool carriage in the collections of the HSAM Foundation, Hall 1 UG, at the Burgdorf storage site.

The composition of the brass artillery shells was evaluated using the SPAMT-Test tool (Degrigny et al. 2010) and were found to contain 30% zinc by weight. These objects are stored in an uncontrolled environment in an above ground metal structure covered with steel panels, at a storage facility near Thun. High daily climatic variations were observed within this building. Temperatures ranged between -5°C and 37°C, and relative humidity between 31% and 87%, with wide variations over a 24-hour period, up to 20°C and 40% RH. For the purposes of this study, this site is ideal for the testing of protection systems on low reactive materials, such as copper alloys.

Figure 2. Copper alloy artillery shells from the HSAM Foundation collections, stored in the main building at the Thun site.

The composition of the metal test coupons used in this project was first planned to be similar to that of the iron carriage and the brass artillery shells. However, with the idea of testing the potential of the corrosion inhibitors selected on a broader range of metals that may be common to collections of historical technical interest, a decision was made to slightly vary the composition of the metal test coupons. Consequently, two sets of 50 coupons each made of building steel, 0.2% carbon and 1.5% Mn by weight, as well as two sets of 50 leaded brass coupons each with a composition of CuZn39Pb2 were purchased from a local supplier as sheets in the following condition: heat laminated and cold cut. As in the PROMET project, the coupons used in POINT measured 75 x 50 x 2.5 mm.

Method

In step 1, performed both at the Laboratoire de Recherche des Monuments Historiques (LRMH) and at the Centre de Recherche et de Restauration des Musées de France (C2RMF), all the steel and brass coupons were artificially corroded in a humidity chamber using temperature and relative humidity cycles to simulate the alteration of real objects[1]. After exposure to the aggressive conditions of the chamber, the steel coupons exhibited localized areas of powdery orange and dark brown corrosion products, and the brass coupons exhibited an overall mottled dark grey to black appearance (see figures 3a and 3b). The surfaces of both steel and brass coupons were rubbed with a cotton swab impregnated with ethanol. The steel coupons were additionally mechanically cleaned using a rotating soft nylon brush to remove any remaining powdery corrosion products, but not the entire surface of the corrosion spots.

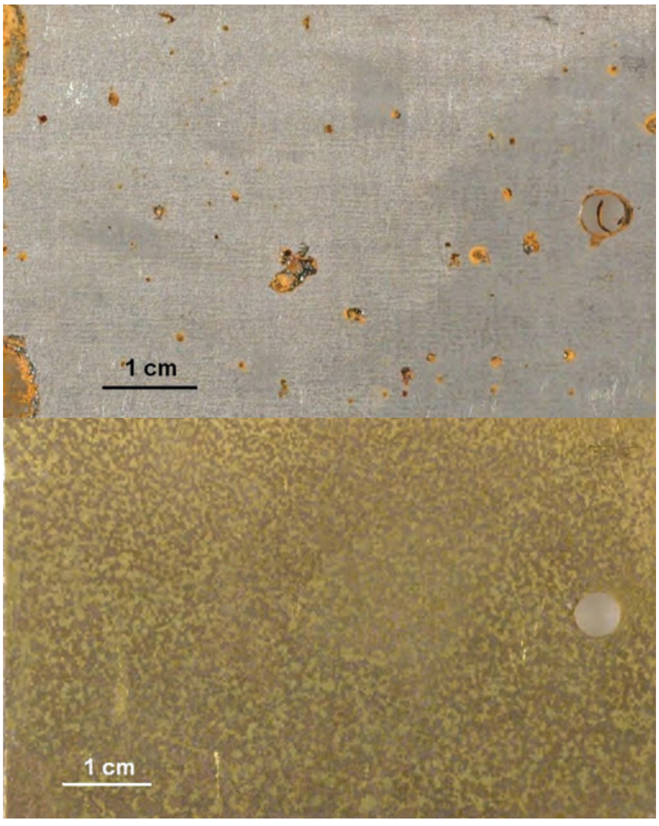

Figure 3. Surface appearance of the steel (*top*) and brass (*bottom*) test coupons after artificial ageing in a humidity chamber.

On the basis of the results obtained from the PROMET research project (Degrigny 2008), sodium decanoate (NaC_{10}) and the carboxylatation solution HC_{10} + H_2O_2 (a carboxylic acid to which a strong oxidant is added) were chosen for further testing in this study. Several preliminary application tests were performed on the artificially aged coupons to determine the most satisfactory solution composition and application method[2,3]. Solutions were assessed visually for their transparency and reversibility with ethanol of the film obtained, as well as the ease of application by brush or spray. After application of the corrosion inhibitors on the first set of 50 steel and 50 brass coupons, the coupons were returned to the humidity chamber[4]. Testing was conducted over a period of three weeks, during which the entire surface of the coupons was examined weekly with a binocular microscope and the reversibility assessed using X-ray microdiffraction (μXRD).

In step 2, the best rated corrosion inhibitors and application protocols (determined from step 1) were applied to the second set of 50 steel and 50 brass coupons, and the artillery shells, in the HSAM laboratory in Thun. Prior to application, the metal surfaces were mechanically cleaned in the same manner as before, without damaging the original surface. As the artillery shells exhibited less surface corrosion, the inhibitors were applied after degreasing the surface with ethanol only.

Both the cleaning of the surface of the military carriage (see Figure 4a) and the application of the inhibitors (see Figure 4b) were carried out on site at the Burgdorf facility where the RH level is much higher than in the HSAM laboratory. This necessitated the use of a hairdryer to help dry the protection systems. Considering that the test zones on the carriage were fully covered by corrosion, a 40 cm long low carbon steel cylinder-shaped spacer was added to the trial. The spacer, like the metal coupons, exhibited only a few corrosion spots on bare metal.

The coupons were placed on a Perspex rack next to the treated objects in storage (see Figure 5).

Figure 4. After mechanical surface preparation (*left*), corrosion inhibitors (3L NaC_{10} and 3L HC_{10}+H_2O_2) were applied by brush on the iron parts of the tool carriage (*right*).

Figure 5. Perspex® rack for housing the metal coupons being tested on site in the HSAM storage facilities.

Results and Discussion

Table 1 gives the list of all protection systems tested in step 1. These remain dry to the touch and do not attract dust after a drying time of only a few minutes, and never more than 30 minutes, depending on the environmental conditions of the room where they have been applied.

	NaC10	HC10 + H2O2	HC10+H2O2 / NaC10
Steel	-3 layers (3L) applied by brush -Applied by spraying	-3 layers (3L) applied by brush -Applied by spraying	1 layer (1L) / 2 layers (2L) applied by brush
Brass	-1 layer (1L) applied by brush -3 layers (3L) applied by brush -4 layers (4L) applied by brush -Applied by spraying		

Table 1. Selected formulations for the protection systems tested in the POINT project.

Step 1 showed that for the steel coupons, sodium decanoate (NaC_{10}), applied in three successive brush applications, performed best with no alteration of the surface appearance noticeable at macro and micro levels. The film formed with the carboxylatation solution (HC_{10}+H_20_2), applied in three successive brush applications, showed alteration after one week, and this damage appeared to contribute to the development of localized corrosion after two weeks (see Figure 6, left hand column). A mixture of the carboxylatation solution and sodium decanoate was also tested, and the results were very similar to those of sodium decanoate.

For the brass coupons, only the sodium decanoate, applied in one to four successive brush applications, proved satisfactory, as the carboxylatation solution caused white stains to appear on the surface of the metal. The application of at least four layers of sodium decanoate led to pooling of the water-based solvent, around which localized corrosion developed (see Figure 6, right hand column).

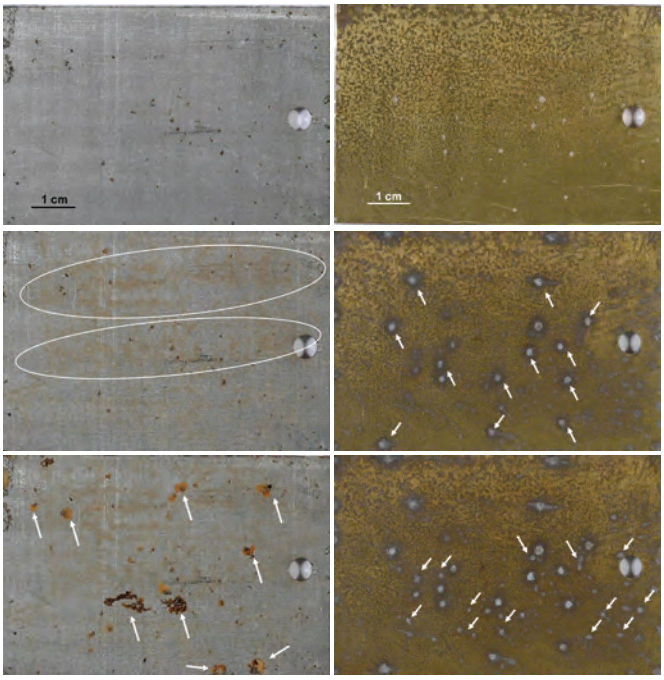

Figure 6. Evolution of the surface appearance of a pre-corroded steel coupon protected with 3 layers of the carboxylatation solution (*left hand column*) and a pre-corroded brass coupon protected with 4 layers of the sodium decanoate solution (*right hand column*). The top row shows the coupons after application of the inhibitors, prior to exposure in the humidity chamber, the middle row after 1 week in the humidity chamber, and the bottom row after 2 weeks in the humidity chamber.

Application by spraying was also assessed and gave limited protection. The presence of carboxylates on the surface of the coupons was confirmed by µXRD[5]. In figure 7, a characteristic peak of iron carboxylate at low angles of diffraction may be observed.

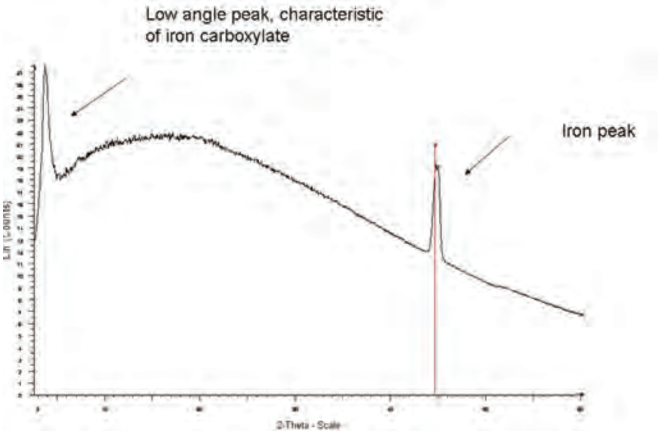

Figure 7. MicroXRD pattern obtained from a steel coupon treated with sodium decanoate.

Satisfactory reversibility and potential re-treatability were essential criteria for the acceptance of the corrosion inhibitors tested in this study. The disappearance of the characteristic peak of iron carboxylate from the µXRD diffractogram was employed to assess whether reversibility was achieved, after the inhibitors were removed by rubbing the surface with an ethanol impregnated cotton swab. Table 2 lists the protection systems that were both effective and reversible and were then the most promising for ageing tests in real conditions. The carboxylatation solution, which did not give very good results on steel coupons in step 1, was considered in step 2 since Hollner had shown that this solution was particularly effective on heavily corroded surfaces, such as the military carriage (Hollner 2009). Spray application was further tested on steel coupons since this method had possible application to large artifacts.

	1L NaC10	NaC10P	3L NaC10	3L HC10+H2O2
Steel		X	X	X
Brass	X		X	

Table 2. Selected protection systems tested on-site.

Step 2 is now in progress. Some areas of the objects selected, the carriage (plus the spacer) and the artillery shells, are covered with the protection systems given in Table 2, and are currently exposed for a period of one year in their specific environments. Exposed next to these artifacts is the second series of coupons, placed on racks and covered with the same protection systems. Non-protected reference coupons are also considered to assess the corrosivity of the environment.

The coupons and the objects are being regularly examined and photographed; initially on a weekly basis, and then at monthly intervals. Every three months, members of the HECR and HSAM meet on site to document all coupons at macro and microscopic levels in laboratory conditions. The efficiency of each protection system is assessed, as well as its reversibility on three coupons. One of them is removed and stored in dry conditions for further scientific examination. Re-treatment with the same protection systems is carried out on the two other coupons, which are then placed back on the rack.

Comparison between the coupons and the objects is carried out, in real-time, to detect any damage to the protection systems applied to the objects.

Conclusion

This study is ongoing at the time of writing, and should be completed by the end of 2010. At the conclusion of the project, it should be possible to comment on the performance of the two corrosion inhibitors tested on corroded copper and iron alloy objects, and compare their performance with the test coupons. Results from this study also will help devise a protocol for the application of the corrosion inhibitors, and provide information to assist conservators and collection managers who will monitor treated objects. The multidisciplinary team overseeing this project will ascertain that standard conservation ethics such as minimal intervention prior to inhibitor application, reversibility, and non-toxicity are respected.

Acknowledgements

This project would not have been possible without the financial support received from the HES-SO (University of Applied Sciences, Western Switzerland), which the authors wish to sincerely thank. Thanks are also extended to the other institutions that supported this project; in particular the HSAM Foundation that gave access to its collections, and the LRMH and the C2RMF which granted privileged access to their accelerated ageing devices and analytical tools. Finally, thanks are due to the AR&D (Applied Research and Development) team at the HECR-Arc for its administrative and technical assistance, as well as conservators Michiel Brunott and Ludovic Rumo involved in the conservation of the HSAM Foundation collections at the Burgdorf site.

Endnotes

[1] Humidity chamber parameters: 16 hours at a temperature of 40°C, and 100% relative humidity (RH) followed by 8 hours at a temperature of 20°C, and 60% RH. The copper alloy coupons were handled without gloves (to instigate corrosion) before being exposed for 62 hours. The steel coupons, handled with gloves, were exposed for 131 hours.

[2] The sodium decanoate solution (0.1M) was prepared as follows: In a 1 liter beaker, 4g of NaOH was dissolved in 300mL of distilled water. After dissolution of the NaOH, 17.58g of HC_{10} was gradually added using a spatula. Distilled water was then gradually added to make up the solution to 1 liter. The carboxylatation solution (HC_{10} 30g/L + 0.1M H_2O_2) is prepared as follows: In a 1 liter beaker, 30.61g of HC_{10} was dissolved in 500mL of ethanol, and stirred with a magnetic stirrer (dissolution is rapid). Next, 8.59mL of H_2O_2 was added, followed by distilled water to make up the solution to 1 liter.

[3] The application method used for both the steel and brass coupons was as follows: the coupons were laid flat and one layer of the corrosion inhibitor was applied with a flat brush followed by immediate air drying at a 45° degree angle with hairdryer or clean compressed air (both gave similar results); repeat for multiple layer application; dissolution in an ethanol bath in case of problem with application. Spraying: using protective gloves and mask, the coupons were laid flat in a fume hood and the corrosion inhibitor was sprayed onto the surface at an angle of 45° to cover the entire coupon; immediate air drying (45° degree angle, by hairdryer or clean compressed air); dissolution in an ethanol bath in case of a problem with application.

[4] Humidity chamber parameters: 16 hours at a temperature of 40°C and 90% RH, followed by 8 hours at a temperature of 20°C, and 60% RH.

[5] Rigaku type RX tube; copper anticathode λ= 1,54186Å; 200μm collimator; Rigaku R-Axis IV type 2D detector imaging plate, treatment with FIT 2D and EVA software, analysis carried out under a low incidence inferior to 8°.

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Materials

Steel and brass metal coupons
Société Kaufmann & Fils
Marché 8-10 / CP 2146
CH-2302 La Chaux-de-Fonds
Switzerland
Tél. : (41) 32 911 10 50
Fax. : (41) 32 911 10 51
Email: info@kaufmann-fils.ch
Web-site: www.kaufmann-fils.ch

Capric or decanoic acid HC_{10} ($CH_3(CH_2)_8COOH$) 98%
Sigma Adrich Chemie GmbH
Buchs, Switzerland
Tel.: (41) 81 755 28 28
Fax.: (41) 81 755 28 15
Email : fluka@sial.com
Web-site : https://www.sigmaaldrich.com/sigma-aldrich/home.html

Pure soda (in pellets) and H_2O_2 (35%)
ROTH SOCHIEL E.U.R.L
3, rue de la Chapelle
Boîte: B.P. 11
67630 Lauterbourg, France
Tel. : (33) 3.88.94.82.42
Fax. : (33) 3.88.54.63.93
Email : info@rothsochiel.fr
Web-site : www.carlroth.fr

95% ethanol
VWR BDH Prolabo
Rue Neuve 7
1260 Nyon, Switzerland
Tel. : (41) 44 745 13 13
Fax. : (41) 44 745 13 10
Email: info@ch.vwr.com
Web-site : http://ch.vwr.com

Authors

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Q & A SESSION

Vasilike Argyropoulos: Thank you that was very interesting. Do you know what the darkening is being caused by because we haven't found that with Poligen that we used on iron bladed knives. With time there's been no darkening and so your results are very interesting. And my second question is: You tried to take off the Poligen with ethanol, is that correct? Why not sodium hydroxide which is what is recommended by the manufacturer, as that works very well.

Guillaume Rapp: Sorry what was recommended? Sodium hydroxide?

Vasilike Argyropoulos: Yes, ethanol may not work well, but sodium hydroxide will, so it will be reversible. You can take it completely off if you try sodium hydroxide. So was there a reason you and Christian wanted to use ethanol possibly –

I'm just wondering.

Guillaume Rapp: Why not sodium hydroxide – because I didn't know this was the correct way to do that. I carried it out with simple methods with what I have – common solvents.

Vasilike Argyropoulos: Why not acetone for example? Why ethanol, I'm just curious? Did you look at other solvents as well?

Guillaume Rapp: I must answer that we tested with a range of non-polar and polar solvents and we are currently continuing this as we don't know how to dissolve this layer, but later I found out that ethanol was possible to use on this layer and so I used that.

Vasilike Argyropoulos: And the darkening? Are you going to do further analysis to determine (like FTIR analysis) what is possibly causing the darkening? We are not finding that so if you want we can do the analysis for you.

Guillaume Rapp: It is interesting that you didn't have this problem of darkening at all, because we noticed that after the first hours of application and [another problem is that] I think our layer is much too thick. This question about the thickness of layers is very important. In our project it was considered what to use methodically that could be used on huge amounts of objects. So it is a methodical problem for us, not really a product problem. The question for us was: 1. How many layers should we apply to overcome the problem?

Vasilike Argyropoulos: Did you measure the darkening using colorimetry? Or was it just visual?

Guillaume Rapp: For the moment it is only visual and we only monitored this visually by photographs. Every 3 months we removed the coupons from the rack and we kept them apart and it is intended that these be analyzed further.

Vasilike Argyropoulos: So do you think the darkening might be related to the thickness of the coating that you are applying? Because you did apply thicker coatings than PROMET. You had 3 layers correct? That was your decision, to go with 3 layers? Whereas we had 2 layers on the PROMET coupons.

Guillaume Rapp: We had 2 layers with Poligen as well.

Vasilike Argyropoulos: And you had darkening?

Guillaume Rapp: Yes and it was the Poligen 91009, that was applied without dissolving it. So it was a clear product. I don't know if you used dissolved product or not?

Vasilike Argyropoulos: I think we did both but I can't remember off-hand to be honest.

Guillaume Rapp: Because for me as a conservator it was a bit painful to apply such a thick layer. Even the first layer for me was much too thick. And it changed the readability of the surfaces too much in my opinion but we did that because we were ordered to.

Vasilike Argyropoulos: Did you have problems with bubbles as well, because some people find that a problem. I assume you used the synthetic vs. the natural fibre brush [for the application method]?

Guillaume Rapp: Yes, we had problems. The question is in what way to use the product because if you shake it to unify [the solution composition] we create bubbles. We could notice the bubbles very clearly on the surface. Some of them disappeared after a while but it is also a little strange and of course the real thickness of the layer is affected by these bubbles. We should maybe treat it under vacuum if we wanted to remove these.

Vasilike Argyropoulos: Ok, thank you.

Maickel van Bellegem: I'm curious about the definitions of retreatability and reversibility. If it is not possible to remove the wax, and you would have to retreat it with an aqueous solution, then that could affect the retreatability. Or is your definition only to apply the same treatment?

Guillaume Rapp: Yes it was to reapply the same treatment in terms of retreatability. With regards to reversibility – it is to completely remove the layer. This has to be assessed finally in the project – for how much we have really reversed the application. For the moment we have not carried out this analysis.

Maickel van Bellegem: Ok, thank you.

Olivier Berger: I am a little bit surprised that you are not going back to the people working in this field. Like people from Quebec, from CCQ [Centre de conservation du Québec] are working with Carnauba wax for now more than 25 years. And they have good results and now I am also using that in Switzerland when dealing with an aggressive environment. But you cannot use it alone, it is too hard a wax. So that is why you have to add some Cosmoloid or some other wax in it to have a really protective and efficient layer.

Guillaume Rapp: That is right. We chose the Carnauba wax because it was used by other conservators at the Historic Army Material Foundation. They use it like this on composite objects made of wood, paint layers and metals and they cover sometimes everything with this Carnauba wax emulsion. It gives good results on some surfaces but it may be aggressive or non-protective on other surfaces. The goal of testing it in this way was to test how it might be aggressive to the coupons and maybe to artifacts. But about the people in Quebec using Carnauba wax - I have not contacted them.

Olivier Berger: They have great experience and a great background in using this and they are working with Carnauba wax every day and they have good results. You know that it is a very salty environment when they have snow and they put a lot of salt on the streets, and the monuments are in a very aggressive environment. The Carnauba wax works, but not by itself – Carnauba wax with other waxes could resist a very aggressive environment.

Guillaume Rapp: For me the real properties of the Carnauba wax are not clear, because does it form a real layer or are some parts covered and others give access to water or…?

Olivier Berger: That is why you have to add other waxes to it.

Johanna Wolfram: Just a comment, not a question: Thank you very much and I found it very interesting that you looked at the reversibility and retreatability. We also had a look at the retreatability, but just on the side, and we found that if you remove the Poligen with sodium hydroxide you can apply other coatings afterwards on the same coupon. But even if you don't remove it, you can put all of them on the Poligen. But we didn't look at that in detail, just visually – it doesn't come off or crack or anything like that. So it would be interesting to do more research on that.

Guillaume Rapp: That is interesting. Thank you.

Rozemarijn van der Molen: Just a small comment. You already mentioned that your layers might be quite thick. And it is known that the thicker your layer the sooner you are going to notice discoloration or yellowing of these layers. You were discussing that in the other research there wasn't any yellowing; also some substances yellow in the dark or in light and maybe you both had very different lighting conditions.

Vasilike Argyropoulos: We used colorimetry to measure and we didn't find it. And I don't think you are talking about yellowing – was it yellow?

Guillaume Rapp: No it darkens in a green/grey tone.

Rozemarijn van der Molen: I was just trying to ask both of you actually that maybe the light on your samples, maybe UV, would be different so the discoloration of your layer could turn out different. This was just a thing I wanted to add to the discussion.

Vasilike Argyropoulos: Do you mean the application?

Rozemarijn van der Molen: No. The samples, when they were laying in these racks, and depending on the lighting conditions in that room, that maybe the result could be affected…

Vasilike Argyropoulos: Absolutely, yes. Thank you.

Eric Nordgren: I'm pretty sure from what you presented that this wasn't a part of the tests, but is there any indication of how these things might stand up in actual uncovered outdoor situations? Were these all under covered buildings even if the humidity was high or fluctuating and has there been any testing or planned testing for these coatings in open environments – where they would not be covered? If all of these storage areas were completely covered or whether you had some outdoor artifacts?

Guillaume Rapp: This is an interesting question because one of our storages, which was quite stable was partly underground and was intended for tanks, and the other was a light building used in military domain, and sometimes the wind can enter the building. So this explains the fluctuations – but it is still indoors.

ON THE USE OF ALCOHOLIC CARBOXYLIC ACID SOLUTIONS FOR THE DEPOSITION OF PROTECTIVE COATINGS ON COPPER

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Abstract

This paper describes the use of ethanolic solutions for the deposition of carboxylate coatings on copper, with the objective of developing an environmentally friendly, reversible and retreatable coating for archaeological objects. The coatings were characterized with optical and electron microscopy and electrochemical tests were performed to compare the corrosion currents before and after the application of the coating on standard copper coupons. Preliminary results suggest that treatment of copper with carboxylic acid solutions in ethanol with more than 10 carbon atoms, and pH 7–7.5, improves the corrosion resistance of copper. Nevertheless, the use of ethanolic solutions of carboxylic acids is not suitable for use on cultural heritage material because of the irreproducibility of the results and the blue color of the copper carboxylate.

Keywords: copper, corrosion inhibition, carboxylic acid, carboxylate coatings, ethanolic solution

Introduction

Preservation of cultural heritage metals has many requirements concerning materials and protocols of intervention. The chemical characteristics and the visual appearance of the patina and the corrosion crusts on an object depend on the surface finish, microstructure and composition of the underlying metal, and the environment to which the object is exposed. Every object is a unique combination of metal, a patina or corrosion crust (which may need preservation where it is protective, aesthetically desirable, or carries historical information), and possibly active corrosion.

Active corrosion can rapidly damage or even destroy metal objects: cations migrate from the metal substrate and react with available anions to form the metal salts that constitute corrosion layers. One way to preserve these objects is to isolate the objects from the environment with a protective coating. A major problem with presently available treatments is that some of the products, used as protective coatings and corrosion inhibitors, are not safe for use by conservators. 1,2,3-benzotriazole, for example, is a very effective inhibitor against copper corrosion, but it is also toxic and environmentally harmful with a possible carcinogenic effect (Health Council of the Netherlands 2000). Nevertheless, organic coatings are one of the most important ways to protect metal against corrosive agents. They have been used for a long time in conservation: different forms of waxes and oils were applied to bronze objects by Greek craftsmen to protect this metal (Scott 2002).

Earlier studies have demonstrated the effectiveness of carboxylic acids and sodium-carboxylates as aqueous corrosion inhibitors (Stein et al.1998, Bertrand et al. 2000, Rocca et al. 2001a, Rocca et al. 2001b). Moreover, protective layers of metal carboxylates deposited on the surface from aqueous solutions have been described as effective inhibitors against corrosion of lead, copper alloys and iron (Rocca et al. 2004, Dowsett et al. 2007, Hollner et al. 2007a, Adriaens et al. 2008, De Wael et al. 2010). Longer carboxylate chains provide better protection for the metal surface (Rocca 2001b), but the insolubility in water of the higher molecular weight sodium compounds (i.e. dodecanoate to octadecanoate) prevents aqueous deposition of the coating.

Aqueous solutions have another disadvantage: they can accelerate the corrosion process. This is particularly evident for copper alloys, which are attacked by nantokite (CuCl). Moisture promotes the conversion from nantokite to copper hydroxychlorides, such as atacamite and paratacamite, fragmenting the surface and causing further corrosion until the complete destruction of the metal occurs (Scott 2002). Another drawback of the use of aqueous solutions is that carboxylate layers synthesized from short chain carboxylic acids (four to eight carbon atoms) are soluble and therefore are not particularly waterproof or durable in damp environments.

All carboxylic acids, on the other hand, are highly soluble in alcohols, such as ethanol and propanol (Morrison 2002). The principal aim of this project is to see whether a protective metal carboxylate layer can be deposited simply by soaking the metal in alcoholic solutions containing long-chained carboxylic acids (up to 12 carbon atoms). Three acids were selected for the test: heptanoic acid (HC_7), partly to provide a benchmark with published data, decanoic (HC_{10}), and dodecanoic acid (HC_{12}), to represent the longer chains. A range of immersion times and concentrations was used for each.

The objective of this study was to find a practical and easy method for the deposition of corrosion inhibitors with improved moisture and corrosion resistance, while taking into account specific requirements of heritage preservation, in particular the issue of reversibility and aesthetic appearance.

Experimental

Experiments were carried out on coupons made from 99.9% pure copper (Goodfellow Cambridge, Ltd.). These were 2 mm thick, and 12.6 mm in diameter. The coupons were mechanically cleaned with P1200 grit silicon carbide (SiC) abrasive paper to expose a fresh metal surface. The surfaces were subsequently polished using a polishing cloth and an alumina (Al_2O_3) water suspension (1 μm particle size). To remove any adherent Al_2O_3 particles, coupons were rinsed with deionized water and ultrasonically cleaned in ethanol for 15 minutes.

Alcoholic solutions were prepared using carboxylic acids with different carbon chain lengths. Heptanoic acid (HC_7) decanoic acid (HC_{10}) and dodecanoic acid (HC_{12}) were dissolved in 99% analytical grade ethanol. Different concentrations were prepared at 0.05 M, 0.1 M and 0.15 M. In addition, sodium and potassium carboxylate solutions were made by adding respectively sodium hydroxide (NaOH, 0.5 M in deionized water) and potassium hydroxide (KOH, 0.5 M in ethanol) to the carboxylic acid solution (in ethanol as above) in order to raise the pH to 7. NaOH was added as an aqueous solution to the solution of carboxylic acid in ethanol as it is insoluble in the latter solvent (Zacharie et al. 2009). In contrast, KOH is soluble in ethanol (Aylward 1999). Copper samples were treated simply by immersion in the solutions without agitation for 1, 6 or 24 hours. The samples were not rinsed after immersion, but dried by exposure to air for two hours.

After the treatment, the copper coupon surfaces were characterized by optical (model SMZ800, Nikon Corp.) and electron (Phenom™, FEI Company) microscopy in order to assess the morphology and coverage of the layer. In addition, polarization measurements were carried out in a 0.1 M sodium sulfate (Na_2SO_4) solution. The reference electrode used was a mercury mercurous sulfate K_2SO_4 saturated electrode (MSE); the counter electrode was a platinum wire. All the potential measurements given in this paper are referred to [in?] the MSE reference electrode. A computer controlled potentiostat with the software package GPES 4.9 (Autolab PGSTAT10, ECO Chemie) was used for all measurements. The polarization resistance was measured using linear polarization in a range of ± 20 mV versus open circuit potential (OCP) and with a scan rate of 1 mV/s. The corrosion current density was calculated using linear polarization (± 250 mV vs OCP, scan rate 0.2 mV/s.) and via the Tafel extrapolation.

X-ray diffraction (XRD) measurements were performed on a Panalytical XPert Pro Multipurpose Diffractometer using filtered Cu k-α radiation in order to confirm the presence of a particular copper carboxylate on the sample surface.

Results and discussion

A first set of experiments was aimed at obtaining a homogeneous coating over the entire copper coupon surface using ethanolic solutions of heptanoic, decanoic and dodecanoic acid. The deposited layer was characterized with optical and electron microscopy. Samples that were judged by microscopy to have the most uniform coatings were examined further with electrochemical techniques in order to verify the corrosion inhibition of the carboxylate layer. Finally, sodium carboxylate solutions were tested on corroded samples coated with nantokite, atacamite and a paratacamite-atacamite mixture, prepared according to the protocols described by Leyssens (Leyssens et al. 2006), in order to simulate the application of the coating to archaeological objects.

Ethanolic solutions of carboxylic acids

The results for copper coupons immersed in ethanolic solutions of heptanoic, decanoic and dodecanoic acid for 1, 6 and 24 hours show that none of the solutions produces a homogeneous coating. As an example, Figure 1 shows an optical micrograph of a coupon immersed for 24 hours in a 0.1 M heptanoic acid solution. The deposition of platelet crystals of a blue-green color, characteristic of the heptanoate (Ghermani et al. 1994) is evident. Indeed, all the copper monocarboxylates are blue/blue-green because of the presence of the Cu^{2+} ion, as described by Smith (1995). The XRD spectrum of the same coupon is presented in Figure 2: peaks from the copper substrate are clearly evident, but there is no match with any copper compound listed in the database of the International Centre for Diffraction Data (http://www.icdd.com). However, the database does not contain reference spectra for copper-heptanoate. We therefore reconstructed a reference spectrum by inserting the crystallographic data from Ghermani et al. into the software package Crystallographica v 1.6d (Oxford Cryosystems Ltd.). The match is excellent, demonstrating both that the heptanoate is what had grown, and that the structure on the copper surface is dominated by the 001 orientation (which is why the reflections in the 2Θ range 10º-12º are missing). Figure 3 shows backscattered and secondary electron images of the same copper coupon in which the heptanoate crystals are clearly visible. In general, it was found that longer immersion times and higher carboxylate concentrations lead to an increase in the number-density of crystals deposited. Nevertheless the coatings remained discontinuous.

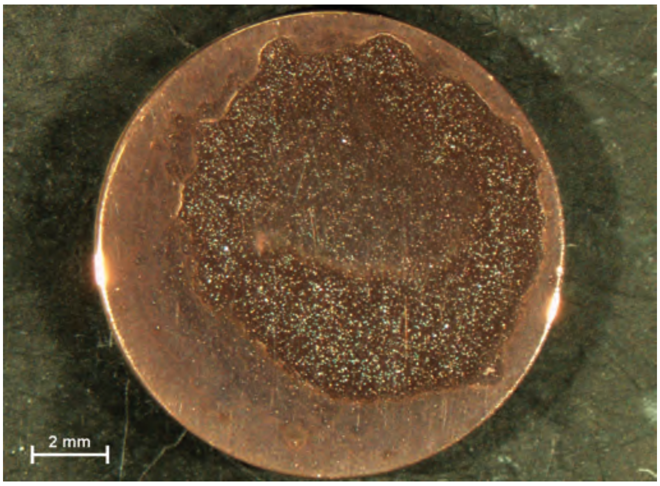

Figure 1. Sample treated for 24h in 0.1M HC_7 (in ethanol).

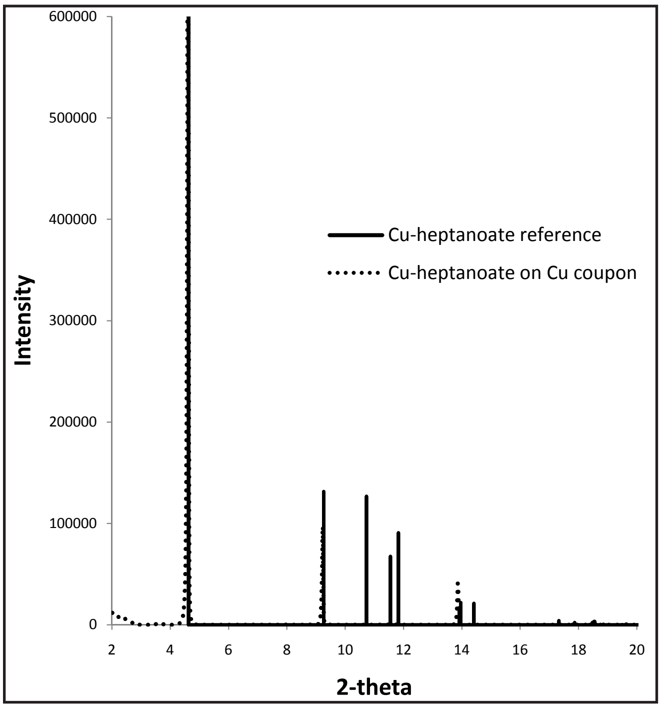

Figure 2. XRD spectrum of copper treated for 24h in HC_7 0.1M (dotted line) and reference spectrum of Cu-heptanoate (solid line).

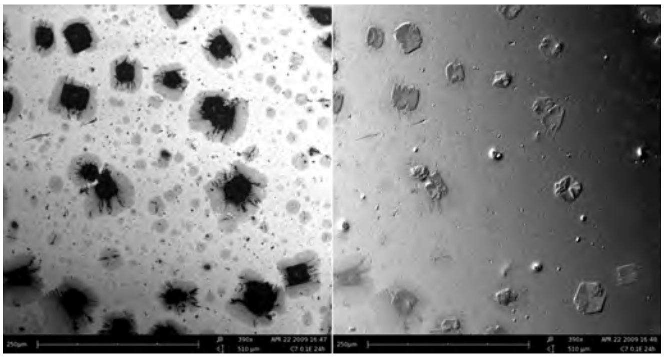

Figure 3. Sample treated for 24h in 0.1M HC_7 (in ethanol): BS (*left*) and SE (*right*) images.

Sodium-carboxylate solutions

In a second set of experiments, copper coupons were immersed in the sodium-carboxylate (NaC_n) ethanolic solution, which was prepared according to the protocol listed in the experimental section. The procedure used for coating the samples was the same as that described for the carboxylic acid solutions.

For the case of NaC_7 with a concentration ≥ 0.1 M, and an immersion time of 24 hours, a homogeneous blue-green dendritic coating of crystalline copper heptanoate (verified by XRD) was obtained. Figures 4 and 5 show optical and electron micrographs of the coating. It is important to note that the layer is not mechanically attached to the surface, but deposited during evaporation of the solvent. Rinsing the sample after immersion will remove the coating. After drying in air, the surface of the coupons is covered by a white layer. Since the copper carboxylates themselves are blue-green, it is likely that the white substance is unreacted sodium carboxylate, as described by previous studies (Hollner et al. 2007b).

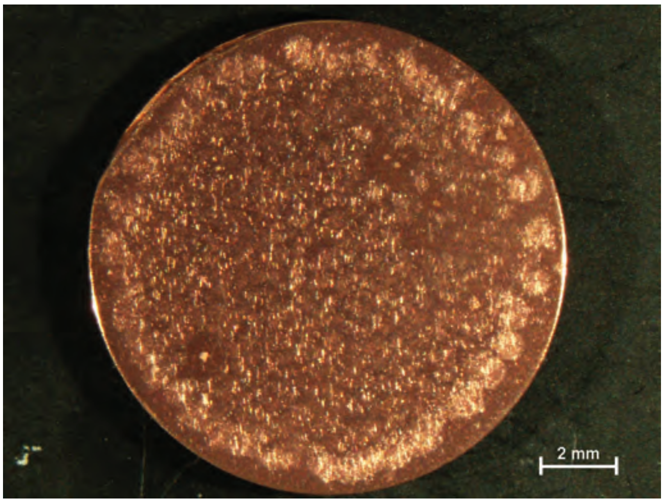

Figure 4. Sample treated for 24h in 0.1M NaC_7 (in ethanol).

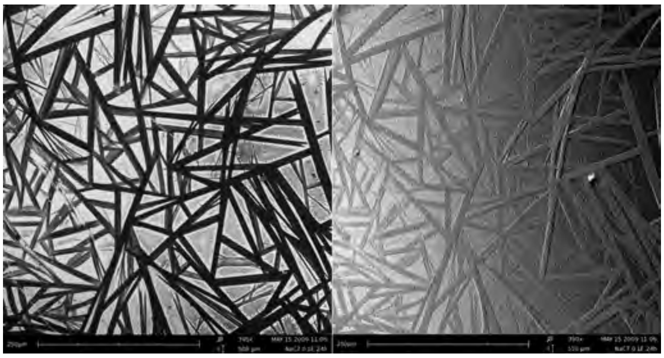

Figure 5. Sample treated for 24h in 0.1M NaC_7 (in ethanol): BS (*left*) and SE (*right*) images.

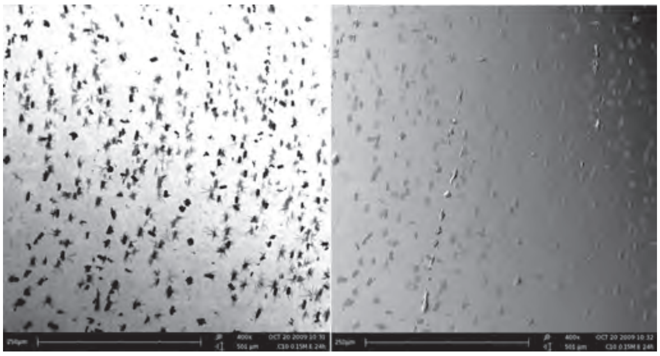

Figure 6. Sample treated for 24h in 0.15M HC_{10} (in ethanol): BS (left) and SE (right) images.

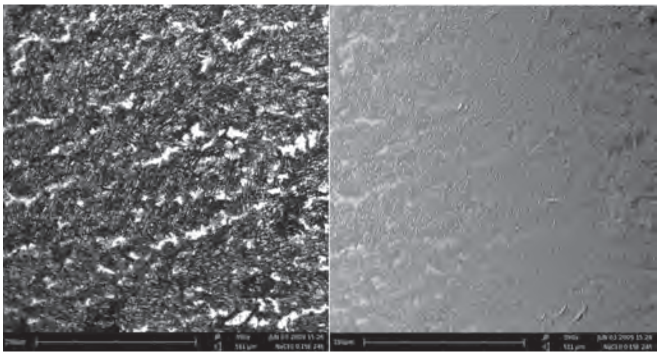

Figure 7. Sample treated for 24h in 0.15M NaC_{10} (in ethanol): BS (left) and SE (right) images.

Figures 6 and 7 show the results from coupons that were immersed in HC_{10} and NaC_{10} 0.15 M, respectively. The difference in surface coverage between coupons treated with HC_{10} or NaC_{10} is evident: the coverage in Figure 7 (NaC_{10} solution) is much more homogeneous.

When depositing from a NaC_{12} solution with a concentration > 0.1 M, the formation of copper dodecanoate was observed on both the polished and unpolished faces (underside) of the coupon. On the unpolished face, still coated with its native cuprite, the dodecanoate layer appeared thicker and more continuous to the eye (see Figure 8). No growth was observed on this face when using the NaC7 or NaC10 solutions.

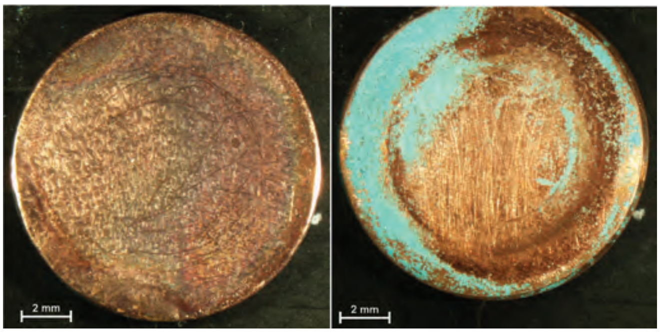

Figure 8. Sample treated for 24h in 0.1M NaC_{12} (in ethanol): front and back side.

The reproducibility of the surfaces produced using sodium carboxylates was significantly worse than that achieved with the carboxylic acid alone. For the former, in repeated growth sequences using the same protocols and times, only a minority reacted to form the surface copper carboxylate. We suspected that this was due to inhomogeneity in the solution with the NaOH/water system not mixing and reacting with the carboxylic acid/alcohol system. However, similar tests using potassium carbolylates (see experimental section) also failed to produce uniform layers. Possibly, agitation might have improved the situation, but this was not investigated here.

A further step in this research involved the measurement of the corrosion inhibition of the carboxylate coatings applied from ethanolic solution using electrochemical techniques. Inhibition was assessed using polarization resistance and corrosion density measurements. For the electrochemical tests, we selected only the samples that produced presented homogeneous coatings. These were:

NaC_7: 0.05M and 0.1M immersed for 1, 6 and 24 hours

NaC_{10}: 0.05M, 0.1M and 0.15M immersed for 1, 6 and 24 hours

NaC_{12}: 0.1M and 0.15M immersed for 1, 6 and 24 hours

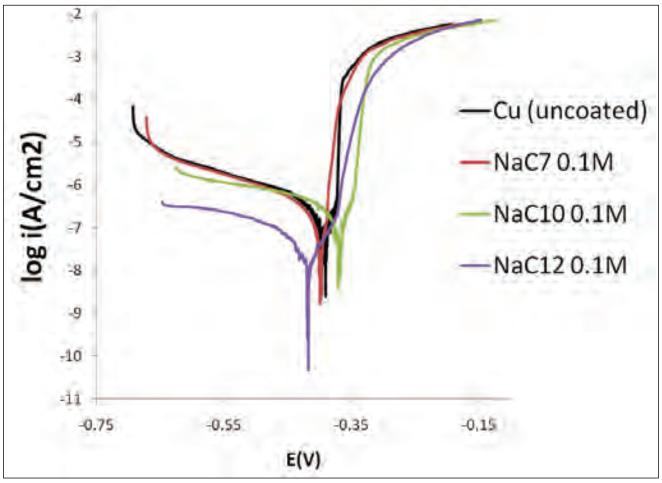

Figure 9. Potentiodynamic curves for different Na-carboxylate.

Potentiodynamic curves obtained from the copper coupons treated with these solutions are presented in Figure 9. Here, the samples were all cleaned and polished as described in the experimental section, and the same concentration of the carboxylate (0.1 M) and immersion time (24 hours) was used. It is clear from Figure 9 that the use of NaC_7 and NaC_{10} to coat the copper coupons does not improve corrosion resistance. In fact, the corrosion potential (E_{corr}) is the same as that of uncoated copper and no decrease in the corrosion current is observed. The treatment with 0.1 M NaC_{12} solution provides better inhibition, as the corrosion current density is slightly reduced.

Table I presents the average value of E_{corr}, polarization resistance (R_p) and current density (i) for coupons immersed in NaC_7, NaC_{10} and NaC_{12} and shows increasing inhibition associated with the length of the carboxylic chain.

Figure 10 displays the potentiodynamic curves recorded on a series of coupons immersed for 24 hours in a 0.15 M solution of NaC_{12} (pH 7). The corrosion density of the

sample	E_{corr} (V)	R_p (kΩ cm^2)	Corrosion current density (A/cm^2)
copper (uncoated)	- 0.44	4.3	1.47E-03
NaC_7	- 0.41	6.5	4.00E-03
NaC_{10}	- 0.38	30	1.60E-04
NaC_{12}	- 0.39	458.2	2.00E-05

Table 1. Selected formulations for the protection systems tested in the POINT project.

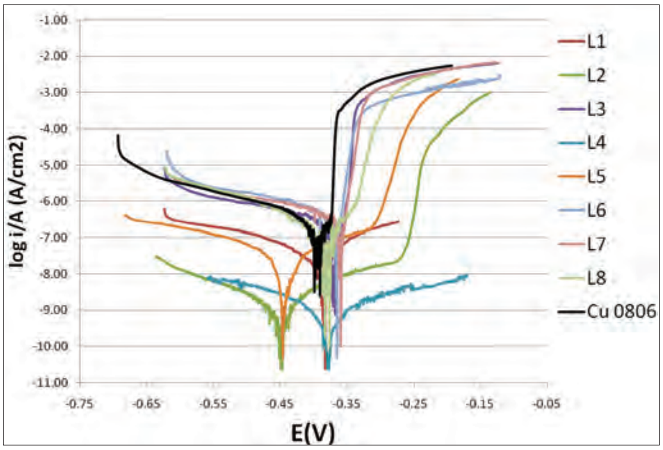

Figure 10. Potentiodynamic curves for samples treated in NaC_{12} 0.15M.

samples is correlated with the quality of the coating. Furthermore, when the coupon does not react with the solution to form a copper-carboxylate layer, the corrosion current is higher, indicating a faster corrosion speed.

Table II presents R_p and current density values for samples treated with the same conditions as those presented in Figure 10: 24 hours of immersion in a 0.15 M NaC_{12} solution with a pH 7. The corrosion inhibition is variable and is dependent on the uniformity of the carboxylate layer. Small values of current density (implying better corrosion inhibition) were obtained from samples characterized by a more uniform layer on the surface (assessed by visual inspection of the micrographs).

Sample	E_{corr} (V)	R_p (kΩ cm^2)	Corrosion current density (A/cm^2)
L1	- 0.371	544.7	1.14E-06
L2	- 0.387	7180.3	4.83E-07
L3	- 0.371	46.1	6.30E-05
L4	- 0.305	34620.5	9.42E-08
L5	- 0.432	923.2	2.40E-06
L6	- 0.376	32.8	6.92E-05
L7	- 0.373	27.0	9.32E-05
L8	- 0.375	20.2	3.83E-05

Table 2. Selected protection systems for testing in natural on-site ageing conditions.

Sodium-carboxylate coatings on artificially corroded samples

In order to assess the effects of carboxylate solutions on real objects, some corroded coupons were prepared for coating application. The coupons were covered with different copper corrosion products (see Experimental section): cuprite (Cu_2O), nantokite (CuCl), atacamite $Cu_2Cl(OH)_3$ and a paratacamite/atacamite mixture. The protocols used produce cuprite and nantokite layers in the order of a micron thick and atacamite and atacamite/paratacamite layers 100's of microns thick. The coverage is uniform as assessed by optical microscopy.

The corroded samples were immersed in a sodium dodecanoate (0.15 M) solution for 24 hours. After 24 hours of immersion a blue-green color was visible on the surface and, in some cases, a white deposit on the blue surface was also visible. The white deposit was thought to be related to the deposition of unreacted sodium dodecanoate.

Figure 11 presents an example of the results obtained; on the left is a corroded copper coupon with a nantokite layer (4 μm thick); on the right is the same copper coupon after 24 hours of immersion in the 0.15 M sodium-dodecanoate solution in ethanol. As usual, the presence of copper caboxylate was confirmed using XRD. The blue-green color is evident once more.

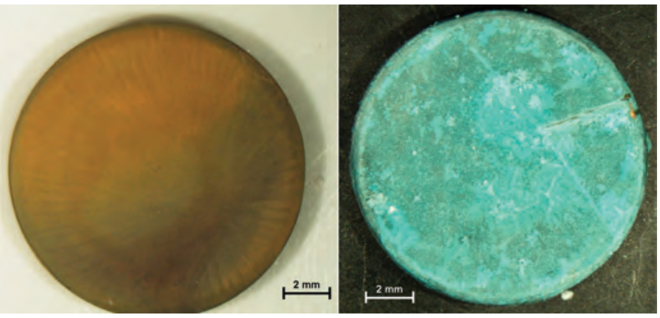

Figure 11. Artificially corroded sample (nantokite layer) before and after immersion in NaC_{12} 0.15M for 24h.

Observations gained from these experiments conducted on copper coupons appear to indicate that a copper-carboxylate layer, deposited through evaporation of a solvent, in this case ethanol, is not suitable for application as a corrosion inhibitor on cultural heritage objects. Noted drawbacks include the fact that they introduce a layer, changing the color and general appearance of the original metal surface and they are not resistant to mechanical damage.

Conclusions

This study shows that application of carboxylate coatings deposited from ethanolic solutions to obtain increased chain lengths is not viable as a conservation treatment. The experimental method tested in this study also posed reproducibility problems in the coating deposition and therefore in the inhibition efficiency. Acidic and neutral solutions containing carboxylic acid of different chain lengths were tested and the addition of NaOH to the solution was found to improve the homogeneity of the layer. The carboxylate layer, which is obtained by evaporation of the solvent, is easily removed and does not appear to create an efficient barrier against moisture and gaseous pollutants. The color and aesthetic appearance of the treated metal were not satisfying; thin layers of carboxylate coating are not effective against corrosion and thicker layers are blue-green in color.

Acknowledgements

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Materials

Copper foil
Goodfellow Cambridge Limited
Huntingdon PE29 6WR England
Tel: +44-1480-424800

P1200 grit SiC paper, Al_2O_3 1µm
Buehler GmbH - European and MESA Headquarters
Postfach 160355
40599 Dusseldorf, Germany
Phone: +49-211-974100

Carboxylic acids (HC_7) (HC_{10}) (HC_{12}), NaOH, KOH, Na_2SO_4
Sigma-Aldrich NV / SA
Kardinaal Cardijnplein 8
2880 Bornem, Belgium
Tel.: +32(0)3-8991301

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Q & A SESSION

David Hallam: I can concur with your results. I tend to find carboxylates and their application somewhat problematic.

Alice Elia: I agree, definitely. And if I can say, C10 also stinks horribly! C12 is getting better it has a sweet smell but C10 is really awful.

Jannicke Nienhuis: You said you didn't rinse the coupons after you immersed, because then you would have rinsed off everything. But isn't that what you want?

Alice Elia: No. I want to deposit a layer and copper carboxylates are soluble in ethanol so the metal was reacting with the solution and when the solvent was evaporating the salt was depositing on the surface.

Stéphane Lemoine: You have to adjust the pH of the carboxylic acid from 4 to 7, is that right? And for this purpose, you add sodium hydroxide?

Alice Elia: Yes.

Stéphane Lemoine: And then you create a carboxylate – a sodium carboxylate?

Alice Elia: Not completely. The acid is partially neutralized. We checked with ethanol and I also tried a solution of isopropanol and the equivalence point was about pH 8.4. So when we arrived at pH 7, the acid was not completely neutralized. So it is a mixture partially of sodium carboxylate and partially carboxylic acid.

Stéphane Lemoine: That's right and on the object you don't create a copper carboxylate entirely, because you have sodium carboxylate too.

Alice Elia: Well, when it is green, it is definitely copper carboxylate. Recently we did some infra-red measurements and some samples treated in water, because I also tested water and not only ethanol. We found evidence that there was both copper carboxylate and a minor quantity of sodium carboxylate residue on the surface. But this was for water samples.

Stéphane Lemoine: Thank you.

David Thurrowgood: Many years ago now I did a student project based around carboxylates, looking at the efficiency of them starting from a chain-length of about 2 to 3 all the way up to 16. I certainly found what you found which was that as the chain length increased the efficiency dropped quite dramatically and they were much harder to dissolve. What I did find, that was very interesting was that C8 was actually very effective both at being able to be formed into a solution and in preventing corrosion. So I have some iron coupons which were tested in an experiment, which have now been exposed to about 12 years in standard museum conditions and in fact haven't corroded in any way. So may I suggest as well C8 as worth looking at as a possible avenue? It was probably the only one of the carboxylates which seemed to remain stable for any length of time.

Alice Elia: Ok, thank you.

Peter Northover: Just curiosity – were you using absolute ethanol? Because as soon as you expose that to the air it is going to pick up water. Does the fact that you have a little bit of water in your ethanol solution of your acid make much difference? If you have pure ethanol you can't keep water out of it unless you are in a sealed container.

Alice Elia: Yes, this is true. It is a problem. But there is nothing we can do about it in fact. Even using isopropanol some water from the air will always come.

Peter Northover: And do you think the water made much difference?

Alice Elia: We stopped using water because we wanted to use longer chains. So it was not really no water at all because we do not want to have water on our samples and also because we wanted to try other compounds.

Coatings And Corrosion Inhibition

Chair: David Thickett
Panelists: David Hallam, Johanna Wolfram, Alice Paterakis, Guillaume Rapp, Alice Elia

Vasilike Argyropoulos: Well I would just like to commend all the speakers it was a very interesting session. It was interesting to see researchers who are either doing their masters or PhD thesis present their work and that there is this type of research going on and that many young faces are doing this kind of research, so I commend you, congratulations. It was interesting to see what impact Poligen had at the Metal 2007 conference and a lot of people picked up doing research, continuing the research for the Poligen. And I guess my question is and maybe we need to discuss this, is why, if Paraloid is so great and conservators love it and Incralac and everything, why is everybody jumping to look at these new products, and is it because there is a need for it, is it because we want to have more things to try and see if we can improve it? Because if Paraloid B-72 and Incralac is doing such a great job, why look at it? I am sure it is not just to do research projects, you know there are a lot of topics out there, so I just guess I want to ask the people in the audience who use these products, you know, why are we interested in looking at these new coatings that are on the market? Question?

David Hallam: I think we are interested in looking at new coatings because the old ones don’t fulfill the needs we require. Many of the old ones work wonderfully in what I would call your standard museum environment, but if you look at the storage tunnels in a mountain in Switzerland, that’s not your standard museum environment, with an RH of what was it, 85%? So, we’re searching for things that work better and we’re also searching for things that are re-treatable. Maintenance.

Vasilike Argyropoulos: I understand for the outdoor environment, but I think what I want from the audience maybe, or maybe from the panel, for the indoor environment in the museum, are we happy with Paraloid B-72 and Incralac, is it enough? I mean Alice, you are a perfect example, you have been working so many years in a museum, because if you talk to conservators in Greece they love Incralac on bronze objects, they swear by it. So, it’s just a question I have.

Alice Paterakis: Well, B-72 is problematic for collections that are stored in high temperatures, so in Turkey and Greece in uncontrolled conditions in the summer you can’t use B-72 because the glass transition temperature is 40 degrees Celsius, whereas I realize Incralac has a higher transition temperature than that. But that’s one of my primary reasons for testing Poligen, I am looking for something that’s as good or better than B-72 and has a much higher melting point.

David Thickett: One thing that I have seen a lot is objects that have been treated by particularly Incralac, and then have gone on to re-corrode. And I think that one thing that we don’t do enough of as a profession is to go back and assess whether our treatments have worked in the longer term.

Robert van Langh: I actually agree with Bessie what she is saying on this and as a field I really think that we should get really much more focused as to what kind of questions do we have in what field because the example that David refers to is more, I would say metal BIGSTUFF, you know or a different field, and I know David that you’re saying that’s not true. I actually think, well it depends apparently as well as to which conference we are talking about, you know because at Metal 2007 it was different than Metal 2010. So I don’t know where we are going to go on Metal 2013 or 16. I just think that it is really necessary to ask ourselves the question what are the real problems that need attention, which focus should we have in which field and what kind of research is really necessary that we should be looking at and addressing in the coming years, so therefore, yes, I completely agree with you. I mean are those the problems that we have right now? For instance in the majority of the museums that you know are represented, or that we perhaps represent and that’s just museums in the cultural heritage field. And then of objects, tangible objects, is that the right well the correct answer, or the correct, how do you say that, approach to it, because I would look at those, I would distinguish those things between something that you can have in your hand and something that is a locomotive or anything like that. Those are two different approaches, completely different approaches and I am willing to put in the stick you know and let’s go and fight about it, disagree about these things and have discussions about it, that’s what I intend to do with this thing.

David Thickett: I think the other thing is that there are also large numbers of small objects in very aggressive environments. Within the UK over 50% of museums are in historic buildings and they are generally not well-maintained museum environments and that’s why...I mean personally, for a while with my work at English Heritage, and we have some appalling environments, we have environments where 85% would be a very good day, you know, I know that we need better coatings than the ones that we already have.

Robert van Langh: Ok but David, I really disagree with you. If you think from a museum point of view there we have already 10 years ago in the Netherlands we said, we have an A, B, C or D collection. A means that it’s really the core business of your museum, B is ok, is really related closely related to…

David Thickett: Is this its significance?

Robert van Langh: Well it's like the significance for the museum, so and D finally, you say, hey get rid of it. We don't have to conserve everything, we have to make choices. So we can say oh, we have a really big problem that we cannot answer within the collection, within D, but is that really a problem?

David Thickett: But some of the material that we have is A, I mean we are talking of you know paintings like Rembrandt in these collections, we are not just talking….

Robert van Langh: Of course….no, no, no, no, and I agree with that and definitely yes that it true but I also think…I also think that we have to take into consideration the significance of the objects that we have, what they represent in the cultural heritage field and therefore what kind of research is needed for what kind of objects. That's the kind of questions that I would like to ask.

And everyone agrees, apparently? I love it, I can sing as well! Any comments on that?

Guillaume Rapp: Not probably on what you say but at least until now we have a problem in Thune with our objects that are military objects, metal objects that for strategic reasons most of them are covered with paint layers. And, it's funny but military paint layers are very, very sensitive to organic volatile components, to very basic solutions and so on. This is why in our project we couldn't take account for instance for Cosmoloid in white spirits, it was not possible because we had whitening of the paints, and this maybe (inaudible)..and also on the most important pieces of the collection and also the least relevant ones.

Karen Stemann Peterson: I agree with David that a lot of important items especially iron objects need coatings that are more protective than Incralac and Paraloid B-72. They tend to not protect enough for some of the storage areas that we can give them and also some of the exhibition areas and it is useful that other products are tested and hopefully some that are not too poisonous to apply and remove again.

I had a question for the former speaker, because I saw those steel panels with corrosion on. You removed just the top of the corrosion mechanically before coating and, well in corrosion science of course opening up areas of… corroded areas that starts, initiates, new corrosion so you start by just giving oxygen access and then do your tests. I was wondering…old-fashioned material as tannin, treating objects with tannin maybe as a pre-treatment for giving good coatings on steel and iron, I don't know if anybody has thought of that going back to tannin. Of course you can remove the loose tannin so you just get a slight darkening of the surface.

David Hallam: Tannates are wonderful in boilers is my feeling. I agree with Robert about the use of significance as a treatment protocol and treatment pre-curser, but I don't agree with what I would consider a very narrow definition of what a museum and historical collection is. I actually think as conservators we should be looking far more towards the commercial world and looking at what commercial….I mean there are some stunning corrosion inhibitors out there and some stunning coatings. Sorry guys we just need to find them and test them.

Ian MacLeod: It's really more of an observation on several of the papers that have been recently presented this afternoon, and I use the words of Neil North the former head of conservation at the Western Australia Museum, and he went on to be very successful and made millions of dollars - corrosion consultant – and he said in all the court cases he went to, 98 – 98.5% of the failures were due to poor surface preparation or failure of the applicator to put on a sufficient thickness of the coating, and it was only in about 1-1.5% [of cases] was the failure due to the actual coating. And I think because of the variability of the results that people have been getting of say comparing one coating with another and getting different results, what you need to do is the ICOM-CC Metals Working Group probably needs to go and define for the next triennium what standards you will be using when testing coatings on artifacts so that next time or in 6 years time when we are having another conference, we will have all of the results and we will know what the film thicknesses were, what the drying times were etc, because clearly films take a long time to mature and if you test something that isn't fully dried out you are really condemning it to an early death, that's all.

David Hallam: Along that line, what I will do is set up on the forum on the ICOM-CC website, a discussion on this, and I invite you all to join it. If you don't we will, we will, progress things that way.

Robert van Langh: David I want to respond to that I mean we don't need a forum we need research by any kind of bright student who actually says well these are the possibilities, these are ways that you can approach this, and this is what we will choose and present it for the next conference, and then you can agree or disagree with that and then you can say yes we should or we should not be doing it like that, but if we make it into a forum discussion then we are not going to get any further.

David Hallam: No, if we do it in a controlled manner I think we can. And if you have a research student who would be willing to do that then great, fine, as well.

Robert van Langh: Well, that would be my question, are professors here now present saying yes, that that is something that I would like to do? And that is something that…this is how we can go further, I am sorry, I am perhaps too pragmatic in these things but you know.

David Hallam: No, but also I think we do actually need to use ICOM–CC website forum as a place for technical discussion. So, lets try and progress that to see if we can do it too.

David Thickett: I think maybe what we should do is use both because it would be great to have somebody pull all of this together but there are a hell of a lot of expertise in this room and it's going to be difficult for those people to find particular publications. Alice has mentioned lots of ASTM standards, there are DIN standards, and there are probably lots of other standards and working protocols that people use. As a group maybe we can pull those together and help that person significantly.

Paul Mardikian: I feel that we are being too wide in scope because the variety of artifacts we have is much wider than what we are describing now with B-72 or wax, the problems are much wider. First of all we need to differentiate the materials, you cannot put in the same bag copper based materials or iron based materials, you cannot put in the same bag artifacts coming from a terrestrial site, artifacts coming from a marine site. The alterations are very different, the problems are different and the problems can be three-dimensional. I mean in marine conservation we do not have a coating problem we have an impregnation problem and you can have several centimeters of the corrosion products that you're trying to preserve in place that you have to isolate from the environment. So those things are very, very wide and each application is different. The use of decanoic acid is possible on a surface that is in relatively good shape, the use of a tannin is possible if you have a surface that is still metallic. If you are dealing with something that has several centimeters of corrosion, those things cannot be applied unless you dip them into solution and you impregnate them. So, we need to be very clear in what we are discussing right now and try to pinpoint the problems of the copper alloys, the problems of the iron artifacts, and always make a differentiation between what is indoors and what is outdoors, because very often we mix everything together and we end up by being all confused. I would never use B-72, I'm sorry, on an outdoor iron object, I would use wax probably, so we need to be clearer because we are creating confusion right here.

Arlen Heginbotham: I think another thing that came to my mind was the importance of, more specifically, coating methods and one of the things that occurs to me is that it may be valuable during the point at which a research program is being designed that a very in-depth discussion with very experienced practitioners might be very valuable so that the application is done in a way that is consistent with the way that it would be done by somebody with a great deal of experience working with it, and I guess beyond just coating methods too, I think that it could be valuable for experimental designs to be reviewed more regularly by people who use the materials in question in the field who have been using them over a period of decades.

David Thickett: I think there is no doubt that by far the best way to do this research is collaboratively between a scientist or a team of scientists, conservator or team of conservators to pull both of those expertise together.

Vasilike Argyropoulos: I just want to say when we started working on the PROMET project we did have experienced people who write standards for ISO and do coating testing for outdoor bronzes and have done many European projects, so there was a lot of discussion on what to do and what standards to use and so we spent a lot of time [on that]. But I want to go back to the issue of standards and how ICOM-CC can help because many of you know about the CEN/TC 346 in Europe for the conservation of cultural property. We have 5 working groups and we are trying to write standards for methods of testing materials, diagnosis of materials, terminology. ICOM-CC has already asked for official collaboration with CEN/TC 346 for terminology and we could do something more with metals. I should say that I am the convener of working group 2 which is on materials constituting cultural property, and I am disappointed to say that we have very few metal experts and I am tired of going to meetings and talking about you know standards and writing standards for mortars, for marbles. The monument people they're very organized and they're there, you're not getting paid for it, and they are creating standards for conservation of cultural heritage. And the question I have to all of us is if we see that there is a need for it, so we have to, more than a forum, we have to start getting together to talk about, ok, let's start out using the same methods so that we can compare our results to Australia, to Greece, and see if they are reproducible. You know I have a lot of questions about the reproducibility of the results based on some of the methods that were used, and so I don't necessarily believe them you know, so I think it is an important issue and how can ICOM-CC working group in metals help this need of standards in the field and how can we collaborate together and how can we get you to join forces with CEN/TC 346 to create standards in Europe?

David Thickett: Bessie, can I just ask - your discussions are very valuable, with the stuff I've read that has come out of PROMET that doesn't appear to have been captured, the discussions about what methods to use, what coupons. Is that available in any way, or could that be made available in any way?

Vasilike Argyropoulos: You know Christian was the work package leader of this and you know we…when you are doing European projects it's crazy as you all know because you have a set of deliverables that you have to get in with a certain timeframe so that you get the money in the end, and you're meeting with a lot of experts and you know, I guess how the discussions went is we talked about what standards were being used with outdoor bronze monuments based on other standards, ISO standards, and then they discussed what would be the base case scenario for what we wanted with these coupons. Was it the best methodology? No. Did we make mistakes? Yes and this is why I have a poster to go back and reflect on the thousands of analysis that we did with reflectance FTIR because we didn't have time to do basic research to look at film thickness to be able to interpret our results on real coupons. We have at least 5 papers that we still have to write on the PROMET results, and there's so much research to be done, but it's a matter of time and money. But you know and so….

Andrew Lins: I did want to just follow up a little on what David commented on about information and technology transfer. It's apparent in the coating industry that fluorocarbon coatings can last easily 40 years if properly applied there is no question of it. The question is, how do you transfer that - a reversible system that can be used in conservation, and we are looking at that, we are looking at it both from a point of view of clear coats as well as pigmented coats. And I will say that the technology transfer is not obvious and easy as there are very different systems involved from what we are normally used to.

David Watkinson: It's good to hear about trying to get something, as Bessie was talking about just then, to compare the materials to begin with, but in a way that's the first stage, it's the first really important stage. But then it's about how you use them in practice in the field because people interpret things in different ways and you have to dot the 'i's and cross the 't's for how you apply these materials to surfaces. I mean in conservation, I think conservator's are notorious, maybe not the best choice of words, but notorious, for actually reading case histories and at the end it just has some throw away comments about 2 coats of B-72 were applied to the object and if you are lucky you will say in acetone and it will tell you its 20%. Now we had a student who ran a project and what they did was they gave minimum information to a group of 10 colleagues of applying coatings in what would appear a similar way, and when you interpret it, it's completely different because people actually apply four coats to let it dry they apply the next coat 20 minutes later, someone else applies it 24 hours later and so you get a completely different pattern and they perform differently because accelerated corrosion on those produced a different result. In talking about this with Brita during the coffee break and she brought a really important point up, is that very often conservators, whether we like it or not, when they apply things to surfaces, they're thinking about what it looks like on the surface as much as whether they are getting this even coat that produces a protective layer, and that's within the mind, and that has been mentioned several times about shine and darkening on surfaces, so its something that is quite important to consider beyond that or at least build it into the testing phase and I don't know if anyone has any comments on that. One thing for Alice, we actually did have a student who did look at Paraloid in terms of temperature, she had a paper recently at the British Museum in the SEM conference there, and we found incorporation of particles at 35 degrees in the surface, it started as low as that so… thank you.

Peter Northover: I really wanted to sort of look at the converse, in that in Europe with excavation companies, what is in their stores, what has Landesamt in Germany have to deal with, there is a huge amount of metalwork we don't have the resources to treat. Initially for archaeology it needs to be preserved long enough so that we can extract the maximum of information both in archaeological terms and in metallurgical terms and maybe the thousands of samples preserved in my office may, in some cases, be all that survives in the end from some objects, and coming towards retirement their disposition is an issue but we need to have sensible ways of deciding what not to treat or how long things will last without treating, but you know, concentrate on the preservation of the information as well as the shape and the appearance of an object - and we need standards there too.

Nicole Ebinger-Rist: We have to think that all of the coatings are temporary, so if you have to deal with thousands of objects, we have about 16 tons of objects we have to deal with, we have the responsibility for, so we need more research and we have to put all the different themes together because we must go further in our research because we need solutions not only for four years or ten years because it's like a boomerang effect - we don't see the objects only one time, we see them very often because ten years goes very fast. So, we have to think about more research with coatings it's very important for us because when we have individual objects we always come back to oh, we have Paraloid B-72 and this is not satisfying for us to have individual objects and to work always with the same coatings so….

David Thickett: Yes I suppose the nightmare scenario is that Rohm and Haas decide that Paraloid B-72 is no longer commercially useful and we no longer have it, imagine where we'd be then!

David Hallam: It's pretty obvious to me that we need to do something about standards and standards of testing, so I would be interested in getting together a list of people who would like to pursue that and maybe we can form a, you know, make that as a sub project backed by ICOM-CC MWG. So, those who are interested pin me to the ground I think lunchtime…no….tomorrow evening it might be. Let's sit down and eat something and talk about it, ok?

David Thickett: (responding to question from someone not at the microphone) Bessie is by far probably the best person to say - how far along is CEN/TC 346 with testing? I know where the preventive [working group] is. I am involved in that.

Vasilike Argyropoulos: We are talking about working group 3, CEN/TC 346 which started around 2000, it's a technical committee, CEN is the standardization of all of Europe and in order to become an expert you have to be appointed from your national standards body, so it would be I guess DIN in Germany, ELOT in Greece, and all the other standard bodies. You become an expert and there are conveners for each of these working groups and what you do is, you may have a standard, you may have a standard that we all believe should be used in the conservation of cultural property of metals let's say, but it needs to be changed slightly to accommodate our needs. So one country will put forward and recommend doing the standard and changing it and the members will vote on it as a pre-adoption. And then there is a call for experts and the experts come together at meetings usually twice a year to work on this draft standard and then it goes back to each mirror committee of each country, they vote on it, they make comments, they send it back and within a 3 year process it becomes a standard and the purpose is to sell them, that's the whole purpose, and so under working group 3 from what I understand because I am not a member of that working group, its mostly for marble, for stone and mortars. There isn't anything for metals and as I said, we are very poorly represented in my opinion in CEN/TC 346 unfortunately and yet we have one of the largest working groups in ICOM-CC, so I think that's unfortunate in my opinion.

Dave Krop: I think this is a really good discussion so far and I want to add some other thoughts similar to Paul. We are talking about standardization as a very good thing, and it is, is allows us to compare what we do in different areas of work from similar foundations, but I kind of agree with Paul with all of the variances in material. Paul said he wouldn't use B-72 where I might use it in a certain situation and so even in the same area we may disagree. What happens if standards are set and within the industry, say, ICOM-CC sets standards and I personally don't like using them and then my treatments fall outside of industry standards, how is that reflected upon, you know, its just…things are so different, we think of coatings as these magic things, you do your treatment, you zip it up in your coating and then if something happens 'oh, oh the coating failed'. Well, maybe its insufficient treatment as well I mean how do you even judge those kind of factors like pre-treatment things, during treatment, how that may affect the coating as opposed to 'standard'? I don't know….. brain dump right here.

David Thickett: I think one thing that's quite important to understand with the CEN standards [European Committee for Standardization] is they are primarily measurement standards; they are methods and ways to measure things. So within CEN you would say measure resistance polarization would be you use a particular cell, a particular thing it's not that you are saying B-72 is the material that you should be using on x, y, or z, its saying that B-72 has had its properties measured in this way and that way and that's a very common misconception about the CEN standard and the other thing is that CEN standards are guidelines, they're not binding legal standards.

Paul Mardikian: I would use B-72, I would, I love it but I would not use it to protect an exterior object that's the point. I think that Robert was saying that we need to define exactly what we are looking for – we have a problem, what is the problem, you need to identify a specific category of artifact and alteration. We have the case right now in the lab of objects made of cast iron that have several centimeters of graphitized layer that have been stabilized the best possible way but still those objects may be reactive and may need to be protected, and it's not a surface coating problem, it's an impregnation problem and it's true that we need to find products that are going to penetrate and seal off the reactive sites and provide a long-lasting protection to those artifacts indoors and the problem is that for many years wax has been used and wax is a wonderful product, but when it gets to removing it, it's a problem. So, for instance, Poligen could be an interesting product because you could then use Poligen to impregnate those objects while they are still wet and like Philippe was pointing out to me, yes, they have a slight higher pH, so, you know you could impregnate those objects and then let them dry and maybe it would work. That may be an alternative to the consolidation of objects from marine sites, you know we are looking at other ways to protect those objects right now and have a way to retreat those objects if need to be. So, those are real problems for us, I am giving you a practical case here.

David Thickett: I think almost all of the authors came up with a list of properties that they wanted for their coatings – I saw a very interesting approach that was developed a number of years ago by the V & A for textiles, totally different, but looking at adhesives, different adhesives for different uses, and what they did was get that list then rank the things, then ranked how important it was for that use. For your use, the penetration would be far more important than the surface film, and then they generated a matrix to say, with their testing, this product is the one that gives the best for that. That might be a useful tool.

Johanna Wolfram: I would like to say something to the standard because I think we still have all local problems, local environment, local objects, local labs, we have our own way to treat objects, our own equipment, so if you standardize all of the research you still cannot expect that if somebody says well this product is good that it is good in your lab, with your objects, so I mean it is all ideas we collect here and you have to try it at your home anyway, so…I am not sure if that will solve our problems we have.

David Thickett: We're only really standardizing the…or the only thing that we could even hope to standardize parts of are the laboratory testing regimes – actually developing that into use on objects is a whole different piece of work and a very large and long-term piece of work.

Tonny Beentjes: I should have mentioned this during the lecture on the waxes. If I could recall correctly that if you use sodium hydroxide on certain cast irons you can actually get stress corrosion. I don't know whether anybody else has experience with that? So it's just a word of caution, I don't think it's all types of cast iron but you have to be careful. It's a similar problem which you get on brass with ammonia, you can get also on cast iron.

Aaron Shugar: Two things: one, I want to bring us back to the fact that we are looking at metals not coatings. I know that coatings are used to protect the metals but we still have to understand the base material we are looking at. And number two, related to that, when you are making standards you are trying to reduce variability and the metals we look at are so variable, every one is different. One cast iron is different to another cast iron, so how do you deal with that situation? Something to think about at least.

Robert van Langh: Well I think it brings us back to the basis of everything, that each object is an object by itself, should be looked at, examined from that [point of view], meaning there is, there is no general rule and we all know that and that's what we teach our students who come into this field within conservation everywhere, so you have to look at each object you know at its own merits so there is no general rule for that. I mean, you must agree with that of course.

Aaron Shugar: This goes against what you were saying before about that some artifacts are disposable, and I don't agree with that, I think that you assess each artifact as it comes in to determine if it is treatable or not and make a decision based on that assessment.

Robert van Langh: My point is if you have various museums which have various collections so, one collection for a museum is of no interest whatsoever, but can be D collection in one museum and A collection in another museum, so that is my point for looking at these things. What happens if you don't look at these things like that? Well, the D collection does not get any attention whatsoever, and they are sort of saying there are no problems with it and they just discard it. So, I think you have to look at those problems and then really say what are we going to focus on, what is of interest and why is it of interest, and finally it all comes down to money, funding, the research that you have for that, do you get funding for that, yes or no. So we can decide as to what's important to our field but I think that we still have to look at the bigger picture and then realize what are we doing and why are we doing that, what is it based upon and I just think it is important to ask those kind of questions.

David Hallam: As I think somebody said before it all comes down to significance and significance varies from collection to collection, and there is a really good website in Australia that has a wonderful publication on significance on it which I have on my USB stick for anyone who wants, which goes through how to look at a collection and then how to use significance to assess what you do to it, whether you put it in the dumpster or whether you conserve it.

Gerhard Eggert: We have to focus, yes one should discuss significance, at the moment it is a very important, very important question. What I try to teach my students is if you focus on this object you're neglecting another one, so even if you don't want to speak of significance to make selections we do, so we have to deal with that. I think, I really think this is another question. I want to focus on the questions posted here which David put up, and yes, there is no one way of natural ageing, conditions are different, we have a lot of variance in the conditions, and we have definitely the problem of accelerated ageing – how does it really mimic what is happening to our things. So yes, standards are good we need standards to have reproducibility of what we are measuring, so scientists love standards, but conservators want solutions that work which is a different approach to that. I love standards but they should not just be one standard on how to test corrosion resistance of a coating or something, there should be, there must be a variability of all the different thing. I really love the Poligen project, they had a different way of assessing how much corrosion occurred, they tested electrochemically in sulfate solution with its SO_2 in the air, so there were slightly different approaches, and we do know with accelerated ageing what is important and what not. So a different kind of experiment on the same thing could have other results, so what is important is trying different methods and see if we come to a common result. Yes at the end it's very difficult, every object is different, but up to now we treat everything with Paraloid B-72 - could that be ok? I don't think so.

David Thickett: No and I think with the variability of objects we have, to say that we have two coatings is quite a… not a good situation to be in.

Eric Nordgren: Just a comment really, or maybe a question, but it seems that in several of the papers here and many others that I've seen where they are talking about things like accelerated ageing tests, they are actually referring back to known standards such as ASTM, so the utility of that I think is pretty clear because it's something you can refer to and know how that was done. I think that's really useful and maybe we can build on that with some agreed standards on what we are talking about with coatings and then use those or refer to them so we speak the same language. But that doesn't mean that we have to have a very narrowly defined idea of, you know, conditions and artifact types, and so I think they can still be useful and still allow for flexibility with different collections, different situations.

CORROSION AND DETERIORATION STUDIES

Session Chair: Alice Boccia Paterakis

CORROSION EVALUATION OF GHIBERTI'S "PORTA DEL PARADISO" IN THREE DISPLAY ENVIRONMENTS

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Abstract

The 'Porta del Paradiso' by Lorenzo Ghiberti, also known as the 'Gates of Paradise', will soon be unveiled to the public after undergoing lengthy conservation. This project is at the stage where it is necessary to define environmental criteria for the long-term display of the doors. In this paper, three possible methodologies for display of the doors are considered: a showcase purged with nitrogen; a showcase with low, controlled relative humidity; an open showcase with a controlled microclimate. Galvanic sensors were used inside the cases to continuously monitor the macrocouple current of the doors and establish which case provided the most stable environment for display. Results to date indicate that the showcase with low, controlled humidity may offer the best solution for long-term display of the doors.

Keywords: Gilded bronze, galvanic sensor, Lorenzo Ghiberti, Porta del Paradiso, monitoring, corrosion rate, macrocouple current.

Introduction

The *Porta del Paradiso,* considered a masterpiece of the early Renaissance, are gilded bronze doors made by Lorenzo Ghiberti between 1425 and 1452 for the eastern portal of the Baptistery of San Giovanni in Florence, Italy. The doors consist of 10 panels, 24 friezes and 24 medallions cast in mercury gilded bronze. A scheme of the doors is reported in Figure 1.

Following the flood that devastated Florence in 1966, the doors were removed from the Baptistery and have been the subject of numerous technical investigations and extensive conservation treatments. These investigations have focused on trying to accurately record the condition of the doors, the techniques of manufacture, and on the choice of the most appropriate cleaning procedures (Alessandrini et al. 1979, Siano et al. 2001, Matteini et al. 2003, Ferretti et al. 2008, Fiorentino et al. 2008).

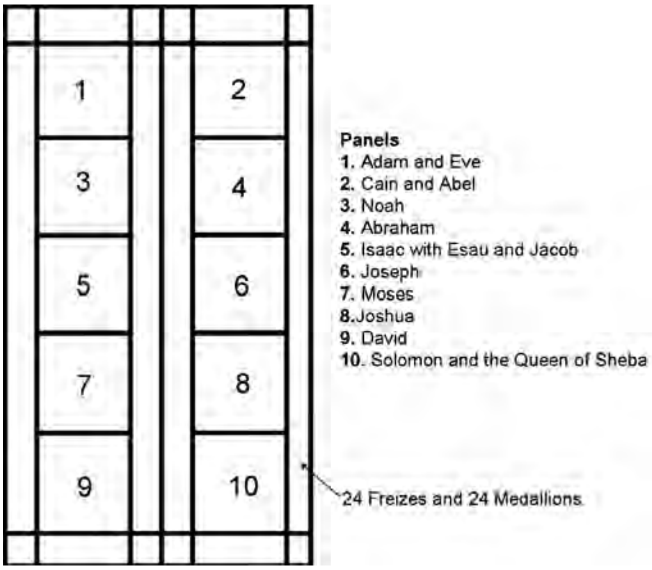

Figure 1. Schematic representation of the Porta del Paradiso by Lorenzo Ghiberti.

The conservation of gilded bronze is an extremely complex subject. Unstable corrosion products can develop between the metal surface and the gilding, and can comprise compounds such as copper chlorides that cannot be completely removed without damage to the gilding. In addition, the situation is made worse by the galvanic coupling between gold and bronze, which accelerates the corrosion processes.

For the Porta del Paradiso, two different cleaning methodologies were used to remove the thick encrustation from the gilded surface of the doors: 1) immersion in a Rochelle salt solution followed by rinsing with distilled water and acetone and/or 2) Nd:YAG laser cleaning (Siano et al. 2001). Despite the careful and meticulous restoration, it was impossible to eliminate all the corrosion products that formed over 500 years underneath the gilding. The corrosion products underneath the gold leaf are still unstable and very sensitive to microclimatic fluctuations.

At the present time the doors are in the final stage of conservation and will soon be re-assembled and unveiled to the public at the Museo dell'Opera del Duomo, Florence. In order to choose the most suitable environment for long-term display, the Opificio delle Pietre Dure (OPD), the conservation institute in Florence where the doors are being treated, have begun a new phase of research to define a suitable long-term display environment for the doors. The display environment will serve two goals: to provide the best conditions for preservation of the doors, and provide an enjoyable viewing experience for the public. This phase, involving specialists from different Italian research institutions, will evaluate the following three display environment options:

1. a showcase purged with nitrogen,
2. a showcase with low, controlled relative humidity (RH) (between 15% and 20%),
3. an open showcase with controlled microclimate. In this option, a dynamic flux of air separates the space occupied by the door sections from the surrounding environment.

Of the two options that require a glass showcase, the nitrogen purged case is probably the best way to achieve a stable environment for the doors due to the complete removal of humidity and oxygen. On the other hand, it is more expensive and complicated option compared to a showcase that maintains a constant low RH level.

A case that maintains a low RH may be a better choice than absolutely dry conditions. On one hand, it is known that by lowering the RH, the rate of corrosion is reduced (Shreir 1994). On the other hand, RH that is too low may favour the dehydration of the patina, which may become brittle. Therefore, it is proposed that the best solution should be an environment with RH slightly below the threshold that inhibits corrosion of the metal substrate. Determining this RH threshold is one of the goals of this project.

Low RH can be achieved using dry air, obtained by means of a compressor connected to an appropriate dryer, without the anoxia risks associated with a nitrogen-purged case. However, the use of showcases significantly limits the public's enjoyment of the doors as they are viewed through glass. The open showcase with controlled microclimate should create the same local environmental conditions as the showcase with low RH, with the big advantage of avoiding a glass panel between the object and the visitor. However, the open showcase solution is not easy to achieve with respect to closed showcases (Maekawa 1998, Shiner 2007) due to significant technical difficulties, such as leakage and the related degree of insulation between the inner and the external environments.

In order to choose the most suitable display option for the doors, qualitative and quantitative data for each case was collected. Unfortunately, traditional electrochemical techniques used to gather quantitative data, such as Linear Polarisation Resistance (Rp) or Electrochemical Impedance Spectroscopy (EIS), cannot easily be applied to a bimetallic object like the doors. A promising alternative is the use of galvanic sensors (Mazza et al. 1977) simulating the doors and allowing the continuous monitoring of macrocouple current that is directly proportional to corrosion rate.

This paper reports the preliminary results from the monitoring of the macrocouple current from galvanic sensors that were placed alongside three sections from the doors in the three display environments described above. The three sections of the doors included in this study are two friezes and one door panel (described below). It also briefly describes the results of the surface examination that was undertaken with micro-Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) prior to placement of the door sections in their respective test environments.

Materials and Methods

The three sections from the *Porta del Paradiso* that were chosen for this research are shown in Figure 2. These sections are:

4. Elia's frieze (frieze number XV), shown in Figures 2a and 3a, was placed in the showcase with low and controlled RH;
5. Miriam's frieze (frieze number XIX), shown in Figures 2b and 3b, was placed in the showcase purged with nitrogen;
6. Noah's panel, (panel number 3), shown in Figures 2c and 3c, was placed in the open showcase.

Before the three sections from the doors were placed

Figure 2. The three sections of the Porta del Paradiso chosen for this study: (a) Elia's frieze (XV), (b) Miriam's frieze (XIX) and (C) Noah's panel.

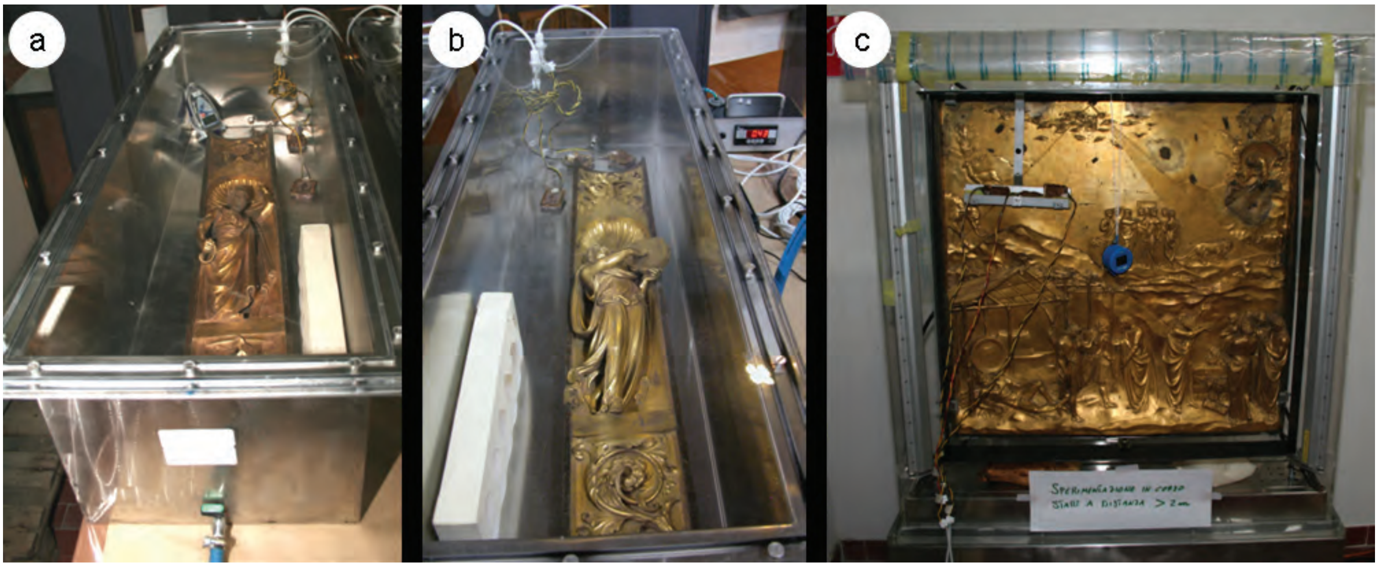

Figure 3. Display case options: (a) the showcase with *low and controlled relative humidity*, (b) the showcase *saturated with nitrogen* and (c) the open showcase *with controlled microclimate*.

in the showcases, their surfaces were characterised by photographic documentation (macro and stereomicroscope), μ-FTIR, SEM-EDS and color measurements to obtain a record of the surface condition at the commencement of the test period (see Figure 4). The results of the preliminary characterisation are briefly summarised below. The analyses will be repeated at the end of the test period and the results compared to confirm whether changes, for example, growth of new corrosion products over the gilding, have occurred to the metal surface during placement in the test environments. Results will be described in detail in a future publication, once the test period is complete.

The surfaces of the two friezes are different, despite their common past conservation history. Corrosion products are visible in several areas on Elia's frieze (see Figure 2a and 4a), which appears to be the less stable than

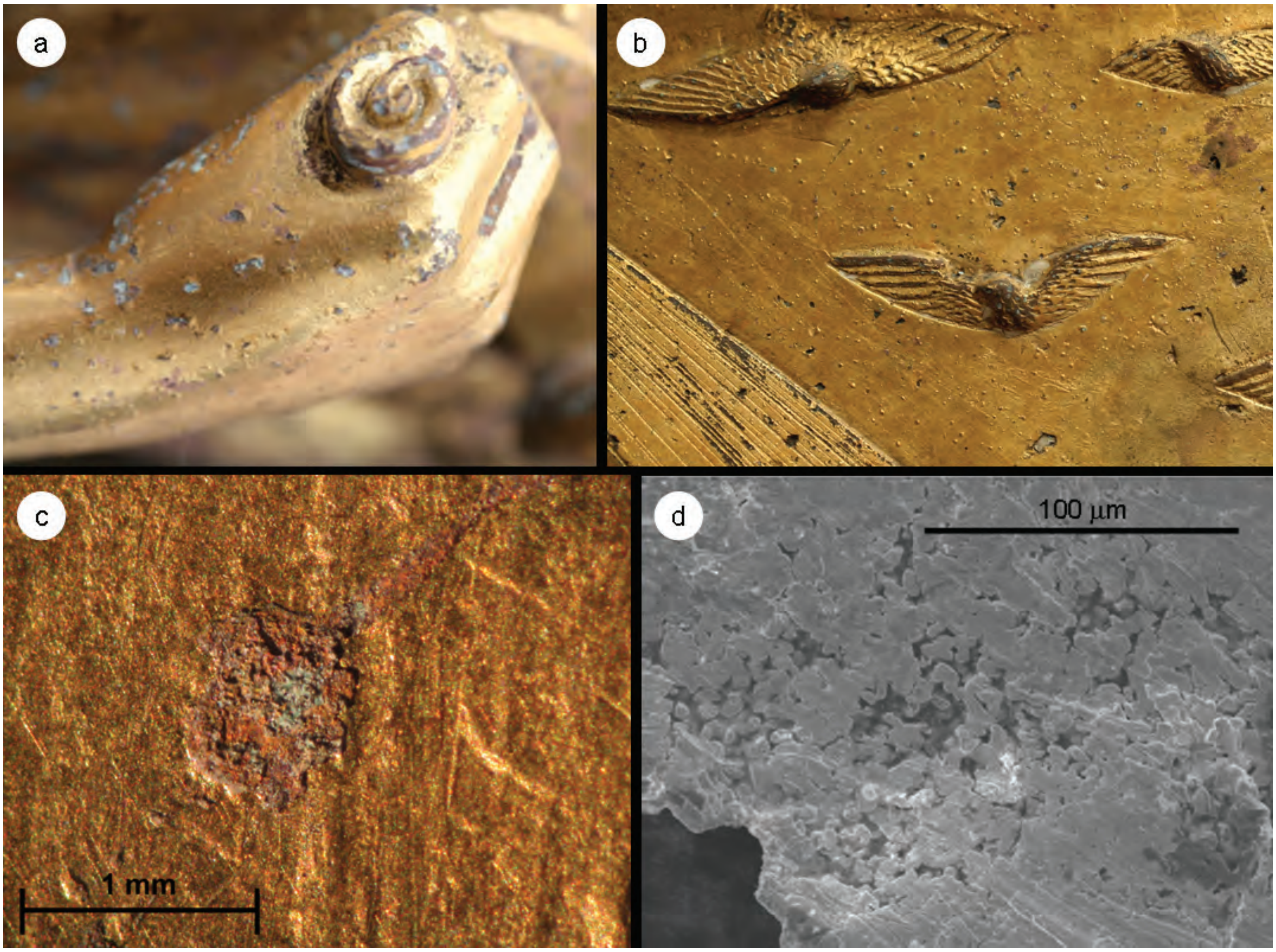

Figure 4. (a) Detail of Elia's frieze (b) Detail of Noah's panel (c) Microscopic image of a corrosion pustule (d) SEM image of the gilded surface.

Miriam's frieze (see Figure 2b), as corroded areas are less frequent over the latter frieze. µ-FTIR and SEM-EDS analyses results revealed the typical residual porosity of mercury gilding (see Figure 4d) and a patina of corrosion products mostly composed of cuprite (Cu_2O), a copper oxide; atachamite, $Cu_2(OH)_3Cl$, a hydroxychloride; as well as antlerite, $Cu_3SO_4(OH)_4$ and brochantite, ($Cu_4SO_4(OH)_6$, both hydroxysulphates. Results from analysis of the surface of Noah's panel revealed micro-blistering of the gilded surface (see Figure 4b), as well as minor pitting and extrusion of green corrosion products through the gilding. These minerals were also identified as copper hydroxychlorides and hydroxysulphates mixed with cuprite and tin oxides.

Display Environment Options

Due to the complex technology required to set up the open showcase with controlled microclimate, experimentation with the nitrogen-purged and the low RH showcases began earlier (July 2009) than that of the open showcase (September 2009). For technical reasons, it was not possible to start the planned conditioning of the two showcases at the same time as the two friezes were placed in the cases. In the meantime, low RH (below 20%) was achieved by the use of conditioned silica gel. Monitoring of thermo-hygrometric conditions in the cases was carried out with wireless data loggers placed close to the friezes, with data recorded every 30 minutes.

The volume of the two closed showcases is approximately 80 litres, they are constructed from stainless steel with Plexiglas lids and are fitted with two taps for the introduction and discharge of gases. The nitrogen showcase was saturated by fluxing (3 liters/minute) with pure nitrogen for approximately two hours. The complete removal of oxygen was verified by an oxygen sensor connected to the discharge tap. A box of moisture absorbers calibrated to 0% RH was also introduced into the showcase to keep the RH low at all times.

In the showcase with low RH, RH of approximately 20% is kept constant as follows: a) before being introduced inside the showcase, the dry air hose is split into two lines. One air line (5 liters/minute) is forced through a water bubbler to make the air humid. The two air lines are then re-joined in an airtight chamber equipped with RH/T sensor; b) two fluxmeters adjust the proportions of dry/humid air to obtain the desired conditions. A box of humidity absorbers calibrated to 20% RH is present in the showcase.

The open showcase has the shape of a parallelepiped, and is 102×102×21.5 cm^3 (H×W×D) in size. The central area, 78×79 cm^2 (H×W), of its front surface is open, i.e. only a 10 cm wide passé partout is left. The door panel is placed in the center of the case. The case is designed so that a volume of dry air surrounds the panel at all times, without the need for a glass cover (see Figure 3c). The efficiency of the system was investigated with accurate profiles taken of temperature, air speed, RH and moisture content in front of the door panel. The RH is the most critical parameter for the panel, and is regulated by the air temperature and moisture content, expressed in terms of the Humidity Mixing Ratio. This ratio is the mixture of moisture and dry air, expressed as the ratio between the mass of moisture present in the air to the mass of dry air. The air speed and Mixing Ratio profiles (see Figures 5 and 6) show that the protective air layer is 20 cm thick, but the Mixing Ratio profile shows that the airflow includes some 60% of ambient air. This reduces by 40% the ambient RH. The airflow profile, measured with a hot wire anemometer in front of the panel shows that the air speed ranges from 10 cm to 20 cm s^{-1}, and is of the same order of magnitude of the airflows, i.e. up- or downdraughts, that are naturally generated in a room for the small temperature differences generally existing between indoor air and walls (Camuffo 1998).

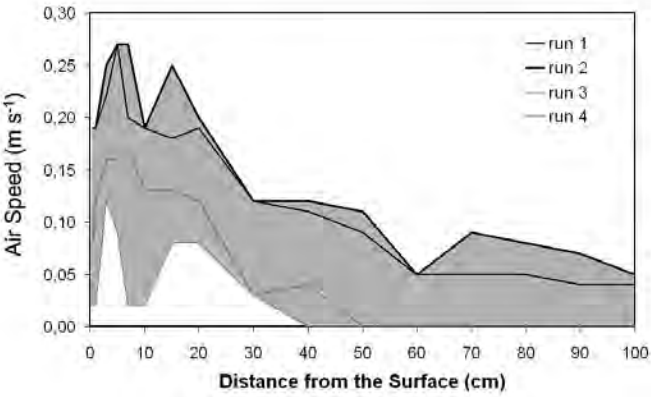

Figure 5. Air speed in front of the panel, at the center. The gray band indicates the range of fluctuations in air speed, and the internal lines the maximum (black) and minimum (gray) speeds at repeated profiles with higher or lower turbulence.

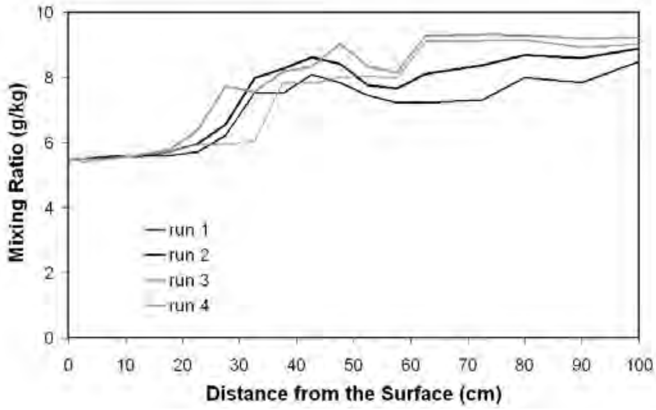

Figure 6. Humidity Mixing Ratio in front of the panel, at the center. Different lines indicate repeated mixing ratio profiles.

The temperature and RH variations for the different display environments are shown in Figure 7. The RH stabilised at around 7% in the nitrogen-purged case, and around 17% in the case with low RH. These results reveal that it was not possible to completely stabilise RH at a specific value in the open showcase. The RH oscillates in the range 16%-39%, but is considerably less than the ambient conditions in the surrounding environment (the laboratory), which remained in the range 40%-70%. The sudden increase of RH that occurred the Oct. 21, 2009 was due to a failure of the air compressor. The open showcase was readily sealed, the RH controlled by the use of silica gel, and the system reactivated on the Nov. 17, 2009. Subsequent, isolated increases of RH most probably have to be ascribed to temporary interruptions in electricity supply that caused temporary interruptions to the compressed air supply for this case.

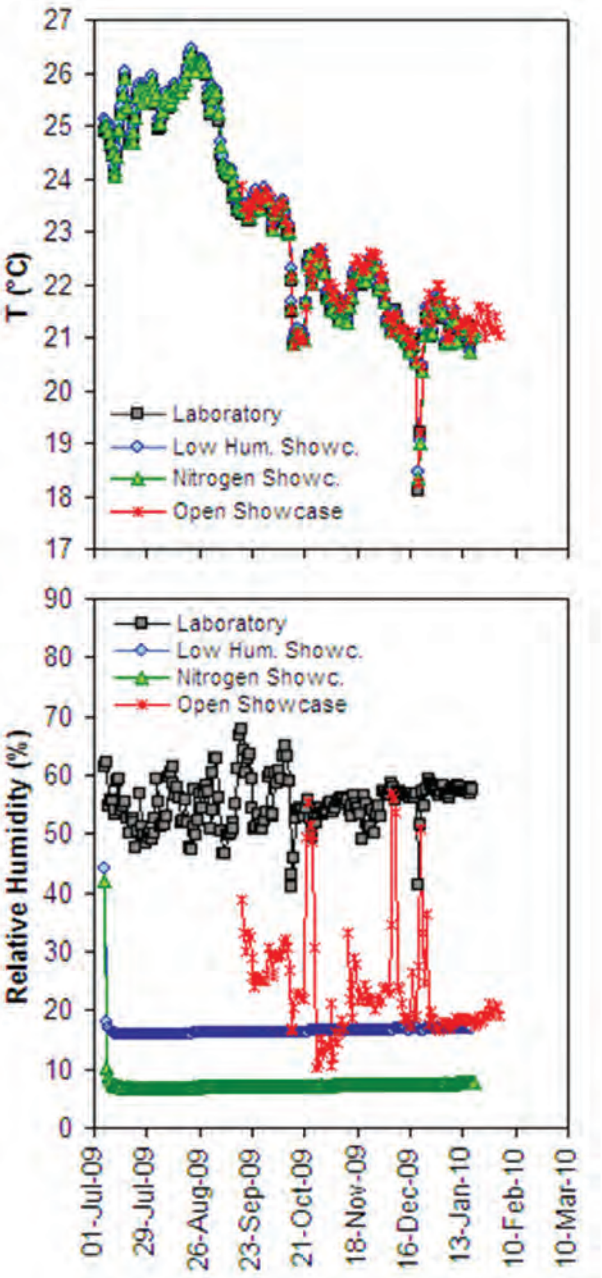

Figure 7. Temperature and relative humidity variations.

Galvanic Sensors

The galvanic sensors used in this study were acclimated to the partially controlled environment of the laboratory for at least two months before being placed in their test environment with one section of the doors. The laboratory has controlled temperature, but no control for RH. Some sensors were removed or changed during the experimentation. The two-month period of preconditioning in the laboratory was necessary for the stabilisation of the sensors and to acquire the average macrocouple current characteristic of each sensor. The sensors, shown in Figure 8, are 4x5x1 cm in size and simulate the most unstable areas of the doors. Three sensors were placed in each case. Three sensors were placed in each case and three additional sensors have remained exposed to uncontrolled laboratory conditions as a reference for the duration of the testing period.

The sensors are described as follows:

- They are a quaternary bronze alloy, with a composition similar to that of the doors (Cu 93,1%; Zn 3,2%; Sn 2,6%; Pb 1,1%) (Bernardini et al. 2000, Siano et al. 2001, Siano et al. 2006, Ferretti et al. 2008);
- They have an artificial patina of corrosion products, consisting of Nantokite ($CuCl$), Tolbachite ($CuCl_2$) and Chalcanthite ($CuSO_4*5H_2O$) in the following proportions 2:1:3. The high chloride content should make the sensors extremely unstable and reactive to humidity, simulating a heavily corroded bronze with unstable corrosion products, as is the case in some areas of the doors;
- They are gilded, obtained by sputtering;
- They each have electrical connections to the bronze substrate and to the gilding for the measurement of macrocouple current. Electrical connections were obtained by means of a conductive silver-based glue;
- Insulation on the sensors was applied in the form of an epoxy resin coating for the electrical connection to the bronze; the coating was also applied to four sides and the back of the sensor.

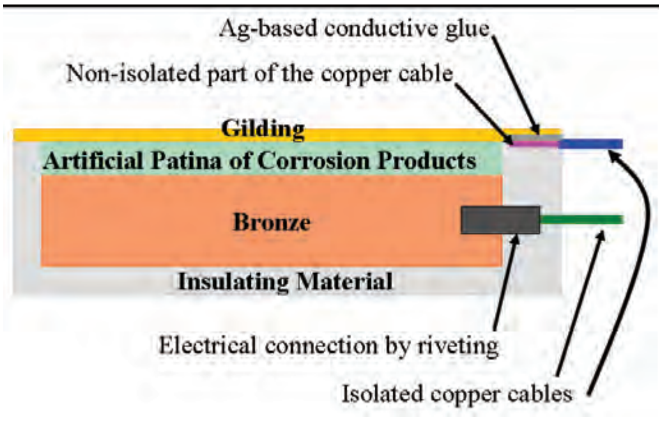

Figure 8. Galvanic sensor.

The best sensors available, characterised by the highest macrocouple current, were introduced inside the three cases. Three sensors were exposed in each case.

Results and Discussion

The macrocouple current, flowing between the gilding and the bronze, is directly correlated to corrosion rate and is continuously monitored by means of a high precision multimeter. Figures 9 and 10 report the macrocouple current recorded during the preconditioning of the sensors, before they were placed into the three cases.

During preconditioning, a high macrocouple current variability, which exceeds more than two orders of magnitude, was recorded, and this variability was interpreted in terms of indoor RH variability. Unfortunately, deterioration of the sensors led to a decrease of the average macrocouple current with exposure time. The most deteriorated sensors were periodically replaced by new ones. Faraday's law allows evaluation of the corrosion rate from macrocouple current density. For this study, the following assumptions were made: the bronze and the gilding have the same surface area, the cathodic process (oxygen reduction) occurs mainly over the gold surface and only the copper is oxidised ($Cu \rightarrow Cu^{2+} + 2e^{-}$).

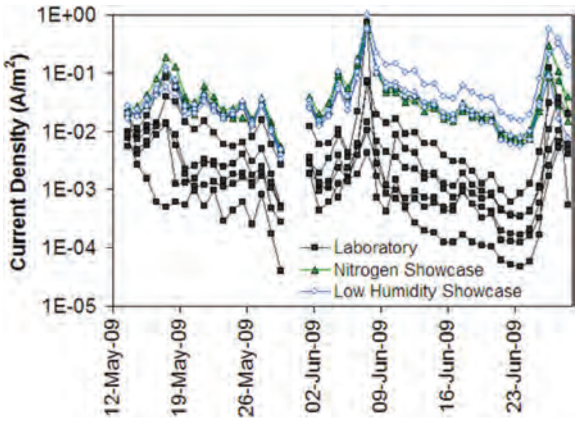

Figure 9. Average daily value of macrocouple current during the preconditioning time before the introduction of the sensors into the showcases: the triangle and circle indicate the sensors chosen for nitrogen and low humidity cases respectively.

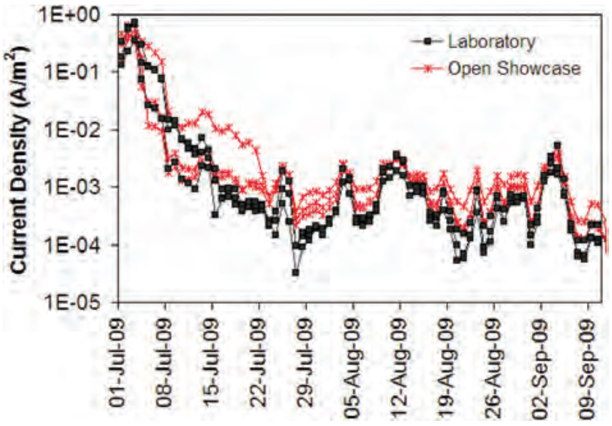

Figure 10. Average daily value of the macrocouple current during preconditioning before the introduction of the sensor into the open showcase; the asterisk indicates the chosen sensors.

As previously discussed, the sensors are designed to represent a gilded bronze with very unstable corrosion products underneath a layer of gilding; that may represent the most unstable parts of the doors. Data obtained from the sensors (see Figure 11) clearly show that any part of the door presenting these conditions could suffer quite high corrosion if subjected to insufficient environmental control, such as the conditions of our laboratory. The reported values are the daily averages among all the sensors that were exposed to the same conditions. The average corrosion rate during the preconditioning time in the laboratory was about 65 μm/y and 80 μm/y for the sensors that were then introduced into the nitrogen and low humidity showcases, respectively, with a peak of about 1 mm/y. The sensors that were placed in the open showcase were more deteriorated, possibly due to the longer preconditioning period. These sensors had a reduced capacity (more than 10 times) in their ability to supply macrocouple current compared to the sensors that were placed into the nitrogen-purged and the low RH cases.

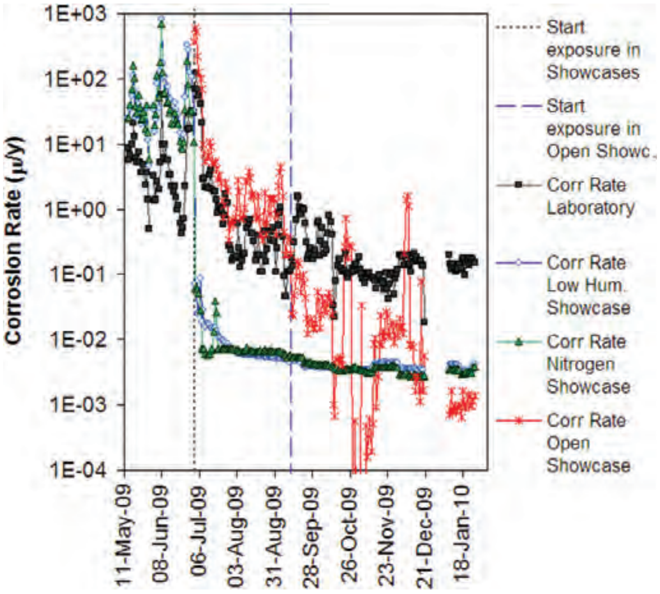

Figure 11. Corrosion rate for all tested conditions: Average daily values exposed under the same conditions. The moment of introduction of the sensors into the two closed showcases and into the open showcase is indicated by vertical dashed lines.

After the introduction of the sensors into the two closed showcases (see Figure 11), the corrosion rate was drastically reduced by more than three orders of magnitude. The effect was immediate for the nitrogen showcase. After one month, however, the two sets of sensors showed almost the same corrosion rate, which continuously decreased with time. After seven months the corrosion rate was about 4 nm/y.

After the introduction of the sensor into the open showcase (see Figures 11 and 12), the corrosion rate was reduced by more than one order of magnitude with an average value during the first 10 days of about 0.1 μm/y. The sudden increase in the corrosion rate on Oct. 21, 2009, is clearly associated with the compressor failure that exposed the sensors to the partially controlled laboratory environment. However, this incident revealed that the sensors respond quickly to RH variations. When the RH inside the open showcase reached values similar to those in the closed showcases, the corrosion rate reached very low values, similar or even lower than the sensors in the closed cases. It should be remembered that the sensors in the open showcase were more deteriorated and therefore supplied a reduced macrocouple current compared with that supplied by the sensors in the closed showcases.

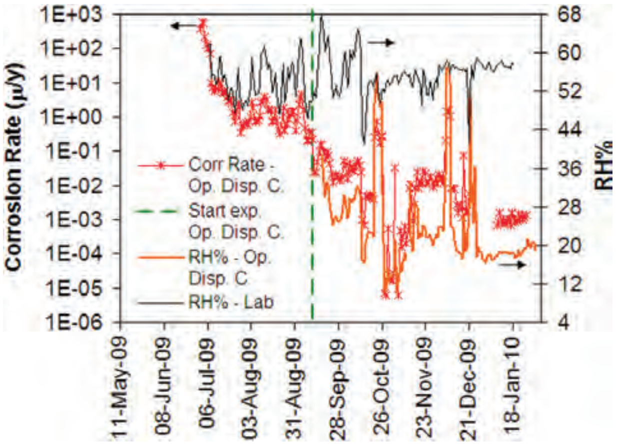

Figure 12. Corrosion rate and relative humidity for the open showcase: average daily values of all the sensors. The moment of introduction of the sensors into the open showcase is indicated by vertical dashed lines.

Conclusion

The research presented here is still ongoing at the time of writing. However, some preliminary conclusions can be drawn:

- Galvanic sensors proved to be a powerful tool for simulating and monitoring the corrosion rate of gilded bronzes. However, further improvements are necessary to obtain more reproducible, reliable and durable sensors.

- There appears no significant differences between displaying the Porta del Paradiso in a showcase saturated with nitrogen or in a showcase under low and controlled RH. However, unstable corrosion products are very sensitive to RH fluctuations, even when corrosion is negligible. Furthermore, very low levels of RH may favour the dehydration of the patina, causing embrittlement.

- The level of RH obtained in the open showcase significantly reduces the corrosion rate, even though it is definitely less efficient than the other two closed cases.

- It is proposed that an improved open showcase that guarantees a RH level below 20% could be as protective as the other two closed cases.

Further experiments are necessary in order to clearly identify the most appropriate RH level for gilded bronze with unstable corrosion products, as found on the Porta del Paradiso.

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Materials

Data loggers
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Tel. +39 059 653274
Fax +39 059 653282 - P.Iva 02309180368
www.giorgiobormac.com

Oxygen sensor: Mod. Mect,
Tirrenia s.r.l., Via Jacopo Ruffini, 2
16128 Genova, Italy
www.tirreniasrl.com

Moisture absorbers (0% and 20%)
Art Sorb, PHASE, Firenze,
Phase restauro srl
Sede legale Via Perugia, 10 - 20122 MILANO
www.phaseitalia.it

Dry air
Nitrogen: 99.99% nitrogen 5.0
Air 0, SAPIO, Arezzo
Sapio Srl
Località Poggio Bagnoli 52020 Pergine Valdarno (Arezzo)
www.grupposapio.it

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Q & A SESSION

Jean-Bernard Memet: Could you explain how you measure your current density, because as far as we know it is very difficult to measure current density in a galvanic cell without an electrolyte. You do not have any electrolyte in your cell, and I wanted to know more about that.

Sara Goidanich: The two metals are the bronze and the gilding and our electrolyte was the artificial patina. This was really a critical point, with setting up the sensors, because depending on the thickness and the composition of the patina, you would have different values of the current that we managed to collect. So if the patina is too thin, then we have short circuits between the gilding and the bronze and we lose some current. We know we have macro-couple currents, but the problem is to detect them. If the patina is too thick or too dry you cannot measure the current but because the patina contains hygroscopic compounds, which are never completely dry, we do get a measurable current. In the end it happens in real cases that we can measure a current but we cannot measure the corrosion because we have a direct connection between the gilding and the bronze, which normally short-circuits the current through the patina. In order to get a current there had to be no connection between the gilding and the bronze. The other was to optimize the thickness and composition of this patina to be able to measure it more readily. I don't think the values we get are the real corrosion rates because I know we lose some current, but the point is that I think the corrosion rate is at least the same value as the current we measure. It might be higher.

Jean-Bernard Memet: Ok, thank you, just another comment. You assume that the surface area of the gilding and the bronze is the same, but this is not the case. But you just have to say 'apparent surface' - because your surface area can vary from 1 to 2…

Sara Goidanich: Yes I think the gilded surface is 2 or 3 times that of the bronze, but the current density is the value you measure – but it is somehow difficult to show the entirety of the processes. So we choose to make some assumptions, but we have the order of magnitude of the thickness of how the corrosion penetrates.

Jean-Bernard Memet: Yes, and it is a relative study. Thank you.

Shelley Sturman: I commend you on this work. It is wonderful to see you doing this. I had a terrific opportunity a number of years ago to study these same door panels and what was most disheartening was to see that the panels that had already been treated and were already in nitrogen cases, were continuing to corrode. There were lots of green blisters all over them, and I was disappointed that people believed that the nitrogen cases were the way to go but they were leaking and they weren't able to stabilize the pieces. I am very happy to see that just controlling the relative humidity will work and am especially hoping to push forward the open showcase if you can do it. How are you controlling the RH%? Are you doing it simply by temperature, are you evacuating, are you on negative pressure – I'm not sure. I don't think you explained it…

Sara Goidanich: There are several reasons for why I didn't go into too much detail about that – first of all, time and secondly, I am not the one that set up these showcases. I can tell you what I have understood from interaction with the other colleagues: We have some air flow from the bottom so the case is closed from the sides with the exception of the front. We have a Passe-Partout around so just the surface is free from the glass and you have some dry air flowing from the bottom. As you see the problem is the mixing ratio so we still have 60 per cent of the air from the surrounding environment that is mixed with the air we are blowing in from the bottom. Sorry if you want more details you will have to contact the other colleagues.

Robert van Langh: I was wondering if you also considered an overpressure – a very low over-pressure of nitrogen? Is there also a possibility to create a controlled relative humidity with the overpressure of nitrogen?

Sara Goidanich: Yes, again you should talk to the other colleagues, but as far as I know, one of the concerns was to not create impressions on the surface because some parts are really unstable. So for instance the airflow that we are using is of the same order of magnitude as the normal airflow you would have in a room. So there is a lot of concern over what could happen to the surface. At least up to now they have not tried, but I am quite sure that Professor Camuffo, or Dr. Siano, or Dr. Mencaglia can provide you with the information but at the moment they are considering heating the airflow slightly by only a few centigrade…

Robert van Langh: Yes, I know and in the Army Museum in Delft, in the Netherlands, they have created showcases – large showcases – where they have a constant overflow or overpressure of the showcase – very minimal – just so that the air from the outside does not come inside and you simply have a continuous flow and that seems to work…

Sara Goidanich: Ok, I will refer that to the colleagues. If they were here, they would answer better than me…

PREDICTING THE CORROSION BEHAVIOUR OF OUTDOOR BRONZES: ASSESSMENT OF ARTIFICIALLY EXPOSED AND REAL OUTDOOR SAMPLES

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Abstract

This paper examines the effect of acid rain on sheltered and unsheltered areas of the patina of a quaternary bronze sculpture of King Louis XIV located in Versailles, France, as well as on artificially corroded G85 bronze coupons. The corrosion behaviour of the coupons was examined through wet-dry tests to simulate the stagnant and leaching rainfall conditions found on the sculpture. The results show that in sheltered conditions, the patina is a multi-layered system with an inner tin-enriched layer covered by copper and lead compounds. In runoff conditions, a tin-rich patina behaves as a thin porous layer allowing significant dissolution of the other alloying elements of the bronze. Therefore, properly aged surfaces, reflecting the complexity of real patinas, are needed for adequately testing corrosion inhibitors.

Keywords: atmospheric corrosion, quaternary bronze, rain, surface characterization, cross-section.

Introduction

Outdoor bronze monuments suffer diverse types of corrosion according to their exposure conditions (Robbiola 1991, Krätschmer 2002). Investigation of Cu-based alloys has been quite extensive. However, significant gaps in knowledge are encountered in practice. It is clearly acknowledged today that bronze alloys behave differently from copper alloys when exposed to rainwater, even if this point is not always taken into consideration (Robbiola 2008, Jouen 2008, Hertling 2008, Chiavari 2008).

The present study concerns the chemical and physical characterization of the patina formed in unsheltered and sheltered areas, taking into account the influence of the alloying elements in a Cu (Sn-Pb-Zn) quaternary bronze sculpture. A complementary approach was adopted in this study; the results obtained from an outdoor monument and on bronze specimens submitted to simulated laboratory conditions are compared. The sculpture that is the subject of this study is the outdoor equestrian statue of King Louis XIV (see Figure1a) at the Palace of Versailles, France. In addition to obtaining 10 samples from the patina, special authorization was granted to the authors to take one sample to prepare in cross-section consisting of the patina and the underlying alloy. While patina surface analyses from this sculpture have already been reported (Robbiola 2008), the investigation of the cross-section is discussed in this paper.

In particular, the influence of different exposure conditions, i.e. stagnant and leaching acid rains, are reproduced on bronze G85 coupons by using the following protocol: stagnant conditions, which simulate sheltered areas on the sculpture, are assessed by wet/dry test (WD), during which the coupon is cyclically immersed in stagnant artificial rain. Rainfall runoff conditions, simulating unsheltered areas on the sculpture, are assessed with the DROP test, during which artificial rain is periodically dripped onto the metal surface of the coupons. The evolution of the corrosion process is determined by monitoring, both the amount of dissolved metals and the bronze surfaces. Surface characterization was performed by X-ray diffraction (XRD), scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) coupled with in situ Raman spectroscopy. Full characterization of the patina, which is the support for the application of protective treatments, plays a key role in designing efficient conservation strategies. Based on this knowledge, pertinent ageing conditions can be determined and consequently representative patinas for testing protective coatings and corrosion inhibitors can be selected.

Figure 1. The statue of King Louis XIV at the Palace of Versailles, France (*bottom*). Detail of the unsheltered pale green sample area of the plume on the statue (*top*). The arrow indicates the sampling area.

Experimental methods

Materials

The sculpture that is the focus of this study and a reference for the laboratory tests on the bronze coupons is the famous equestrian bronze of King Louis XIV. The sculpture was cast around 1836 and is located in the main court of the Palace of Versailles, where it is fully exposed to an urban atmosphere. Different morphologies of decay, usually observed on outdoor copper alloy monuments, are in evidence on this sculpture (Robbiola 2008):

(i) A dark green patina with thick black deposits in areas of the sculpture that are partially or completely sheltered from rainfall;

(ii) Powdery pale green patinas with black islets in areas unsheltered from rainfall.

In addition, heavy green staining on the calcareous stone base, indicating leached green corrosion products, clearly shows evidence of the solubility of the current patina.

Samples of the patina were obtained by scraping the corroded surface in 10 areas on the plume of the hat (see Figure 1b) with a lancet. One sample was obtained from the unsheltered area of the plume with a jeweler's saw; this sample was prepared in cross-section. The cross-section (2 x 0.6 x 0.4 cm^3) was mechanically mounted with a clamp (without using any mounting resin). The bronze plume of King Louis XIV is a quaternary alloy (see Table 1) with a dendritic microstructure, containing a α-Cu matrix with tin (Sn) coring around the dendrites (see Figures 2 and 3a).

The bronze coupons used in the artificial exposure tests were 2.5 x 5 x 0.5 cm^3 in size, and are a sand cast quaternary bronze (G85/UNSC83600), with a composition that was determined by atomic absorption spectroscopy (AAS), and is reported in Table 1. The coupons have a microstructure comparable to that of the bronze plume from the sculpture (see Figure 3b).

To reproduce the average composition of natural rains, samples of rain were collected in Bologna,Italy, and used as a reference with the following composition: Cl^- (1.27mg/L), NO_3^-(4.64mg/L), NH_4^+(1.06mg/L), $SO_4^{=}$(1.9mg/L), $HCOO^-$(0.05mg/L), CH_3COO^-(0.23mg/L), Na^+(0.53mg/L), Ca^{2+}(0.34mg/L), pH = 4.25. Further detailed information on experimental procedures is given in Bernardi (2009).

Artificial exposure tests

The equipment used to perform the wet-dry tests consists of glass-jacketed cells kept at 25°C, with one sample vertically hung in each cell. The volume of the artificial acid rain solution was 300 ml per cell. Each wet-dry cycle consists of 20 minutes of wetting and 40 minutes of drying. Allowing a time of 20 minutes to dry the sample, a reasonable time of wetness (TOW) of 40 minutes can be assumed for each cycle. The weathering solutions were renewed every week, when they became neutral (pH~7).

Rainfall runoff conditions are simulated through a *dropping* device (DROP) where the artificial acid rain is periodically dropped onto the surface of the coupons at a 45°angle, then collected with no recirculation of the used solution. This set up is different from that reported in Bernardi (2009), where continuous runoff was applied during a period of 30 days. In the present study, a weekly cycle of two days dropping (~TOW) and five days drying was set, according to pluviometric data recorded in Bologna. In the WD and DROP tests, the metal concentrations (M=Cu, Sn, Pb, Zn) in the ageing solutions, i.e. the solutions to which the samples were exposed, ($m_{M,sol}$) were determined by AAS. To compare the results, the duration of both tests was set to 30 days of TOW.

Characterization

Compositional information and identification of crystalline phases of the corrosion samples obtained from the patina of the sculpture and from the artificially exposed samples were studied by XRD and by a combined EDS and Raman spectroscopy system integrated in a variable pressure scanning electron microscope (VP-SEM). This combined system allowed the full characterization of the sample cross-sections, by using confocal electron and laser beams (λ=514.5 nm) for acquiring sequential SEM images, EDS and Raman spectra from the same area (laser spot size < 2μm at Full Width Half Maximum, FWHM). More detailed information on this instrumentation is provided in Bernardi (2009).

Periodically, mass variation and mass loss measurements were performed. Mass losses (m_{tot}) of the exposed samples were measured after pickling the patina samples. This was achieved by washing in distilled water (1.75mL.cm^{-2}) for 30 seconds, immersion in HCl 20% v/v (5.3mL.cm^{-2}) for 1 minute, rinsing in water for 30 seconds. All steps were performed in an ultrasonic bath, at room temperature and repeated twice. The pickling solutions were collected and analysed by AAS to determine the amount of each metal M in the patina ($m_{M,cor}$).

In both the WD and DROP tests, the metal concentrations (M=Cu, Sn, Pb, Zn) in the ageing solutions ($m_{M,sol}$) were also determined by AAS. The total amount of each metal M transformed from its metallic state to a cation was evaluated as:

$$(1)\quad m_M = m_{M,\,sol} + m_{M,cor}$$

Roughness profiles were obtained for the coupons subjected to the DROP test, and were performed by stylus profilometry (tip radius: 5 µm) to measure the loss of thickness of the metal due to the corrosion process.

Corrosion rate and dissolution factor

The corrosion rate of each metal M of the alloy, $v_{M,cor}$, at time *t* is defined as:

$$(2)\quad v_{M,cor} = \frac{m_M}{A_{cor}\,t}$$

where A_{cor} is the corroded surface (cm^2). The corrosion rate of the alloy, v_{cor} (µm y^{-1}) is calculated from mass loss measurements (WD) or from thickness loss (DROP).

The tendency of each metal M to dissolve in the environment, or to remain in the patina, is expressed through the dissolution factor f_M as reported in Bernardi (2009):

$$(3)\quad f_M = \frac{m_{M,sol}}{m_M}$$

Results and Discussion

Natural exposure: sculpture of King Louis XIV

As reported in Table 1, EDS of scraped patina samples clearly showed differences in the elemental composition between the sampled patina on sheltered and unsheltered areas of the sculpture.

By comparison to the original alloy composition, a depletion of Cu and Zn is observed in both sheltered and unsheltered patinas. In contrast, Sn enrichment is markedly more pronounced in samples taken from the unsheltered patina of the sculpture.

It should also be noted that in the sheltered areas there was a greater level of environmental elements such as Al, Si, K, Mg, Ca and Cl, mainly related to aerosol deposits. The main corrosion products identified on samples from both sheltered and unsheltered areas were cuprous oxide, cassiterite, brochantite, posnjakite and antlerite. In sheltered areas of the sculpture, quartz and gypsum were also detected in significant amounts. These results are in agreement with the corrosion products usually found on outdoor bronze sculptures (Robbiola 1991, Scott 2002).

Surface EDS analyses published in a previous paper (Robbiola 2008) showed a Sn enrichment in the pale green zones and a depletion in the raised black islets as shown in Figure 1. The examination of the patina samples in cross-section (see Figure 2) reveals that the interface of the alloy/patina under the black islets is strongly enriched in Sn and O. These elements are not detectable on the surface due to the thick crust of the black islets (thickness ≥100µm), that is rich in Cl, Si, Ca, S, C, O and consists of cuprite, posnjakite, antlerite, amorphous carbon and calcite (see Table 2).

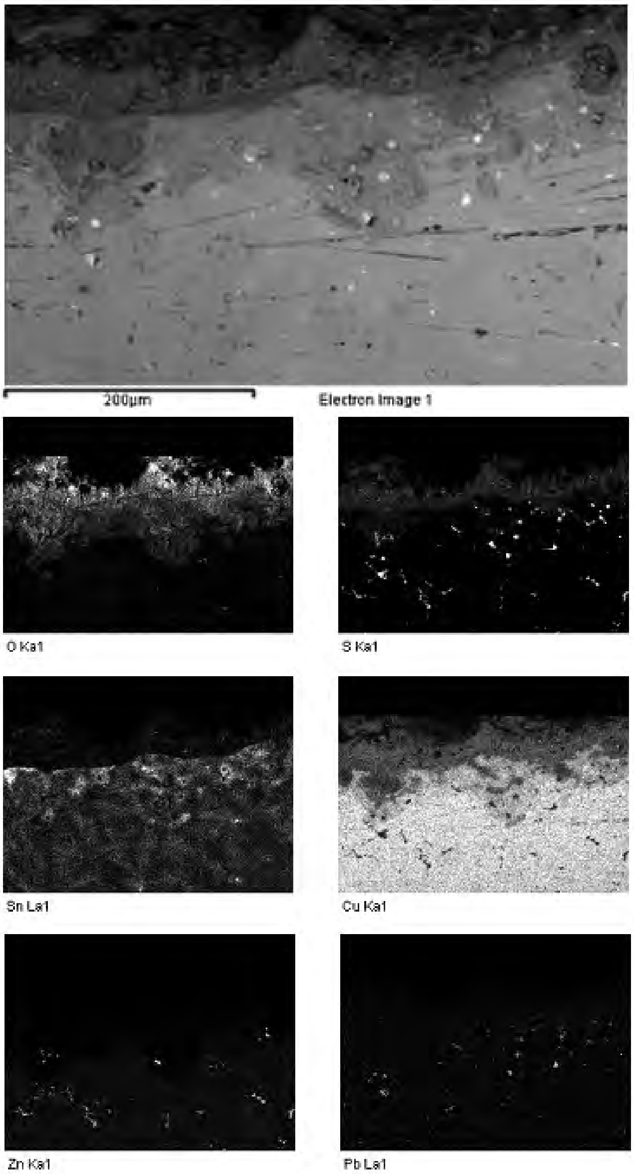

Figure 2. Cross section (BSE image and X-ray map) from the sculpture of King Louis XIV (unsheltered area, black islet).

The substrate underneath the black islets is involved in the corrosive process, appearing like a transitional zone, progressively decuprified and enriched in Sn-oxides. This can be explained by the diffusion/migration of oxygen anions through the thick patina and the subsequent penetration inside the alloy that induces a preferential oxidation of Sn, which forms stable oxides. In contrast,

	C	O	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Cu	Zn	As	Sn	Pb	Ni
Louis XIV alloy[a]											0.4	82	8.2		3.7	5.9	
Artificial alloy[b]												88	2.4		4.4	3.9	0.5
Louis XIV-sheltered patina	18	36	0.3	0.9	3.0	0.2	3.8	1.2	0.5	1.1	1.4	31	0.9		1.2	1.3	
WD patina	3.8	12						0.6				77	1.5		5.4	1.7	0.5
Louis XIV- unsheltered patina	9.0	35		0.1	0.2	0.7	3.1	0.3		0.7	1.9	26	0.9	0.8	17	3.9	
DROP patina	3.0	34					0.3					17	0.8		41	3.2	

[a] (Robbiola 2008), [b] (Bernardi 2009)

Table 1. EDS analyses (wt%), of the bronze sculpture of King Louis XIV, 1836, Versailles, and artificially aged quaternary bronze samples (Time Of Wetness ~30days).

cross-sections of pale green areas, where black islets are absent, are thinner and do not reveal any significant transition zone in the underlying alloy. The pale green patina is very thin, powdery, strongly enriched in Sn, O and S (see Figure 3a) and mainly consists of cuprite, Sn (hydrated-hydroxi) oxides, posnjakite, antlerite and anglesite (see Table 2).

	WD patina	Louis XIV-sheltered patina	DROP patina	Louis XIV-unsheltered patina
Cuprite Cu_2O	X	X	X	X
Brochantite $Cu_4SO_4(OH)_6$				X
Antlerite $Cu_3SO_4(OH)_4$		X		X
Posnjakite $Cu_4(SO_4)(OH)_6 \cdot (H_2O)$				X
Tin Oxides SnO_x			X	X
Massicot PbO	X		X	
Nantokite, Eriochalcite $CuCl$, $CuCl_2 \cdot 2(H_2O)$	X			
Anglesite $PbSO_4$	X			X
Cerussite, Hydrocerussite $PbCO_3$, $Pb_3(CO_3)_2(OH)_2$	X			
Quartz SiO_2		X		
Gypsum $CaSO_4 \cdot 2H_2O$		X		

Table 2. Compounds detected on the surface, through Raman and XRD analyses.

In both cases, the passivation of Sn in the patina favors the corrosion of Cu and Zn from the alloy that becomes strongly depleted of both these elements, as shown in Figures 2 and 3. This phenomenon is accompanied by the migration of metal cations through the patina to the external surface, where they are leached by rainfall (Cu, Zn) or involved in the precipitation of external corrosion products (such as Cu-containing compounds).

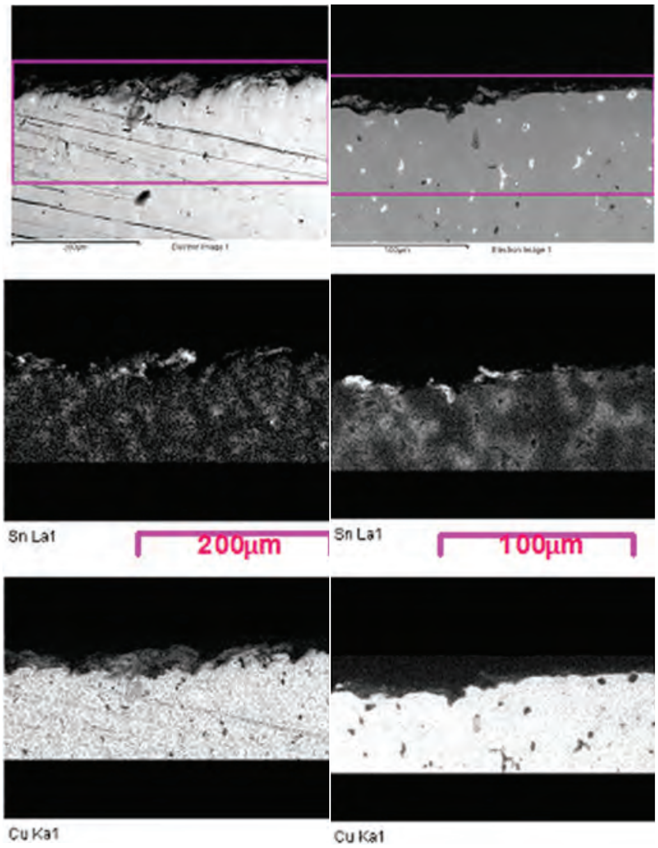

Figure 3. Cross-section, BSE image and X-ray maps of unsheltered patina, pale green areas: King Louis XIV (*left-hand column*); dropping test (*right-hand column*). The analysed area is surrounded by pink lines.

Artificial Exposure tests

Laboratory exposures performed through the WD and DROP tests allow a comparison of the behaviour of G85 bronze coupons in stagnant and leaching rain. In both conditions, EDS analyses of the bronze coupon surfaces (see Table 1) show oxidation of the alloy, that is, a decrease of Cu and Zn concentration and a relative enrichment of Sn, coupled with an increase of environmental elements, such as O, C and Cl as a consequence of the formation of corrosion products (see Table 2). No corrosion products containing Zn were found on the surface in any of the bronze coupons exposed to simulated conditions in the laboratory, or in the sheltered and unsheltered samples obtained from the patina of the sculpture, due to the high solubility of zinc products in this environment (Graedel and Leygraf 2000). In addition, copper sulphates typically found on outdoor bronze statuary, were not detected on the bronze coupons. Artificial ageing in this study focused on the direct effect of the rain without considering the action of gaseous sulphur oxides adsorbed in the water film at high relative humidity (RH), as may occur in real outdoor conditions. Moreover, the $SO_4^=$ concentration in the artificial rain reflects the decrease of atmospheric SO_x in the last decades. However, in the artificially exposed coupons, lead sulphates were detected and this was ascribed to the preferential formation of these compounds that are thermodynamically more stable with respect to copper sulphates (Bernardi 2009).

The corrosion product layer formed on the coupons in the WD test is heterogeneous in composition and contains copper oxide and chlorides, lead oxide, carbonates and sulphates. In contrast, the patina formed on the coupons subjected to the DROP test (see Table 2 and Figure 3 (*right-hand column*) essentially consists of Cu and Sn (hydrated hydroxi) oxides. In the former case, Sn products are not detected because they are localized in the inner layer of the patina covered by Cu and Pb compounds, as shown by cross sections reported by Chiavari (2010). In the latter case, a relevant superficial Sn-enrichment is evident, complementary to the progressive Cu and Zn depletion (see Table 1 and Figure 3(*right-hand column*)). The absence of lead carbonates or copper chlorides is due to the leaching of metal cations from the surface, preventing the precipitation of these salts. This is confirmed by the high concentrations of Cu and Pb found in the leaching solution (see Figure 5). Hence, the Sn-enriched layer remains fully exposed to rainfall. This picture describes what happens in an unsheltered patina, as illustrated in Figures 3 (*right-hand column*) and 3 (*left-hand column*), which compares the real sample (pale green area) and the cross-section of the laboratory sample (formed in the DROP test). Similar features can be seen in both patinas: a thickness of only a few μm, a strong depletion in Cu coupled with enrichment in Sn cations, and no internal oxidation of the underlying alloy.

In both simulated conditions, the alteration of the alloy proceeds with loss of thickness and mass, much more pronounced in the case of the DROP test. Specifically, as evident in Figure 4, the corrosion behaviour of samples follows a power law

(4) $m_{tot}=At^n$,

which describes the typical kinetics controlling the atmospheric corrosion of metals (Graedel and Leygraf 2000).

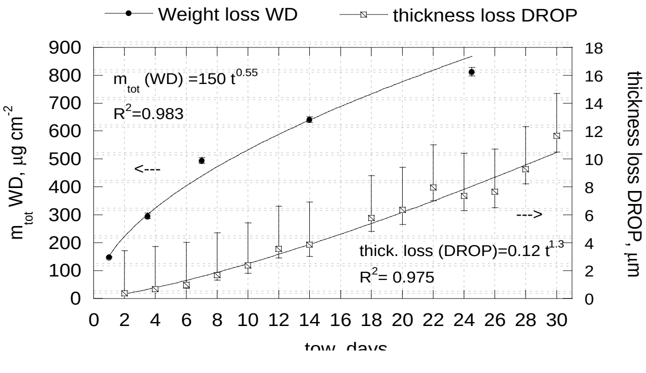

Figure 4. Weight loss for WD samples, and thickness loss for DROP samples versus time of wetness (TOW).

In the WD test, the calculated n value (equation 4) is ~0.5. A corrosion mechanism, controlled by migration of metal cations or environmental anions through a growing partially blocking patina, can be assumed. The evolution of the corrosion rate, deduced from Figure 4, shows a decreasing trend, due to the growth of the patina ($v_{,cor}$ range from 15 to 6 mg cm^{-2} yr^{1}).

On the contrary, for the DROP test, a rather linear trend is observed, that is, n~1, indicating a very porous and unprotected patina, with the corrosion phenomenon mainly determined by the supply of acid rain to the surface. In this condition, both v_{cor} of the alloy and $v_{Cu,cor}$ and $v_{Zn,cor}$ are one order of magnitude higher than those obtained during the WD test (see Table 3).

	$v_{M,cor}$ (mg cm^{-2} yr^{-1})				v_{cor}	
Exposure	*Cu*	*Pb*	*Zn*	*Sn*	*mg cm^{-2} yr^{-1}*	*μm yr^{-1}*
WD	3.6±0.6	1.7±0.6	0.3±0.2	0.080±0.003	6.02±0.03	6.7±0.1
DROP	29.3±0.1	4.3±0.1	2.7±0.1	0.15±0.01	36.5±0.2	49±7

Table 3. $v_{M,cor}$ calculated from ($m_{M,cor}$ + $m_{M,sol}$) and v_{cor} calculated from m_{tot} and thickness measurements, respectively for WD and dropping test, at TOW~30days.

The quantitative analyses of metal cations in solution and in the patina show a different behaviour of the bronze according to the exposure conditions. In stagnant, sheltered conditions (WD), the concentrations of metals dissolved in the environment are much lower than those remaining in the patina, which is in contrast to what occurs in rainfall runoff conditions (DROP), where the majority of oxidised metals are leached by the rain. This is clearly shown by the calculation of the dissolution factors of the different alloying elements f_M (see Table 4).

Exposure	f_{Cu}	f_{Zn}	f_{Pb}	f_{Sn}
WD	0.35±0.01	0.9±0.2	0.41±0.05	0
DROP	0.96±0.01	1.00±0.06	0.70±0.02	0
Louis XIV [a] (unsheltered pale green area)	0.95	0.99	n.d.[b].	n.d.[b]

[a] (Robbiola 2009), [b]not determined

Table 4. Dissolution factors for Wet & Dry (WD) and Dropping (Drop) tests at TOW~30days.

In fact, f_{Cu} and f_{Pb} increase during the WD test but always remain below 0.5: Cu and Pb tend to precipitate as corrosion products. In the DROP test, f_{Cu}, f_{Zn}, and f_{Pb} are markedly higher than in the case of the WD test. It also confirms that the leaching action of the rain hinders the patina formation: more than 90% of Cu and Zn in the patina dissolve in the rainwater (independently from the Cu and Zn in the original alloy). Concerning Cu and Zn, the *f* values obtained for the DROP test are in good agreement with results obtained from unsheltered areas of the sculpture of King Louis XIV. The results also agree with other outdoor quaternary bronze monuments with different percentages of alloying elements exposed to urban atmospheric conditions (Robbiola 2008). In all cases, f_{Zn} is close to 1, indicating that Zn products are soluble in all conditions. By contrast, Sn is totally insoluble (f_{Sn}~0), as also found by other authors (Jouen 2009). In both conditions, all oxidised Sn remains in the patina as insoluble corrosion products forming a Sn-rich layer, permeable to the migration of other metal cations from the alloy.

In fact, with increasing exposure time, the ageing solutions are progressively enriched in the other alloying metals, which dissolve with different trends and extents (see Figure 5). It is worth noting that the dissolution of the bronze coupons exposed to leaching rainwater is at least one order of magnitude higher than those exposed to stagnant conditions.

The dissolution of Cu shows a parabolic trend in the WD test, indicating an acceleration of the phenomenon, i.e. a progressive patina destabilisation. Conversely, in the DROP tests the linear trend of dissolution shows the complete permeability of the patina with Cu cations. In both conditions, Pb dissolves with logarithmic kinetics, revealing a progressively slowing kinetics, whereas Zn dissolves with a linear trend.

Despite composition of the original alloy, the higher values of the metal ratio Pb/Cu in solution compared to the same ratios in the original alloy show a preferential dissolution of Pb with respect to Cu during all test periods. As previously reported (Bernardi 2009), the excess amount of dissolved Pb has been associated with the preliminary polishing treatment of samples, which smears ductile Pb on the surface, and to the action of Pb globules as local anodes in the Cu-rich matrix, corroding preferentially.

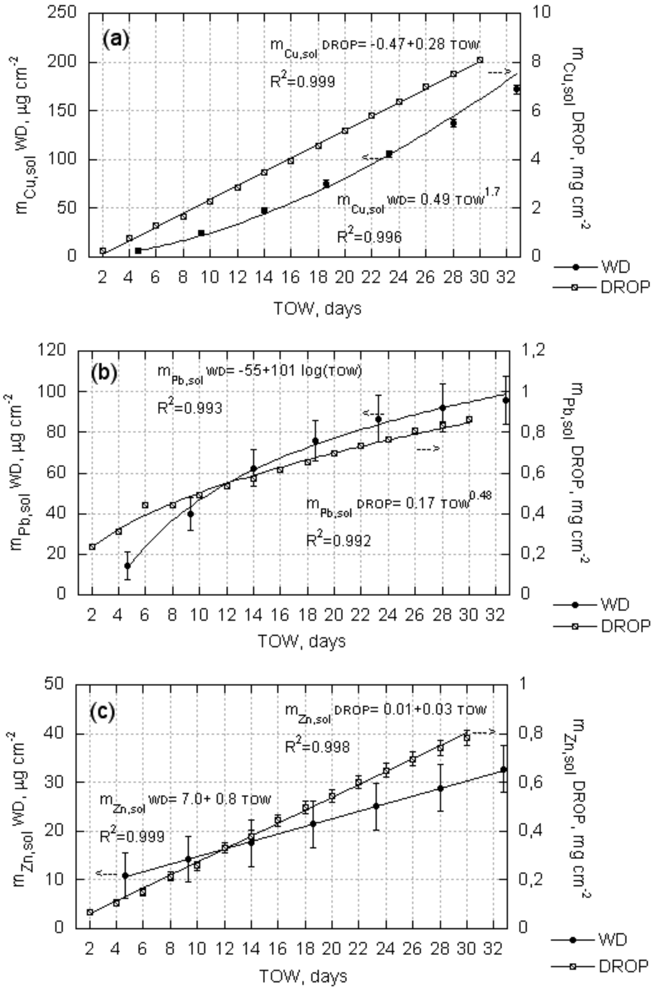

Figure 5. Metal content in the ageing WD and DROP solutions with time of wetness (TOW): (a) Cu, (b) Pb, (c) Zn.

Conclusion

The comparison between corrosion product samples from the outdoor sculpture of King Louis XIV and that obtained from artificially corroded bronze coupons has yielded a better knowledge of patina formation. These results have demonstrated how the composition, the protectiveness and the formation kinetics of a patina depend on its sheltered or unsheltered exposure to rainfall. In stagnant conditions, the patina is a multilayer system: a Sn-enriched layer covered by Cu and Pb compounds. Conversely, Zn dissolves completely. In runoff conditions, the patina is a thin porous layer, strongly enriched in insoluble Sn oxides, across which Cu, Zn and Pb cations migrate; more than 90% of these cations are leached into the environment.

The agreement found between the results obtained from laboratory tests and those obtained from real samples also has an interesting outcome on testing procedures for developing new protective coatings. In fact the patina, which is the support for protective treatments, proved to have different characteristics according to the exposed areas. Artificial patination recipes, based on the deposition of Cu-compounds, are insufficient to reproduce the complexity of real patinas, in particular as far as the leaching action of rainwater is concerned. In fact, the remarkable depletion of Cu and enrichment of Sn observed in unsheltered areas, a process that sometimes also involves the underlying alloy, requires the use of properly aged surfaces for adequately testing of corrosion inhibitors.

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Materials

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Web site www.microglass.it

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Q & A SESSION

John Scott: What a wonderful presentation Cristina, thanks a lot. We've seen before the discussion of the role of the tin compounds in the partial protectiveness against the corrosion of outdoor bronzes. So I just wanted to ask you what you think, although most of your study was in artificially produced patination, about the role of the tin compounds in the patinas that form outdoors on actual sculptures and the relationship of that to the rate of corrosion of the underlying bronze? I'm not sure you really address this in your talk. You point out tin compounds are not soluble in your tests, and most of your attention in your tests clearly and wonderfully is to artificially produced patinas and their qualities. What kind of extension do you have then for the relative degree of protectiveness of the patina or patches of patina on outdoor sculptures? Do those tin compounds, as suggested much earlier by Robbiola etc., have an effect on what part of the patina erodes and whether the patina could be considered protective at all?

Cristina Chiavari: Could be conserved?

John Scott: Could be considered to be something that slows the corrosion of the bronze underneath when you have a sculpture outdoors and it is developing its patina under natural weathering. This is different to your model of course and in your study you show that the tin compounds are not soluble and so then they form a part of the patina that is left behind after erosion or during erosion in weathering situations. It's been suggested before, that part of the role of that tin is to slow the corrosion.

Cristina Chiavari: I don't think so actually – it is completely porous. It can slow down general corrosion, but it is not really a strong effect because it is a completely porous patina, and in some cases it also enhances corrosion. So I don't think it helps really to [inhibit corrosion].

John Scott: So this really is a new, a really new contribution, because from other people's work we thought that the more tin in the bronze exposed outdoors the slower the corrosion of the underlying metal would be, for instance bell metal.

Cristina Chiavari: Generally, maybe. But in runoff conditions, it is really that the ratio of the element changes.

John Scott: I guess it's true that your study doesn't address the microstructure of actual weathered patinas but patinas that form in your experimental conditions. But your take-out from this to the application outdoors would be that the microstructure of the patina close to the metal, for instance the copper-rich patina, the oxide-rich patina, that seems to be where the tin-compounds tend to form and become part of the patina matrix on the surface… your feeling is that that this has no effect on the rate of corrosion of the underlying metal?

Cristina Chiavari: Yes yes, the general tendency of the atmospheric corrosion of metals is as you suggested, you have a slowing [down] of the kinetics, with longer times and this role of tin is not really a protective one… this tin layer, this tin-enriched layer is not a protective layer – this is [for] sure.

John Scott: So it is sure that it is not at all protective because in a lot of the studies looking at these outdoor patinas, in the cycling of wetness and dryness, it has shown the importance of the formation of microcracks and pores, which are then plugged and filled by the formation of new corrosion products. This may possibly, or maybe not according to what you are saying, have an effect on the access of corrosive environmental materials to the surface, which is what causes corrosion. So you still feel that there is no effect of the tin oxides on the permeability of that patina to the environmental corrodants? That's your opinion?

Cristina Chiavari: Yes.

John Scott: Thanks for your work, it's really good to see.

Cristina Chiavari: Thank you.

Tom Chase: It is a wonderful paper and I was glad to see that Luc Robbiola's name was attached to it. It's nice to have something from him at this meeting. As always it's a very incisive and revolutionary view on corrosion. I was particularly glad to see you doing the drop-testing, as I think that is very relevant. We've looked at drop formation and the formation of the run-off channels on sculptures in Washington and I was surprised to see that once they've formed, they continue to form, they continue to eat in. Superficially you would think that when the sculptures are wet in a rain event, run-off would change as it does on your car windshield, but no, it runs down the same channels and just simply deepens them. As John was saying, that is not protective at all. I was also particularly glad to see that 41% tin in the drop-test, that's the same amount of tin that we often see on the surface of Chinese bronzes. I've wondered why you get that 41% tin when we do surface X-ray fluorescence analysis on corroded bronzes. I am going to go back and look at that again. The last thing I wanted to say was that the paper that I presented with [Mike Notis and Al Pelton] about Pourbaix diagrams and bronzes comes to the same conclusion which is that the most stable thing is the tin oxide and that's the last thing you come up with in corrosion so thank you very much it's a wonderful paper.

Cristina Chiavari: Thank you.

Andrew Lins: I just wanted to make a brief comment about the difference between laboratory experimentation and real life and the fact is that in most outdoor bronze exposures, there is a considerable factor in determining what species remain on the surface. In particular the presence of nano-particles of tin oxide, which in my experience are seldom found on objects which are over 100 years exposed, has to be considered. The other comment to make toward John Scott's comment about enhancement of tin on the surface: we know and have known for a long time that the alpha-delta eutectoid is very resistant to corrosion and it is the preferred species that remains on the exterior, after the alpha-phase dissolves. But thank you for your paper, very nice.

Cristina Chiavari: Thank you.

Sara Goidanich: I would like to thank you Cristina. We have been exchanging data and opinions for quite a long time and thank you for [mentioning] something I really care about, which is the run-off. We normally think that corrosion [leads to insoluble products] and that run-off is not corrosion. We found the same as Cristina on our samples exposed outdoors. We also measured corrosion rate and we found that they are not the same, so sometimes you have really high run-off [rates] and really low corrosion rates, so about tinning - the first question, it does depend, as Cristina said, if the film is porous, then tin cannot be protective. In other cases you find that tin does protect against corrosion. But, apparently, as Cristina showed, it does not help to stabilize the rest of the corrosion products that are leached easily in the same way as pure copper. So I think your work is very innovative and we really should think about these aspects of run-off and also about the composition protocol for testing new products for external use. Thank you Cristina.

Cristina Chiavari: Thank you.

Peter Northover: Just a couple of comments about the tin-rich corrosion products. They are a lot more universal than people realize. This is something that we published in an MRS [Materials Research Society] Archaeology proceedings.

The paper was about increased spatial resolution and analyses and we were using high-resolution scanning Auger spectroscopy with the spatial resolution of about 20 nm across, that was able to show up the intergranular corrosion cracks in bronze sheet. At 2 microns wide, you could see all the cuprite, but between the cuprite and the bronze, was a layer of tin dioxide which was 70 nm thick. This was in an archaeological sample. So no conventional microscopy will show it, you probably won't see it in the SEM, but there is a layer of tin corrosion products there. We have I think two examples in Britain. I was commenting on the evil nature of grave environments for the corrosion of bronze. We have one or two early Bronze Age bronze daggers which are completely decuprified. We have a mechanically stable entity which is composed entirely of tin corrosion products. We have another example from an archaeological collection where the bronze was sitting in stagnant air for 3000+ years and the corrosion products on the surface are less than 1 micron of tin dioxide, so I always think the thing that gets left out most in conservation studies is what happens to the tin. You've added to our knowledge of what happens to the tin, thank you.

Cristina Chiavari: Thank you.

Molly Carlson: I have no experience with outdoor sculpture but I have a question: In Maine, on the coast, on some of the islands, they are doing forestry studies to measure the pH of the fog. And I'm wondering since we can have a pH of 2-3 – what would be the effect of an acidic fog on a sculpture this way?

Cristina Chiavari: Yes, a few years ago in France I studied [the effect of] a pH 5.6 and a pH 2 [on the] electrochemical behavior of a green patina. I performed voltammetry and impedance under these conditions and I saw that at pH 5.6 I have copper compounds dissolving, but at pH 2 I also have tin compounds dissolving. So one of the questions we are also asking at this point is that very frequently we find pH 2 in localized measurements on outdoor sculptures, so maybe the destabilization of the patina is not only due to the destabilization of copper compounds but also of tin compounds.

THE DELHI IRON PILLAR: A STUDY OF THE CORROSION FORMED IN AREAS OF SURFACE DEFORMATION

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Abstract

The Delhi iron pillar has long been considered a corrosion resistant structure. Recently, a fast growing deterioration in the form of yellow colored corrosion has been observed, especially in an area on the surface that suffered impact from a cannon ball in the 18th century. This type of corrosion is causing accelerated corrosion of the structure. Close observation of the pillar surface shows that large areas below the impact site are developing iron oxides of different colors on the surface. This paper discusses the possible causes of this deterioration and suggests a plausible scenario to explain this phenomenon. Based on historical information concerning the development of dents in the surface of the pillar, a laboratory-simulated dent was formed on a piece of iron with similar composition to that of the pillar. Electrochemical impedance spectroscopy (EIS), and cyclic polarization were performed on the sample. The results corroborate our proposed mechanism for the deterioration of the pillar. It is concluded that the dented area is subject to tensile stress and is simultaneously exposed to a corrosive environment, and is therefore corroding preferentially to the rest of the pillar.

Keywords: Delhi Iron Pillar, rusting, impedance spectroscopy, rusting mechanism, Raman spectroscopy, rust, iron corrosion

Introduction

Qutub Complex, a world heritage site in Delhi, India, is a complex of monuments and buildings dating to the 12th and 13th centuries A.D. The structures include Qutub Minar minaret, Quwwat-ul-Islam Mosque, Sultans' tombs and other monuments. The majority of the structures in the complex are Islamic. The Delhi iron pillar, which now stands in the centre of the mosque complex, stands at a height of approximately 7 meters (see Figure 1). The pillar is tapered towards the top, with a diameter of 30 cm near the top and 62 cm at the base (Lal 1996). The pillar weighs approximately 6,000 kg, is made from wrought iron, and is believed to have been commissioned by the Hindu ruler Chandra (375–414 AD). The pillar has an inscription in Sanskrit at an approximate height of 2 m from the ground.


Figure 1. The Delhi Iron Pillar in situ at the Qutub Complex.

The Delhi iron pillar is of immense importance from a historical, archaeological, metallurgical and scientific standpoint. The pillar has been standing intact in the hot and polluted environment of Delhi for more than 1,600 years. For almost two millennia, the pillar has remained essentially free of corrosion. However, deterioration has been observed recently, and it is thought that the high level of pollution due to substantial increase in vehicular traffic in the last decade or more around the pillar is leading to its deterioration. On parts of the pillar around the large dent caused by the cannon ball, yellow, unstable corrosion products have developed and appear to be contributing to accelerated corrosion of the structure in this area. This damage is also visible on the inscription that lies under the dent, and the presence of cracks is another sign of the deterioration. Close observation of the pillar surface shows that large areas below the dent and around the cracks are developing iron oxides of different colors. The most alarming situation concerns the large dented area that may be the result of a direct hit from a cannon ball fired by either Nadir Shah in 1739 or by Ghulam Quadir in 1787 (Hearn 1995). The impact point is roughly 10 cm in diameter and 6.5 cm in height. The elliptically shaped dent gives the impression that it may have resulted from a direct hit from a cannon ball, and close observation indicates that the deformation is concave in shape (see Figure 2).

Figure 2. The large dent in the Delhi Iron Pillar. An accumulation of yellow corrosion around the dent and associated cracks is evident. Arrow indicates area where severe pits are noted on the surface.

The dent is on the northwest side of the pillar, approximately 4 meters from the ground. The yellow colored corrosion appears at the periphery of the dent and is more intense above the dent in comparison with the area below it. Interestingly, the dented area itself shows negligible corrosion but small pits are observed all over this area. The cracks that have developed adjacent to the dented area also exhibit the same pattern of small corrosion pits. On the lower part of the dent, on and around cracks that have formed on the opposite side, (the southeast side), very severe pitting is noted (see Figure 2).

The pitting is more pronounced on the pillar's inscription. Due to corrosion, parts of the letters show accelerated deterioration (see Figure 3).

Figure 3. The fourth century A.D. Sanskrit inscriptions on the pillar below the dent and associated cracks have shown accelerated deterioration in recent years.

Possible causes for the corrosion

Corrosion at the periphery of the dent

Although the exact causes for this peculiar yellow corrosion can only be ascertained with detailed scientific analysis of the iron and the corrosion, some possible explanations can be offered based on the published literature. Past studies have shown that the pillar is made of inhomogeneous phases of wrought iron with a minor content of carbon (C) silicon (Si), and phosphorus (P) (Hadfield 1912, Hadfield 1922, Balasubramaniam 2000). Many theories have been proposed for the corrosion resistant nature of the pillar. According to these theories, factors such as the mild climatic conditions of Delhi that existed in Delhi prior to the increase in vehicular traffic, the favorable composition of the iron, its large mass, and, hence, large heat capacity, in addition to the presence of a thick passivating corrosion layer that has formed on the outer surface of the pillar, may be responsible for its corrosion resistance (Wranglen 1970, Raj 2005). Of these many theories, the most convincing is the one based on the presence of a thick layer of phosphorus rich corrosion products that have formed a protective passivating layer on the iron surface.

Elemental analysis of corrosion products from the pillar report that C, Si, and P are present, plus a trace amount of Cu. This layer is impervious to the environment around the pillar (Ghosh 1963). Although the exact thickness of this layer is not known, indirect measurements using a magnetic gauge showed it to be in the range of 200-300 μm (Raj 2005). This finding suggests that the composition of the pillar varies from one area of the pillar to another, as illustrated by its non-uniform rust pattern and variable thickness of the corrosion layer. However, a non-uniform chemistry would have caused very severe corrosion of the pillar due to the formation of micro and macro corrosion cells on the surface, which has not occurred here. Another possibility is that the pillar has thick layers of slag of varying thickness across the pillar creating dissimilarities in the metal. The dent on the surface of the pillar as shown in Figure 2 exhibits plastic deformation and cold work from the impact of the cannon ball, and, as a result, is subjected to residual compressive stress. Metal at the periphery of the impact zone should be subjected to tensile stresses. Macro corrosion cells would be expected to form at the area of impact, acting as the cathode in the area of residual compressive stress, while, at the periphery, the area under tensile stress serves as the anode. Corrosion of iron takes place at the anodic sites of the cell, that is, at the periphery of the dent which is under tensile stress as follows:

$$Fe \rightarrow Fe^{2+} + 2e \qquad (1)$$

The ferrous cations, Fe^{2+} and electrons move to the cathode through the conducting electrolyte (here moisture/dew etc.) and the conducting metal respectively, and form ferrous hydroxide as follows:

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \qquad (2)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (3)$$

The generation and accumulation of corrosion takes place at the cathodic sites of the corrosion cell. Since the slag in the microstructure of the iron around the periphery of the dent is cathodic, rust accumulation should have taken place at the periphery of the dent. Observations show that rusting is more pronounced at these locations, as shown in Figure 2.

The hydroxide generated in equation (3) transforms into different forms of iron oxide depending on the conditions prevailing at the corroding interface. If an excess of corrosive gases are present in the environment, especially polluting gases and chloride, the iron oxides formed at the cathode will be unstable. If this rust is conducting and porous, unabated corrosion reactions shall proceed on the surface.

The corrosion of the pillar is more severe in the winter (due to condensation of dew) than during the monsoon seasons (July to mid-September and late January to mid-February). In winter, the unstable, yellow corrosion (probably iron oxy-hydroxide) accumulates at the periphery of the dented area, and accelerates the corrosion process as a result of depolarization effects of ferric ions on cathodic reactions:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \text{ --------------------------- } (4)$$

Due to the washing effects of the monsoon rains on the corrosion, corrosion at the periphery of the dent is often less visible, although the damage continues below the dent and cracks.

Localized corrosion

Corrosion formed at the periphery of the dent and around the cracks is washed away with monsoon rains, condensing fogs or dew, and migrates to the lower parts of the pillar. The rust particles then become trapped in the inscription and slowly deposit there as loose oxides. These oxides act as a good reservoir of moisture and corrosive gases and get absorbed into rust particles that have migrated from the dent to the inscription and other areas below the dent, to act as a conductive electrolyte for continuing corrosion. The ferric ion (Fe^{3+}) of this loose rust has an accelerating effect on corrosion reactions as in equation (4). A careful examination of the structure below the dent and cracks clearly shows this localized type of attack on the surface of the pillar (see Figures 4 and 5). When comparing sections of the pillar below the dent (see Figure 4) with those above the dent (see Figure 5) we find no crack or dent present above it. These observations demonstrate that the rust generated at the periphery of the large dent in the pillar is having detrimental effects below it. This corrosion has become more pronounced during recent years, and the probable cause for the enhanced corrosion is discussed below.

Figure 4. Localized corrosion below the dent on the pillar due to rust initially formed at the periphery of the dent and cracks. Arrow indicate areas where pits have formed below the dent.

Figure 5. No pitting corrosion has formed above the dent on the pillar.

Comparison of a photograph of the pillar's inscription taken around 1970 (see Figure 6a) with a recent photograph (see Figure 6b) shows that an appreciable amount of deterioration has taken place since 1970. Some of the letters of the inscription are severely damaged from weathering, have lost definition, and are on the verge of fusing together. The entire inscription may become illegible within a few years if no interventive measures are taken.

Figure 6. Photograph of inscription taken in the 1970's (*left*) Detail from a recent photograph of the inscription (*right*). Arrows indicate one of the damaged letters of the inscription.

Experimental

In order to test the theory that the recent corrosion on the pillar is caused by tensile stress, the surface of a low alloy steel plate of composition 0.16% C, 0.08% P, 1.25 % chromium (Cr) and 0.32% copper (Cu) was deformed using a compressive load so that the surface was distorted by about 1 mm. Electrochemical impedance spectroscopy was carried out on the front of the deformed test surface (concave deformation), on the back (convex deformation), and on part of the steel surface that was not deformed. EIS was carried out in an Society of Automobile Engineers of Japan (SAEJ 2234) solution of 0.5%(w/v) sodium chloride (NaCl), 0.1%(w/v) calcium chloride ($CaCl_2$), and 0.075%(w/v) sodium bicarbonate ($NaHCO_3$), (Simpson 1998), which simulates the atmospheric conditions for corrosion (Townsend 1999). The data shown in Table 1 demonstrate that the impedance of the deformed surface under compressive stress was about 1.5 times higher in comparison to the stressed surface.

Sl. No.	Part of steel	EOC (mv- .C.E.)	R_p (Ohm- cm^2)	α
1	Surface having compressive stress	-685	1730	0.60
2	Surface having tensile stress	-692	1205	0.56
3	Plane steel coupon	-640	6800	0.64

Table1. Electrochemical impedance data for indented steel plate exposed in SAEJ solution.

Further, the corrosion potential of the compressed surface had shifted more to the positive side than the unstressed surface. It is of interest to note that the polarization resistance of both the tensile and compressively stressed steel are mean that they are more prone to corrosion than the normal steel surface with deformations. However, polarization resistance of normal steel is considerably higher in comparison to the previously mentioned two stressed surfaces. The impedance plots in the form of Nyquist curves are shown in Figures 7 and 8. An induction loop for the area of tensile stress (see Figure 7) indicates that this surface is undergoing some changes during the EIS, which might correspond to the development of pits on the surface.

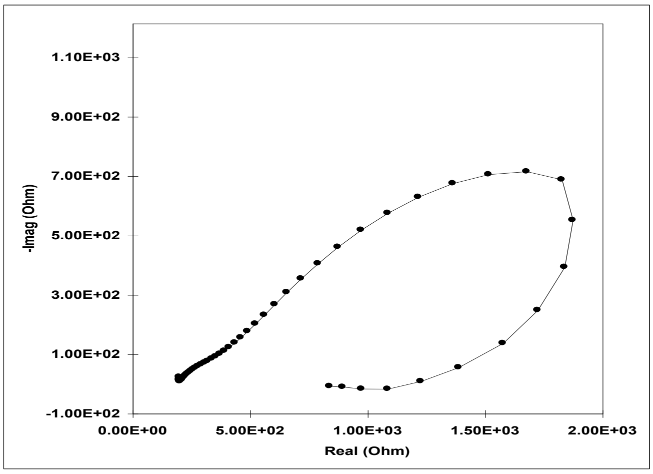

Figure 7. Impedance plot for part of the steel test plate under tensile stress, tested in a SAEJ solution.

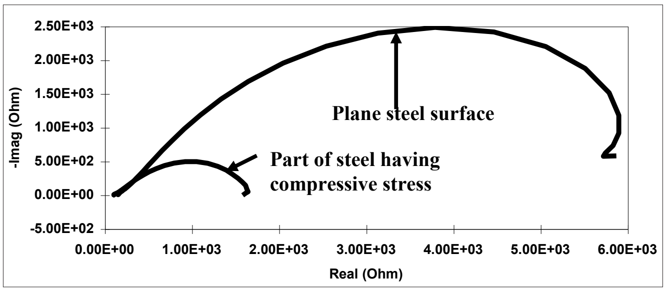

Figure 8. Impedance plot for part of the steel test plate under compressive stress and no stress, tested in a SAEJ solution.

These findings suggest that the compressive straining of the steel has made its surface more passive in comparison to the stressed surface, thus explaining the rust pattern at the periphery of the dent in the Delhi iron pillar. It should be noted that the above data was collected on freshly deformed surfaces. The development of rust after long exposure in an outdoor environment is expected to be of a different nature. Both the mechanism and kinetics of the corrosion reactions may also differ. Preliminary work is ongoing and once stable rust has formed on the three steel plate surfaces described above, the surfaces will be examined using micro Raman spectroscopy and X-ray diffraction (XRD).

DC cyclic polarization studies of the two deformed test surfaces also produced the same trend as noted during the impedance studies. The compressed surface produced lower current density in comparison to the surface under tensile stress (see Figure 9).

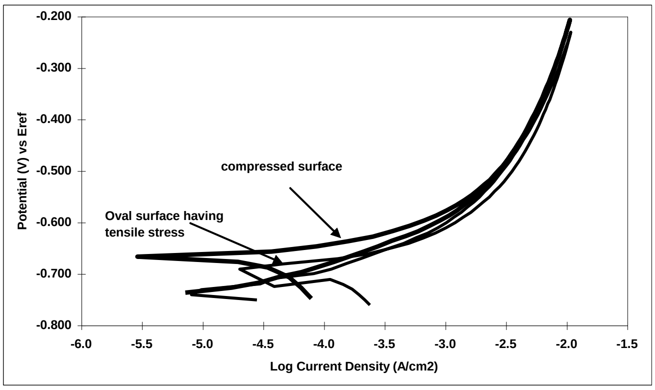

Figure 9. Cyclic polarization of the steel surfaces under compressive and tensile stress.

Urgent precautionary measures needed

Urgent interim measures are needed to prevent or minimize the damage occurring on the Delhi pillar as a result of localized corrosion, until a final report with recommendations to control the corrosion at the periphery of the dent and below it, is completed. These measures are:

(a) Provide a canopy above the pillar in order to avoid the accumulation of moisture during the rainy season and dew in the winter season.

(b) Cover the dent and cracked sections of the pillar with transparent polycarbonate sheet to further protect the pillar.

These measures should be considered temporary. A permanent solution for the preservation of the pillar can only be determined after a full series of non-destructive tests are performed. The technical analysis could include mapping the chemistry of the iron from the top of the pillar to the base, paying close attention to the dent and surrounding areas, characterization of the yellow rust accumulated adjacent to the dent, Raman spectroscopy, XRD, and energy dispersive X-Ray analysis.

Some may argue that little visual deterioration has taken place since the pillar was hit with a cannon ball more than 200 years ago. Undoubtedly, due to its composition, the pillar has some self-passivating properties especially in a mild corrosive environment. However, in a polluted environment where acidic gases such as carbon dioxide, sulphur dioxide and nitric oxides are present, the corrosion resistance of the iron pillar is at risk. As little as 50 years ago, the Delhi climate was not as polluted, and corrosion of iron with a good composition like the pillar, was not a concern. In 1953, Hudson reported that the corrosion rate (thickness loss) of carbon steel exposed in Delhi was 2.5 µm / year (Hudson 1953). A recent study by the authors has shown that the thickness loss of carbon steel exposed in Delhi's environment today is 14 µm/year for the same duration of exposure (Singh 2008). This indicates that the corrosive conditions in Delhi have increased by about six times during the last 50 years. Owing to continued industrialization and pollution, corrosion of exposed iron and steel is expected to be more aggressive in coming years. A simple extrapolation of the data suggests that in the next 15 years, the pillar should experience the degree of damage that occurred in the last 50 years. For this reason, it is vital to establish preventive measures before it is too late.

Future Scientific Studies

A solution to this corrosion problem may only be found once a clear understanding of its causes is determined. Earlier studies are either non-conclusive or speculative in nature. The papers published by Hudson in 1953 (Hudson 1953) and by the National Metallurgical Laboratory of India in the 1960s (Ghosh 1963, Lahari 1963, Lahari 1967) are probably the first studies that generated scientific data on the corrosion resistance of the pillar. A number of publications in recent years, especially by Balsubramanyam et al have helped considerably in unraveling the causes of the formation of the protective surface on the pillar (Balasubramanyam 1995, Balasubramanyam 1997, Balasubramanyam 2002). However, most of their work was performed by taking iron samples from other structures believed to be contemporary with the Delhi iron pillar. None of the above studies shed any light on localized corrosion taking place on the periphery of the dent and below it. Moreover, the theory put forward by earlier researchers for development of a protective rust layer on the pillar with time, should be verified using newer scientific techniques. The authors hope that the initiative taken in the present work will result in the development of a better approach towards preservation of the pillar.

Studies that remain to be performed:

1. Mapping the chemistry of the pillar from the top to the base, using modern non-destructive portable instrumentation.

2. Ascertaining the type of corrosion formed at different locations on the pillar, using Raman spectroscopy, X-ray diffraction, energy dispersed X-ray analysis (EDXA), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma mass spectroscopy (ICP-MS).

3. Monitoring the corrosion rate of iron samples exposed at the pillar site, with a composition similar to that of the Delhi iron pillar.

4. Determine the electrochemical potential of a possible slag-phosphate fill material, to be used to fill the cracks and dent in the pillar. The electrochemical potential of the fill material should match the potential of the pillar. Once the potential of the fill material is determined, fill the cracks and dent in the pillar with the appropriate material.

5. Continue simulation research on steel samples in the laboratory and study the mechanism and kinetics of corrosion, and finding the nature of rusts formed on their surfaces exposed at a site near to the pillar.

Conclusion

Studies have shown that rusting at the periphery of a large dent on the Delhi iron pillar is caused by the formation of corrosion cells. Surface areas under compressive stress behave cathodically and tensile stressed areas act anodically. The mechanism for pitting and rusting of the pillar is described and some suggestions are given to prevent further deterioration of the structure. Further study of the large dent in the pillar is continuing through the simulation tests, and the steel test samples are currently exposed to the atmosphere awaiting the formation of corrosion for future study.

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Authors

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Q & A SESSION

No questions were asked.

THE EFFECTS OF FINGERPRINTS ON SILVER

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Abstract

Sweat deposited by human fingertips can corrode many polished metal surfaces. Sweat consists of salts of light metals, particularly chlorides, traces of heavy metals, and organic compounds, such as fatty acids and urea, in solution in water. The combination of chlorides and fatty acids are the source of the corrosion. This paper describes the monitoring and characterisation of fingerprints on fine and sterling silver using a combination of microscopies and microanalytical techniques. Particularly useful were optical metallography, high-resolution scanning electron microscopy with energy dispersive X-ray spectrometry and 3D visualisation, and compositional mapping using monomer ion beams and time-of-flight mass spectrometry. These techniques have charted the evolution of the fingerprints and have conclusively demonstrated the damage caused.

Keywords: silver, fingerprints, corrosion, characterisation, microscopy, ion beam analysis

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Introduction

For silver on exhibition, the two greatest disfigurements are tarnish, a process involving airborne sulphur, but more complex than the formation of a simple sulphide deposit (Hallett et al. 2003, Dowsett et al. 2003), and fingerprints formed by sweat from human fingertips. It is accepted conservation practice to wear gloves when handling silver objects. This is because fingerprints, apart from being visually distracting through leaving a surface deposit, will also corrode the metal, leading to loss of the original surface; both the specific mechanism of this process and the nature of the products on silver are not known.

The literature on corrosion by perspiration is relatively limited and is generally concerned with corrosion in industrial and other contexts, and with forensic aspects of fingerprints. The article most frequently cited in conservation literature relating to fingerprints is that by Burton, Pye and Brookes (1976), which deals with corrosion on iron and steel in industry but does give a useful discussion on chlorides in sweat. An article on the mechanism of the deposition of fingerprints by Thomas and Reynoldson (1975) discusses how a fingerprint is deposited and changes over time. The authors also examine the difference in the rate of change of composition in both eccrine (aqueous) and sebum (lipid) rich prints. More recent papers, for example, by Archer et al. (2005), also examine changes in the various components of fingerprints over time, in both dark and light environments, but over a much shorter timescale than that of the experiments described in this paper.

The process of corrosion induced by sweat is described in a paper by Bailey and Zaccardi (1983) that looked at the corrosion rates of copper and other metals by human perspiration. However, this did not specifically cover fingerprints. A review in Chemical Engineering News (Jacoby 2006)) about the work of research student Brittany M. Baguley, noted that in addition to the naturally occurring fingerprint secretion, traces of nicotine, sunscreen and cosmetics also can be found.

As might be expected, the vast majority of work on fingerprints has been done in the area of forensic science. However, this work is primarily concerned with the methods of deposition, content of the fingerprint itself, or methods to enable the fingerprint to be detected over longer periods of time. Recently, there has been an expansion in fundamental studies of fingerprints, both recognising their corrosive effects (Bond 2008), and offering new ways of characterising their structure (Williams and McMurray 2007). A result relevant to conservation obtained by Bond was that the intensity of corrosion was strongly dependent on humidity and that keeping a sample in a desiccator greatly retards corrosion. However, no new results are reported on silver and this paper aims to fill that gap.

Sample material and preparation

Rectangular coupons 20 x10mm were cut from fine (99.9%) and sterling (92.5% silver, 7.5% copper) silver

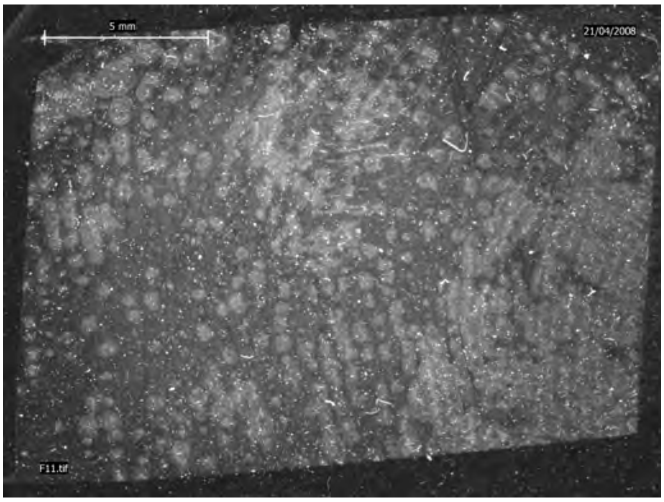

Figure 1. Fingerprint on fine silver after six months.

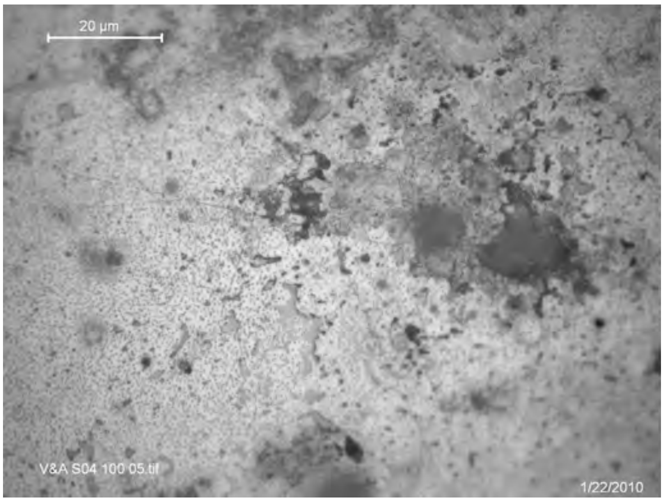

Figure 2. Detail of fingerprint on sterling silver after 25 months.

strip. The coupons were hot mounted in a carbon-filled thermosetting resin, ground on successive grades of silicon carbide paper from P600 to P4000, and polished with 6µm, 1µm and 0.25µm diamond paste. In December 2007, a thumbprint was placed on each coupon then half the samples were left in an open tray in a regularly used office and the rest placed in a well-sealed box. The samples were monitored periodically using optical and infra-red (IR) microscopy and non-contact surface profiling.

An important part of the experiment is at the end to clean off the surface contamination in such a way that the corrosion products can be removed without obscuring the damage. Various attempts were made to wash off the fingerprints without abrasion, the most successful used Swarfega, a commercial hand-cleaner for removing grease. The sample is first rinsed under running hot water then coated with a thin layer of Swarfega. After one minute this is rinsed off under running hot water. The final stage is 15 minutes in de-ionised water in an ultrasonic bath before blotting dry on absorbent paper. If necessary, the washing cycle is repeated.

Optical and infra-red microscopy

The samples were regularly examined at low magnification using a Leica M165Z stereo zoom microscope (see Figure 1) and at higher magnifications using a Reichert Polyvar metallographic microscope with normal incident and polarised illumination and differential interference contrast. Initial monitoring at intervals of a few days was unnecessarily frequent and the samples were subsequently checked at intervals of eight to 10 weeks. At the same time, non-contact surface profiling was carried out with a NanoFocus confocal microscope and infra-red spectra obtained using a Varian UMA 600 infra-red microscope. It was anticipated that changes in the profile and composition of the fingerprints might occur as corrosion products were produced, dust accreted and organic compounds evaporated or oxidised. Our observations were that the initial maximum height of the deposits was in the range 1.6 - 1.8µm, which had not altered in six months. The measurements were taken on similar, but not necessarily identical regions in every case. The total height range across the print was 0.1µm to 1.8µm. The profile of the print stabilised in a relatively short period of time, between 10 and 20 days, after application. However, while the geometry of the fingerprint remained stable, marked differences gradually developed between the effects on fine silver and on sterling silver, and these differences were systematic. That is, the same effect appeared on all the coupons of each group and there was no correlation with the order in which the prints had been applied. The initial fingerprints showed a pattern of ridges with clusters of particles and areas of moisture within the ridges. Over two months, very small crystals were beginning to form in the deposits and within six months the sterling silver surfaces were covered with pieces of dust, fluff and fibre, (see Figure 2). The fine silver surfaces showed only small pieces of dirt, and no fluff or fibre. However, the fine silver coupons were beginning to show areas of tarnish, which have continued to develop (see Figure 3).

There was evidence from the IR spectra of a thin film coating the fingerprint on both fine and sterling coupons. This confirms an observation of Thomas and Reynoldson (1975) that a thin film was deposited on a surface under the fingerprint so that the droplets on the fingerprint had the same contact angle irrespective of the surface energy of the substrate. The composition of the film has yet to be identified and there were clearly differences between the fine and sterling silver in this respect. Combining the results from optical microscopy, the NanoFocus, and the infra-red microscopy supported our observation that the pattern of the fingerprint was stable, but that the nature of the film did change with time, probably drying and allowing contact with the air sufficient to tarnish the fine silver. On the other hand, the film on the sterling silver encouraged the adhesion of dust particles from the air. It is unreasonable to suppose that it had a significantly different composition, so it may just have been thicker and the bonding to the surface may also have differed. The IR spectra of the prints themselves showed evidence for ammonia, hydrocarbons, urea, amino acids, cholesterol, fatty acids, wax esters, phospholipids, squalene and choline, all of which could be present in a fingerprint.

Scanning electron microscopy

Routine monitoring of the samples was performed

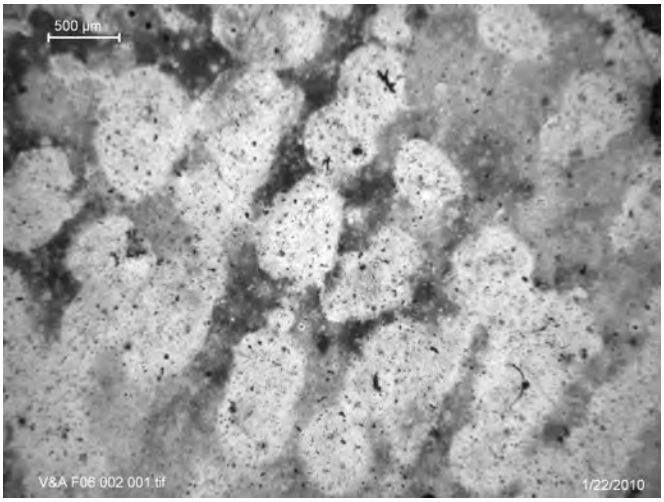

Figure 3. Detail of fingerprint on fine silver after 25 months: dark areas are tarnish.

with a JEOL 840A instrument, while high resolution images were taken with a JEOL 6480. Both instruments are equipped with an Oxford Inca energy dispersive X-ray spectrometry (EDX) system, while the JEOL 6480 additionally has Alicona MEX 3-D visualisation software.

Small area and point EDX analyses showed the presence of carbon, calcium, oxygen, sodium, sulphur, chlorine and silver in the fine silver coupons, and carbon, calcium, oxygen, copper, aluminium, silicon, sulphur, silver and less obviously chlorine in the sterling silver coupons. The sodium was present as sodium chloride crystals, which appeared to be more common on the fine silver. The aluminium recorded on the sterling silver was in a large particle with the silicon, calcium and possibly sulphur, suggesting an airborne soil particle. Organic particles were mainly fibres, for example, from paper or tissue, with few skin scales. Because the experiments were made in an environment where silicon wafers are processed, sub-micrometre particles of silicon were observed.

Copper-containing particles appeared in the sterling silver surface within two-three weeks, and by 15 months the growth of deposits on the copper-rich regions was very visible. In the mature samples, both cuprite and copper oxychlorides were observed in these deposits. After washing, a sterling sample showed only the presence of silver and copper. Clearly the copper-rich phase is attacked quickly and metal steadily removed. After two years (see Figure 4) both copper oxychlorides and silver chlorides can be detected, the silver chlorides being formed either from silver in solution in the copper-rich phase, or at the phase boundary. The implication is that the copper-rich phase in sterling silver is attacked quickly, but the early stages of corrosion are more difficult to follow in the fine silver. Nonetheless, mature samples clearly exhibit silver chloride particles growing at pits in the fine silver surface (see Figure 5). Three-dimensional software was used to enhance the visualisation of the particles and measure their size. The ones selected (see Figure 6) project about 0.5μm above the surface. An unexpected result of the corrosion process was the growth of fans of silver chloride at the boundary between the coupons and the mounts, possible assisted by moisture in the crevice at the edge of the sample. This growth has occurred on both fine and sterling samples and has caused intense pitting along the edges of the samples (see Figure 7).

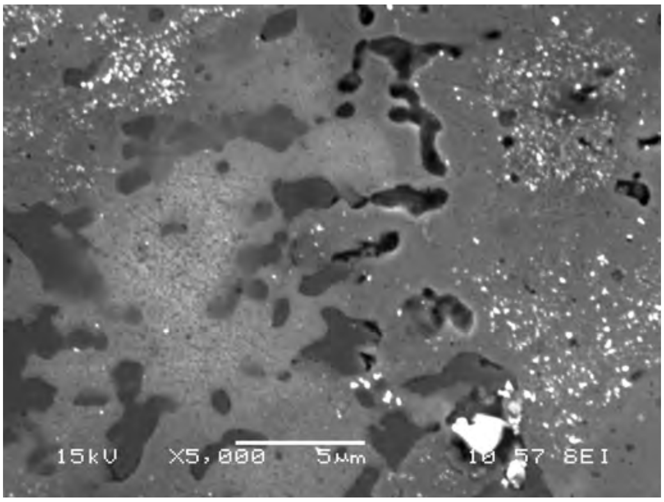

Figure 4. Pitting of copper-rich phase in sterling silver after two years.

MeV-ToF-SIMS

MeV-ToF-SIMS is a novel method of molecular surface analysis currently under development (Nakata et al. 2009). In conventional secondary ion mass spectrometry (SIMS), molecular ions are sputtered from the surface of the sample using a focussed beam of heavy ions, such as oxygen or gallium with an energy range of 20 to 50 keV. The sputtered ions are mass analysed using a time of flight (ToF) or other form of spectrometer to identify the molecular composition of the sample. In Mev-Tof-SIMS, the primary ion beam is of much higher energy, typically 10 MeV. The effect of this is that the beam creates an electronic excitation of the surface molecules leading to very efficient desorption. Initial indications show that ion yields of around 1,000 times higher are obtained allowing much lower beam currents compared with keV SIMS. Other advantages of Mev-ToF-SIMS are that the excitation of substrate ions, especially if the substrate, is electrically conducting, is much reduced, leading to enhanced surface sensitivity. In addition, other ion beam analysis techniques, such as particle induced X-ray emission (PIXE) and Rutherford backscattering (RBS) can be carried out simultaneously allowing quantitative elemental analysis. Potentially the process may be conducted in air, since the range of the high energy primary ions is several centimetres at atmospheric pressure.

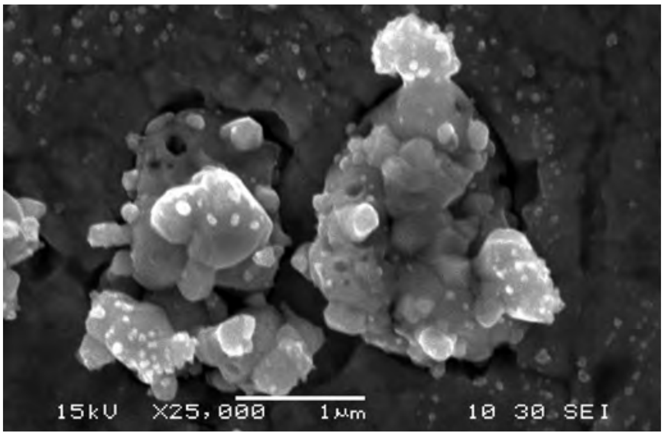

Figure 5. Detail of silver chloride crystals in pits in fine silver.

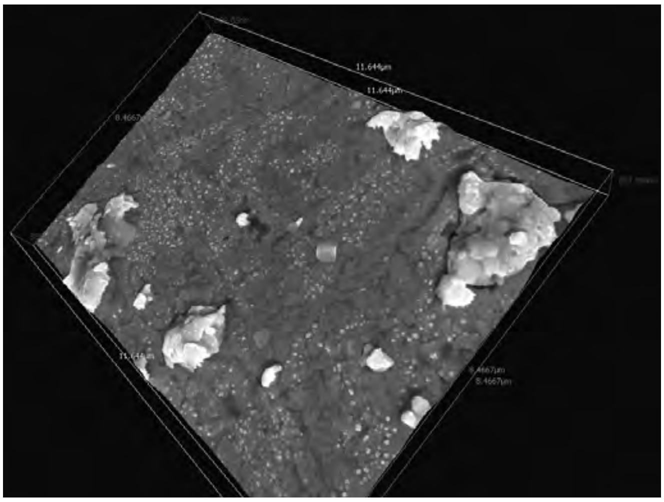

Figure 6. 3-D rendering of silver chloride clumps (one half of a stereo pair).

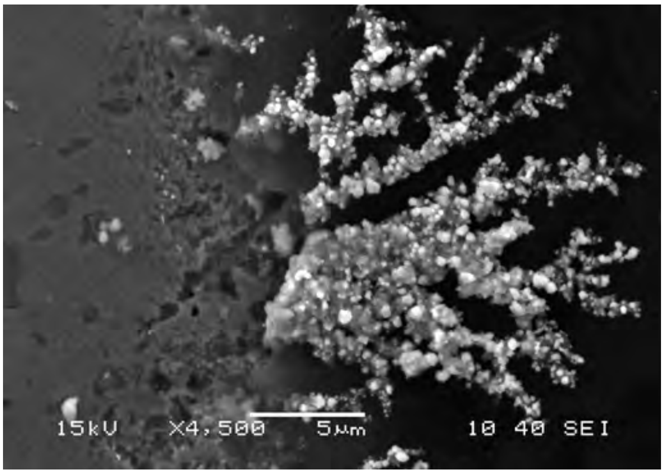

Figure 7. Fan of silver chloride crystals at edge of sterling silver coupon.

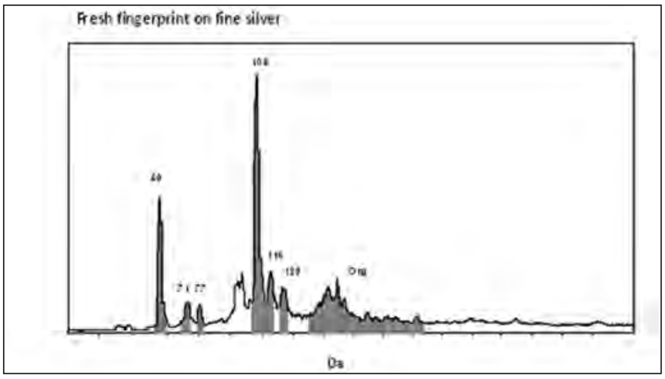

Figure 8. Mass spectrum from fresh fingerprint on fine silver.

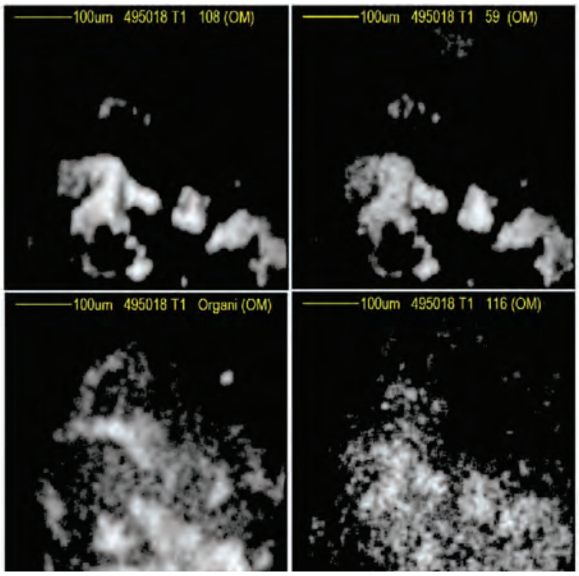

Figure 9. Distribution maps for species at 59, 108, 116 and >125Da.

At the University of Surrey Ion Beam Centre, 10 MeV $^{16}O^{4+}$ ions are focussed to a diameter of 1 – 2 µm using magnetic quadrupole lenses (Simon et al. 2004) and the beam can be scanned across the sample over an area of up to 2.5 x 2.5 mm^2. The secondary ions created by the interaction of the beam with the surface are mass analysed using a linear time of flight mass analyser with a length of 500mm. The mass resolution obtained using this system is ~1, but this will improve with time.

Experiments were carried out on a fresh fingerprint on fine silver and 18 month old fingerprints on fine and sterling silver. The mass spectrum of a small region (500 µm^2) of the fresh fingerprint on fine silver is shown in Figure 8. Because the data is collected as a three-dimensional data cube (x,y,M) distribution maps of any mass number or mass spectra corresponding to selected areas or points can be generated after the experiment is complete.

Strong peaks are observed at masses of 59, 71, 77, 108, 116, 123 and a band from 125Da upwards; maps at 59, 108, 116 and 125Da upwards are shown in Figure 9. The map for 108Da corresponds to silver and shows that even after only 12 hours silver has entered a particulate structure on the surface. The map also demonstrates how silver ions are not desorbed from the conductive silver substrate. The silver is strongly associated with a peak at 59Da. This mass corresponds to sodium chloride. While it is reasonable to see the formation of sodium chloride (NaCl) crystals on the surface after a few hours, especially after the sample has been placed in a vacuum, it is not so easy to understand how NaCl is removed as a single species. The group of peaks above 125Da gives a complementary distribution to that of silver, and comprises a number of organic species yet to be individually identified. Other distinct peaks also correspond to organic compounds but have a rather different distribution, as mapped for the peak at 116Da. Some of these peaks correspond to short chain fatty acids so that the map may depict the lipid component of the fingerprint.

Conclusions

These experiments show conclusively that fingerprints actively corrode both fine and sterling silver. Observations from optical microscopy for sterling silver, and MeV-ToF-SIMS for fine silver, show that the reactions can effectively start with the placing of the fingerprint. Possible mechanisms are not discussed here but experiments comparing natural and simulated perspiration (containing lactic acid and sodium chloride) give similar removal rates on copper, so a combination of chlorides and fatty acids are also involved in the corrosion of silver. As expected, the fine and sterling silver differed in the location of the corrosion and the resulting products, but it was not expected that other behaviours would differ, for example, protecting the sterling silver from tarnish but not the fine silver. The visible pitting of the surface means that removal of silver is required in order to clean the fingerprint, possibly as much as 2µm at a time, although this has yet to be quantified. In practical terms, this means that abrasion caused by liquid solutions employed for tarnish removal, which typically involve an acid (sulphuric or phosphoric) and thiourea, while attacking the silver surface, may not do so to a depth sufficient to remove the fingerprints. In the forensic world, though, the fact that fingerprints etch metals is a useful aid to their preservation.

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Materials

Fine silver and sterling silver strip, 15mm wide x 2mm thick for coupons

Silicon carbide grinding papers from P600 to P4000 grades and 6µm and 1µm monocrystalline diamond suspension in water

MetPrep Limited
Curriers Close, Charter Avenue,
Coventry, Warwickshire,
CV4 8AW, United Kingdom

Swarfega (contains alkanes and cycloalkanes, propylene glycol, tetrasodium EDTA, sodium benzoate, etc.)

Deb Limited, Denby Hall Way,
Denby, Derbyshire,
DE5 8JZ, United Kingdom

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Chris Salter graduated in Metallurgy and the Science of Materials from the University of Oxford in 1976. He currently works for BegbrokeNano as a materials characterization specialist, and he is part of the Electron-Microscopy Research support group of Department of Materials, University of Oxford. He is also a specialist in ancient and historic iron and associated materials.
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Q & A SESSION

Molly Carlson: On that elemental map that showed the high peak of silver, did you find any silver chloride salt?

Peter Northover: We found no peak that would correspond to silver chloride, so that's a 108 and 37 so that's a 145 so there was no clear peak for silver chloride. There didn't appear to be anything sensible at 108 other than silver because there's nothing organic there at that quantity so we took that to be particulate silver. We didn't really see a peak for chlorine so maybe the chlorine has ended up with the sodium. But there is still a lot to learn with these spectra – it's a fairly new science for us, but that is our best explanation so far. But there is particulate silver, even in 12 hours of a fingerprint being on silver, forming on the surface. So basically don't put your fingerprints on silver. Make your curators wear gloves or recruit ones with dry skin!

Tim Foecke: If anyone is interested in the cleaning material [used in the surface preparation] in the US it is sold under the brand name of 'Goop'. I come purely from a physical-mechanical-metallurgy background and I've seen a lot of comparison materials where people have something in the laboratory trying to draw comparisons especially with corrosion to things in the field, and one of the things you really need to be careful about is what is the residual stress state of your particular material. If you compare something that is cast to something that is forged for example, because if you have residual tensile stress on the surface your stretching the bonds of the atoms beyond the equilibrium position which decreases the amount of energy you need to react something into a corrosion product. So how confident are you in your comparisons of your test samples to something that may have been hammered into shape?

Peter Northover: Well, these are cut from rolled and annealed strips of silver. So the introductory slide of myself holding my slightly tarnished christening mug, which is due for polish fairly soon anyway so I thought it was safe to take that as an example of how not to treat silver. My feeling is that the samples we are looking at are pretty close to that. But in another aspect of looking at silver in experiments using backscattered electron diffraction, where you need to take all the residual strain out of the surface, this can be done by just using the conventional metallographic etch with ammonia and hydrogen peroxide since this takes off all the strain you've left by polishing… you can get a strain-free surface – so we could do that too.

Tim Foecke: You get strain-free but if your sample is not sufficiently thin, you may not be residually stress-free.

Peter Northover: Well, there's always a problem with the hydrostatic stress putting it into the mounting press, but I think it is probable that some of our objects are more stressed than some of our samples.

Amanda Morrow: This is more of a comment than a question but I have a numismatic background so this was absolutely fascinating to me. On uncirculated silver coins, if there is a fingerprint on it, the fingerprint will show up in the eventual corrosion, but the fingerprints won't show up on circulated coins and I guess that would be something interesting to look into. Do you have any thoughts?

Peter Northover: The difference is that you're not handling the coins as the coins come into your collection, whether they get cleaned or not. Because coins have been handled, they will be corroding generally, because any deposit left by the fingers will probably be spread fairly uniformly. But they will still gradually etch the silver. Whereas with a fingerprint just put and left will etch a specific pattern into the silver which is a bit more disfiguring. In an uncirculated coin which has been handled minimally, one fingerprint is really going to show up.

PANEL DISCUSSION

Corrosion And Deterioration Studies

Chair: Alice Paterakis
Panelists: Sara Goidanich, Cristina Chiavari, D.D.N. Singh, Vanessa Cheel, Peter Northover

Paul Mardikian: I'm curious about the level of relative humidity – that's a question for Sara. You said that if it gets too dry you may have stresses in your corrosion products and I wanted to know a little more about that and what you found out. It's pretty interesting because usually we try to dry as much as possible and so if you are saying there might be stresses due to the dryness and then the sudden re-hydration of the corrosion products, I'd like you to comment on that.

Sara Goidanich: This is really a preliminary conclusion, but what we have observed with our samples is that, for example, if we cure our patinas before gilding them in dry conditions then the sensors are much less stable compared to sensors that were cured in the laboratory. I should underline that we are talking about really unstable corrosion products, so most probably it's not the average situation of real artifacts. But when you have those copper chlorides, yes, we have seen that if it gets too dry then when you leave it even a few a days in the laboratory it can move, the patina can detach and I don't think this is really a corrosion problem. It's more a problem related to the transformation you have on the patina. Again, these are really preliminary results, I'd really like to study it more in detail, but I'm still applying for money for that. So I hope to have a more clear answer to that [in the future]. You can study the level of hydration, you have the means to do that, so it's not impossible. Considering the corrosion rate, of course, we have to stop it, so this is the first step. But also we should consider the transformation that we have of the patinas because most of the compounds we have, especially when we have an unstable situation, are really hydroscopic. They do transform. They move and change volume.

Tim Foecke: One of the things you can consider is using X-ray diffraction to measure the stresses at various locations around the dent. You can use a technique called sin squared psi, where you measure the location of the diffraction peak as a function of tilt angel of your detectors, and that will give you a straight line plot of sin squared of the tilt angle versus measured d-spacing, the slope of which is proportional to the stress. And if you find that indeed you do have a large tensile stress around the area, at the risk of putting forth a heresy, you are going to have to do one of two things either get the environment away from it or get rid of the stress, and to get rid of the stress you could simply heat it. Put a large induction coil around it, surround it with whatever atmosphere you want, and simply give it a 500ºC bake or 400□C bake for several days (you can trade temperature for time), and relax out the stresses and let the structure recover somewhat and that may alleviate your problem.

We have used the X-ray diffraction technique to measure the stresses in situ on the cables in the Brooklyn Bridge, for example.

D.D.N. Singh: Unfortunately, we were not successful in getting [a sample] of the rust from the surface, but another colleague did XRD and Raman on the rust and he found that it was magnetite and maghemite. So that reinforced our approach of explaining why that the corrosion is taking place so fast and the other surface is not getting rusted. It is because of the formation of maghemite film on the surface…. I have not included that with what I have presented here, as that was a different laboratory. One of my colleagues, Achal Pandya is trying to get rust samples from the surface of the pillar so that maybe by the next Metals committee meeting we will be able to give more findings in this area.

Bruno Pouliot: This is a question mostly for Peter. In your study so far, have you found a relationship between the time that the fingerprint is left on and a recommendation you could make on when it should be removed? When you see a fingerprint first on a silver piece, should you just go and remove it? Or if some of the harm has already been done after a certain period, is it OK to leave it for another two years before you clean it? What would be your recommendation based on your observations so far?

Peter Northover: My feeling is that you either remove it as soon as you make it or it does eventually become stable. This is a project done with no funding in our spare time, and with a lot of help from Vanessa doing the monitoring, but it does seem to reach a steady state. And so if you spot a fingerprint and you don't know how long it's been there, probably it doesn't matter so much and you can leave it for a long while because we have demonstrated that the fingerprint attacks the silver straightaway. To avoid having to remove metal unnecessarily to polish it, it is best, if you can, to remove the fingerprint straightaway.

Vanessa Cheel: What we don't have is measurements of the pitting that has continued to happen over two or three years, so we can't say how much damage is being caused, it certainly is happening. You've got minimal pitting – something happens immediately, but it happens relatively slowly, so you've got a day or two before you need to send the housemaid in to clean last night's silver. But you probably want to be cleaning your silver within six months of putting fingerprints on so you can carry on handling it for six months, and then you're taking off some damage but it's not a vast amount of damage and then it appears to accumulate at a slower rate over the next 18 months or two years.

Bruno Pouliot: Yes that's very interesting, because at Winterthur we coat most of the silver that we have on display in period rooms, so therefore it is coated with a cellulose nitrate lacquer and we've been doing this systematically since the 1980's. So in the summer of '09 we did a survey of 1500 objects that were lacquered, and interestingly we found a few that had fingerprint corrosion despite the lacquer. My immediate thoughts were how is this happening through the coating, but then we realized that they must have been touched before the coating was applied, and even despite the coating, what happens is that, although we haven't done the type of analysis that you've done, but the fingerprint residues undermine the adhesion of the coating to the silver and eventually a tarnish pattern forms where the fingerprint was, and you could even tell where the thumb print touched more because this is where the coating will begin to lift. It will be interesting for us to figure out if the pattern and type of corrosion that develops is identical because it does develop underneath a compromised coating.

Peter Northover: The real reason why we haven't got the measurements that we'd like is simply the practical problem of cleaning the fingerprint residues off without noticeably damaging the damage that had been done, so we could measure it. It proved to be a major headache, getting rid of the fingerprint so we could, with [Alicona] MeX software, just measure the profiles of the pits. We are not entirely sure whether we got that right yet, so that's why we haven't added that result in. We are not sure we can produce a convincing measurement that is entirely due to the effect of the fingerprint.

Maickel van Bellegem: I treated a silver object that had a [finger] print. I gave it a relatively light clean. Visually it was clean, but after a while when it came back from loan you could see the fingerprint again. Possibly, the etching effect of the fingerprint creates a variation of the surface and susceptibility to tarnishing. It creates damage.

Peter Northover: So the consensus from collective experience seems to be that fingerprints are as serious of a problem that we thought they were when we started.

Molly Carlson: I have two questions for Dr. Singh. Concerning the cast iron decorative top to the pillar, do you think that is a later addition or is it original to the pillar?

D.D.N. Singh: It has been found that it is cast iron and maybe that it was fabricated later on. It was fabricated later on because it was damaged by some of the invaders, so that part is newer compared to the lower part. At that time that cast iron technology was not available, fifteen hundred years back when this pillar was made. My perspective is that it is totally cast iron. This means that it was made by someone later on, maybe two or three hundred years back.

Molly Carlson: Do you see any extra corrosion of the cast iron touching the original pillar?

D.D.N. Singh: Cast iron corrodes slowly compared to pure iron, that's why in one of the slides I have shown the corrosion rate of cast iron of the top was much slower compared to the body of the pillar. When the rust develops on the surface it converts into stable rust, that is called maghemite, then the corrosion rate becomes 50 times slower compared with cast iron or other steel.

Molly Carlson: The part of the pillar that is underground – were you able to look at that for a sample?

D.D.N. Singh: As a matter of fact, unfortunately when this pillar was erected people did not know about galvanic corrosion. So, in the bottom of the pillar that is underground, to keep it in a standing position, they had put a very huge block of lead because it is very heavy. This lead and the iron are very important in galvanic corrosion. When the pillar was excavated in 1960 by the Archaeological Survey of India, it was found that the lead was there. So, the proposal was that the lead should be removed and zinc should be put there instead as it will be sacrificial and protect the iron. Unfortunately this was not allowed at that time by the Government, so it [the lead] is still there, and although we don't know, if you see that interface at the floor level and just above, you will find very clear severe corrosion is taking place because of galvanic corrosion.

James Crawford: I have a question for Sara regarding the display cases of the doors. During your discussion you outlined the nature of the open display case. I was wondering, during your presentation you mentioned conceptually how the closed display cases work, and I wanted to know how the closed cases were controlled in terms of relative humidity?

Sara Goidanich: It is explained in the paper, however, the closed case we purged with nitrogen and then it was sealed. We had a detector for oxygen content and then we just checked that the oxygen was completely removed. The showcase with low and controlled humidity is a continuous very slow flow of air; we have two lines of air, one is completely dry and other one passes through a water-bubbling system. Then there is a chamber before the showcase where the two air air flows are mixed and then you monitor the humidity in this chamber before entering the showcase so that you should be sure to have more or less the same levels of humidity. In addition, we added absorbers in both of the showcases, so if for any reason like temporary failures of the system, the absorbers should guarantee the required level of humidity.

Sara Creange: This for Peter – I want to thank you for this study because I think it is something that everybody in conservation is encountering all the time and wondering how serious a problem it is. We also get it [fingerprints] on gold, gilt objects and brass where it is especially difficult to get rid of. A few practical comments, something that would maybe help you to get your fingerprints off without abrading too much is an ultrasonic bath with some surfactants as well. I think there is no good answer to that anyway, but..another tool that we are looking into acquiring at the Rijksmuseum is the Herox microscope with which you can very easily measure depths of etched lines. It would be nice to do a study of the etching over time in different materials.

Peter Northover: Yes, we did try ultrasonic with surfactants and it didn't help too much.

Lisa Young: We did a study on aluminum alloys on space suits about 10 years ago and found the same thing with the etching with the sweat from the astronauts and I didn't know to go to the fingerprint route to find someone who was studying the same thing. But we were getting those large peaks - I think Lyndsie [Selwyn] did the analysis – of sodium chloride in our corrosion products. They were completely being eaten away. I don't know if anyone else has seen this on aluminum alloys. They are only about 40-50 years old, and none of the other alloys that were in contact with sweat have these problems – like the neck, or buttons on the spacesuits.

Peter Northover: It might make sense from what I am hearing to try and recruit a student to look at fingerprints on a variety of materials and if you go to the fingerprint literature, and there are some references in the written paper about recipes for artifical sweat to do even more controlled experiments.

Lisa Young: I am interested because the sweat from the astronauts, although they were sometimes in the suit 12-18 days, it seemed to have been wicked to the surface by an inner glove they wore and then held the sweat against the aluminum. But because it is not direct contact like the fingerprint we need to do more work and find out if that is really true.

Rosmarijn van der Molen: Do we know for certain that fingerprints do not eat through our lacquers?

Peter Northover: It is likely, given what's in a fingerprint, that certainly it will attack some organic coatings and possibly not attack others.

Vanessa Cheel: The content of your fingerprints depends on what you have been eating, which is why my fingerprints and Peter's fingerprints have had different effects on all the things we've handled.

Tom Chase: This is for Sara. I'm very interested in the corrosion test cells that you were using for the data. You showed one slide that showed that they seem to degrade with time, so the signals were changing with time. That is very interesting and I think some more research along those lines would be good. Perhaps you would want to include a membrane or something more porous to hold the corrosion products between the gold and the bronze so that you would get more rapid exchange of species. I am wondering if those are mostly measuring humidity?

Sara Goidanich: Honestly I do think we have quite a good exchange with the environment the way we obtained the gilding. It was really a thin layer and unfortunately since our corrosion products were moving a lot, changing the relative humidity, we broke the layer. So the problem of the degradation of the sensor was that we were losing the continuity of the gilding so at the end of the experimentation, the samples that were in the laboratory had just a very little border of gilded surface, and the rest had just gilded patches. So what we would reduce was the cathodic area so this is the reason why we decreased the current that we can detect with time. I will consider your suggestion because now I am trying to have a different kind of gilding, we are trying gold leaf that will be definitely less porous, so this is something I don't like but I noticed that especially in some conditions I can see the [corrosion] products coming out from the gold leaf, so I believe there is quite a good exchange with the environment. The other point is that we didn't want to introduce anything that normally we wouldn't find in real cases. We are already a little bit far from reality because we know that when we produce artificial samples, it's never the truth so we are trying to remain as close as possible to the reality.

Tom Chase: There are two things I would like to mention. Fred Freikor, years ago, was making similar cells, not gilding, with plates and intermediate membranes to measure time of wetness outdoors, and this was a very useful concept. You might look back at Fred's publications about these. And the other thing is to make relatively reproducible membranes, high voltage discharge will be able to penetrate through and give you a penetrable membrane, and you might want to look into that too.

Sara Goidanich: We tried, not high voltage, but electrochemical patination, and surprisingly the patina was too conductive. I didn't have time to study why but it seems that some parts of the alloy, I don't know if it was lead or some other part, was included in the patina we were obtaining by electrochemistry. So it was maybe more representative of the real cases but not good for our purposes because if the patina is too conductive then we lose the macrocouple current and we do not detect it. I will try with higher voltages but I am worried that it will be the same problem.

Jean-Bernard Memet: This is a question for Cristina, I wanted to know if you had done some analytical tests on the corrosion products, not on the sculpture but on the base of the sculpture? Cleaning the base of the sculpture – in France for example – is a huge problem for restorers, because it is very difficult to clean it without affecting the mineral substrate. We are working now on it, and it is very difficult to have a good method to do it. I was wondering if analyzing the composition of these corrosion products on the base will not serve as an indicator of the solubility or insolubility of the corrosion products on the sculpture itself?

Cristina Chiavari: Partially, yes I think, I have never analyzed these products, but I think that they should be carbonates (copper, lead), or sulfate, maybe with marble you can have these types of reactions. Obviously the more compounds you find on the base of your sculpture, this means that you patina is soluble. But we have never analyzed copper salts, which interact with marble. Of course it's an indication of the solubility of the patina. But you will never find tin compounds, I am quite sure.

X-RAY FLUORESCENCE ANALYSIS

Session Chair: Tom Chase

AN EVALUATION OF INTER-LABORATORY REPRODUCIBILITY FOR QUANTITATIVE XRF OF HISTORIC COPPER ALLOYS

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Abstract

This paper reports the results of a study conducted to evaluate the current state of inter-laboratory reproducibility when conducting quantitative XRF analysis of historic copper alloys. Fourteen institutions, primarily from the museum community, participated in the study, using a total of 19 X-ray fluorescence instruments. The design of the study was based largely on ASTM standard E1601, Standard Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method. *In addition to addressing overall inter-laboratory reproducibility, we also attempt to evaluate the accuracy of individual laboratories. By determining correlations between accurate results and experimental methods and procedures, we are able to propose recommendations regarding best practice and ways in which reproducibility might be improved.*

Keywords: inter-laboratory reproducibility, X-ray fluorescence, copper alloys, fundamental parameters, ASTM E1601

Introduction

Since at least the late 1950s, a number of papers have been published that report quantitative analyses of historic copper alloys based on X-ray Fluorescence Spectroscopy (XRF). With the recent widespread introduction and adoption of relatively low-cost, portable XRF spectrometers, the pace of publication of such data is increasing and is likely to accelerate further. Although we welcome these advances, the rapid proliferation and publication of XRF data raises a host of important questions concerning the accuracy and inter-laboratory comparability and reproducibility of published data. While within laboratory conclusions based on quantitative XRF analysis may be interesting and instructive, comparing data between laboratories, or even between different instruments within a laboratory, can be problematic. Traditionally, such issues have been dealt with via formal or informal inter-laboratory analyses in which common reference materials are measured (e.g., (Glascock 1999, Hein 2002)). Since W. T. Chase's signal 1974 paper, 'Comparative analysis of archaeological bronzes' (Chase 1974), we know of only one other published study that has attempted to evaluate the inter-laboratory reproducibility of quantitative XRF on historic copper alloys (Northover and Rychner 1998). Neither of these publications focused primarily on XRF, but rather on reproducibility *between* techniques. Both publications also focused on copper alloys where the primary alloying metals were tin and lead.

Building on an earlier workshop and XRF round-robin organized by the Getty Conservation Institute, the National Gallery of Art in Washington hosted a seminal meeting in 2007 of representatives from seven museums to address issues surrounding the sharing and comparability of quantitative XRF data between institutions. That meeting, sponsored by Robert H. Smith and the Center for Advanced Study in the Visual Arts, focused on these issues particularly as they relate to the analysis of Renaissance bronze sculpture. Moderated by then Senior Curator of Sculpture, Nicholas Penny and Head of the Object Conservation Department, Shelley Sturman, the participants agreed that the ability to compare data would be valuable, but enumerated a host of problems and obstacles to be overcome before meaningful inter-laboratory comparisons could be made. This study is a direct product of that encounter.

The program described here is an attempt to evaluate the current state of inter-laboratory reproducibility of quantitative XRF analysis of copper alloys. We conducted, interpreted and summarized data generated from a carefully designed study informed by ASTM standard methodology (ASTM 2006, ASTM 2003). By quantifying the extent of reproducibility, we hope to provide valuable quantitative guidelines for practitioners who might wish to compare their own quantitative data with that generated by other laboratories, or who might wish to pursue meta-studies based on the work of many laboratories.

Our study sought participation primarily from laboratories in the museum community whose interests include a focus on historic copper alloys. In addition, we sought to include a variety of instrument types, supported by a variety of quantification procedures and software.

In addition to addressing overall inter-laboratory reproducibility, we also attempt to evaluate the accuracy of individual laboratories. By determining correlations between accurate results and experimental methods and procedures, we are able to propose some recommendations regarding best practice.

Methods

Research Design

Seventeen institutions agreed to participate in the study. Of these, many hoped to produce multiple data sets by using more than one instrument or by processing data from one instrument using multiple methods. Therefore, the maximum number of data sets anticipated was 30. In order to maintain anonymity throughout the study, each institution was assigned a laboratory number for each anticipated data set. This number was known only to the members of that institution and to the program coordinator (Heginbotham). Fourteen, or 82%, of the institutions turned in complete results and the total number of data sets included in the study is 19. In one case, the same instrument was used to produce three data sets by processing the same raw spectra using three different methods[1].

Eight instruments were used in the study. These include Bruker/Keymaster Tracer, Bruker/Roentec Artax, EDAX Eagle 3, Elva-X light, Innov-X XT-260, Niton Gold, Spectrace Omega 5, and laboratory-built models. While many laboratories chose to use the manufacturer's proprietary software for quantification, many others used or created customized solutions, ranging from spreadsheet-based analysis, to complete programs written in-house, to the use of X-ray analysis software available on the Internet.

The design of the study was based largely on ASTM standard E1601, *Standard Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method*, following Test Plan A. Each participating laboratory was asked to analyze a set of 12 samples of metal (designated A-L). The same sample set was circulated to each participant via a traceable shipper over the course of eight months. The test samples consisted of three types: 1- cuttings obtained from reference materials[2] (RMs) n=4; 2- pieces of historic metal, n=6; 3- small ingots prepared by the lead author, n=2. The range of elemental compositions included in these samples was tailored to imitate the broad range can be found in historic copper alloy artifacts from the Bronze Age through the 19th century. A table presented in the *Results* section below provides brief descriptions of the 12 samples, their approximate compositions, and the range of concentrations determined for each element.

On each sample, a circular site was selected for analysis with a diameter of approximately 9 mm. These sites were first flattened with 220-grit silicon carbide abrasive paper. They were then polished with successively finer grades of Micro-mesh™ abrasive cloths, finishing with 4,000-grit. All polishing was done wet in ethanol, and fresh abrasive was used for each sample. The sites designated for analysis were clearly circumscribed on each sample with a stylus, ensuring that the material analyzed would be the same across laboratories. The samples were individually bagged and placed in a padded case for transport. Participants were asked not to touch or otherwise disturb the sample sites.

Per ASTM standard E1601, each laboratory was asked to conduct triplicate analyses of each area on each sample according to their standard in-house procedures. Participants were asked to conduct analyses that would yield a result representative of the entire area. In addition, the three measurements were to be acquired in immediate succession with as little variation in procedure as possible.

Data Recording and Accumulation for Analysis

Each participating laboratory completed a standardized reporting form in spreadsheet format for each instrument used. If the same instrument was used in conjunction with more than one quantification method, a separate form was completed for each method employed. For every analysis, participants were asked to report on a minimum of 12 elements. These elements were Mn, Fe, Ni, Cu, Zn, As, Ag, Cd, Sn, Sb, Pb and Bi. Space was provided to report on additional elements if they were detected. If a quantitative result for a requested element could not be obtained, analysts were asked to choose from the following responses: BDL – below detection limit/not detected; Trace – element present in a small amount but not quantifiable; Present – element present in a significant amount but not quantifiable; N/A – element not analyzed for/not detectable by this instrument. Data for each sample from all laboratories were compiled in a master database for evaluation.

The reporting form provided to the participants also requested extensive detail about the instrument, software, and procedures utilized in each laboratory. Participants were asked to provide information about their instrument manufacturer, model, anode material, and detector type. Participants also reported on operating parameters, including voltage (kV), current (mA), measurement time, spot size, filters, typical number of live (valid) counts collected by the detector per second, and average dead time. Participants also reported the software and methodology used for quantification. This included the full name and version of software, the type of method used, the number of standards used, and the frequency of calibration checks and recalibration. In addition, participants were asked to report their errors and detection limits for each of the 12 elements listed above, and to specify how these values were determined.

Assessment Methods

Reproducibility Statistics

In general, our evaluation followed the guidelines presented in the ASTM E1601 (test plan A). For each set of triplicate results for a particular element in an individual sample, the mean result ($\bar{x}$) was calculated. The overall group mean ($\bar{X}$) was then calculated as

$$\bar{X} = (\Sigma \ \bar{x}) \ / \ p$$

where p = the number of laboratories reporting a quantitative result for that element. For each $\bar{x}$, the laboratory difference (d) was calculated as

$$d = \bar{x} - \bar{X}$$

The standard deviation of all laboratory differences ($s_{\bar{x}}$) was then calculated for each element in each sample as

$$S_{\bar{x}} = [\Sigma(d^2) / (p\text{-}1)]^{1/2}$$

These preliminary calculations allowed the calculation of a between-laboratory consistency statistic, designated as h, that provides a normalized measure of the difference between the reported result and the overall mean value of all laboratories' results for the same element and standard:

$$h = d / s_{\bar{x}}$$

Comparison of the h statistics to a table of critical values allowed outlying results, that is, results that deviated significantly from the overall group mean, to be identified and flagged for follow-up. Laboratories with flagged results were contacted and asked to check their records to see if any errors in procedure, analysis, or transcription of results could be identified. If any such errors were identified, the data were corrected, but if no errors were found, the data were retained as originally reported. Of 1,718 h statistics that were calculated, 48 (2.8%) were flagged as identifying outliers and 20 corrections were made by four laboratories.

Once errors were corrected, reproducibility statistics were calculated for each of the 12 requested elements in each sample. The reproducibility index (R) is a measure of precision and represents the expected variability of results when a method is used in different laboratories. Specifically:

> *Use R to predict how well your results should agree with those from another laboratory: First, obtain a result…, then add R to, and subtract R from, this result to form a concentration confidence interval. Such an interval has a 95% probability of including a result obtainable by the method should another laboratory analyze the same sample. For example, a result of 46.57% was obtained. If R for the method at about 45% is 0.543, the 95% confidence interval for the result (that is, one expected to include the result obtained in another laboratory 19 times out of 20) extends from 46.03 to 47.11%* (ASTM 2003).

The reproducibility index was calculated as:

$$R = 2.8\{(s_{\bar{x}})^2 + [(\Sigma(s^2) / p)\ (n\text{-}1) / n]\}^{1/2}$$

where s = the standard deviation of each laboratory's replicate measurements and n = the number of replicates (in this case, three[3]).

Finally, the percent relative reproducibility index ($R_{\text{rel}}\%$), which represents R as a percentage of the overall mean, was calculated according to the formula:

$$R_{\text{rel}\%} = 100R / \bar{X}$$

Lower Limits

A lower limit (L) was calculated for each element (with the exception of copper) below which the method is not considered reliable. This calculation was made according to the formula

$$L = 100R / e_{\max}$$

where R = element reproducibility index determined for the sample with the lowest concentration of the specific element, and $e_{\max}$ = maximum acceptable percent relative error. In this case, $e_{\max}$ was set to 50% based on ASTM guidelines.

Accuracy of Overall Median

It was hypothesized that the overall group median $\bar{\chi}$ would likely be a good approximation of the true concentration of each element in a sample. If true, then $\bar{\chi}$ values could be used to gauge the accuracy of individual laboratories for samples A-H. In order to verify this hypothesis, the accuracy of $\bar{\chi}$ values was evaluated for the four RMs (samples I-L). For each certified value (X) in the RMs, the percent error of the median was calculated:

$$\%\ \text{error} = 100(\ \bar{\chi} - \text{X}) / \text{X}$$

Certified values that fell below the method's calculated lower limit (L) for that specific element were not considered in evaluating accuracy. The mean percentage error for all elements in the RMs was calculated using the absolute values of all percentage errors where X > L.

Ranking of Laboratories

The accuracy of each laboratory/instrument combination was evaluated on an element-by-element basis. For each quantitative result from a given laboratory, the laboratory difference from the assumed 'true' value (d_t) was calculated. For the four RMs (samples I-L), this was calculated as

$$d_t = \bar{x} – X$$

(recall that $\bar{x}$ = the laboratory's mean result and X = the certified value). For the non-reference samples (A-H) d_t was calculated as

$$d_t = \bar{x} - X_m$$

where X_m = the median value of all laboratory results.

If $X_m < L$ (the method's lower limit as defined above), then X_m was considered to be unreliable as a measure of the true value; therefore no *d* values were calculated and the element was not used for ranking purposes. As an added precaution, if fewer than 10 laboratories reported data for an element in a given standard, no *d* values were calculated and the element was not used for ranking purposes.

A normalized accuracy statistic (h_a) was then calculated by dividing the laboratory difference by the standard deviation of laboratory differences.

$$h_a = d_t /(\Sigma(d_t^2) / (p\text{-}1))^{1/2}$$

where p = the number of laboratories reporting a quantitative results for the element in the given sample.

For each laboratory, all h_a values for a given element were combined to generate a mean accuracy score ($S_{element}$) for that element according to the formula

$$S_{element} = \Sigma(h_a^2) / n$$

where n = the number of quantitative results reported for the given element for all 12 samples. Scores close to zero reflect results that are consistently close to the assumed true value[4].

All 19 laboratories reported quantitative results for Cu, Zn, Sn and Pb (hereafter referred to as the 'major elements'). An aggregate score for major elements (S_{major}) was calculated:

$$S_{major} = S_{Cu} + S_{Zn} + S_{Sn} + S_{Pb}$$

Only 15 laboratories reported quantitative results for all four of the elements Fe, Ni, As and Sb (hereafter referred to as the 'minor elements'). An aggregate score for minor elements (S_{minor}) was calculated for these laboratories:

$$S_{minor} = S_{Fe} + S_{Ni} + S_{As} + S_{Sb}$$

Only eight laboratories reported quantitative results for Bi, so S_{Bi} was not included in the calculation of S_{minor}. S_{Ag} also was rejected for inclusion in S_{minor} because the reproducibility of results for Ag was so poor that the median results (X_m) were not considered to be valid indicators of the true value.

Mn and Cd were sporadically reported by only a few laboratories, making any meaningful comparisons or calculation impossible. Consequently, discussion of these elements is omitted.

Correlations Between Accuracy Scores and Methods

Accuracy scores were compared with the descriptions of instrument specifications, operating parameters and methodology provided in the laboratories' reporting forms. In an attempt to identify 'best practices', we sought to identify characteristics that were common to the most accurate laboratories. No attempts were made to be quantitative in this assessment. Rather, general correlations were identified by simple graphical plotting of the data.

Results

Table 1 provides a summary of laboratory data collected in the reporting forms. Table 2 gives brief descriptions of the 12 samples along with their approximate compositions, and the range of concentrations covered by the set as a whole. For samples A-H, the values are based on the overall group median; for samples I-J, values are as listed by the manufacturer of the RM. Lower limits for samples A-H were defined as described in METHODS. The complete quantitative data reported by all laboratories is available at the following address:

http://www.getty.edu/museum/conservation/papers.html

Reproducibility Statistics and Lower Limits

Summary statistics as per ASTM for the eight most commonly identified elements are presented as a group in Table 3. For each element, the samples, or test materials, are sorted by overall mean weight percent. The method's lower limit (L) for each element is shown on the right side of the relevant sub-table except in the case of copper, for which no lower limit was calculated. A dashed line through the center of each sub-table separates materials whose overall mean concentration falls below L (above the line) from those where the mean is greater than L (below the line). The latter group constitutes the samples for which the method is considered valid. The mean value of the $R_{rel\%}$ statistics for these samples is shown at the bottom right of each sub-table. This statistic provides the most succinct summary, for each element, of the analytical reproducibility that may be currently anticipated within this group of laboratories, based on a 95% confidence interval.

Evaluation of Accuracy

Data for the four RMs are presented in Table 4. This table shows the group's overall median ($\bar{\chi}$) for all elements where reference or certified values are given. Percent errors are shown for elements where $\bar{\chi} > L$. The results show that, on average, $\bar{\chi}$ falls within 5% of the certified value in cases where $\bar{\chi}$ lies in the range of validity for the method. It was determined that $\bar{\chi}$, if greater than L, could be used as a reasonable approximation of the true value for the purposes of evaluating the accuracy of individual laboratories.

Laboratory Number	Tube target	Detector Type	kV	mA	Acqusition Time (s)	Spot size (mm)	Filters (element)	Counting rate (cps)	Quantification method	Number of Standards
1	Rh	PIN	40	2.5	90	6	Al Ti Cu	3500	Empirical	27
2	W	PIN	45	7.5	100	8	Ni Al	4800	FP	0
3	Re	PIN	40	1	400	6	Al Ti	5000	FP w/stds	29
6	Rh	SDD	50	0.6	600	0.05	Ti Co Pd	8000	FP w/stds	19
7	Re	PIN	40	1	400	6	Al Ti	6000	FP	0
8	Mo	SDD	50	0.8	300	0.9	None	30000	FP w/stds	4
9	Rh	Si-Li	40	0.1-0.3	300	0.054	None	10000	FP	0
10	Rh	Si-Li	45	1	100	8.5	Rh	6800	FP w/stds	8
12	Mo	SDD	50	0.6	150	0.07	none	4800	Empirical	12
13	Au	SDD	40	40	400	8	Ag	95000	FP w/stds	8
14	Rh	PIN	40	1.4	120	6	Al Ti	6000	Empirical	73
15	Rh	PIN	40	1.8	60	6	Al Ti	6300	Empirical	45
18	Rh	PIN	40	1.8	180	6	Al Ti	7300	Empirical	46
19	Rh	PIN	40	0.1	600	2.6	Ni V	700	FP w/stds	19
22	Re	PIN	40	1.5	400	6	Al	6500	Empirical	36
23	W	SDD	50	0.2	200	1.5	Ni	16000	Empirical	5
24	Ag	PIN	35	6	60	10	Al	5000	FP w/stds	5
27	Rh	PIN	40	0.003	300	5	Al Ti Cu	6250	Empirical	125
28	Rh	SDD	50	0.35	200	1.5	None	60000	Empirical	15

Table 1. Summary of laboratory data.

Sample:	A	B	C	D	E	F	G	H	I	J	K	L		
Description	Chinese Coin (unknown date)	Italian Upholstery Tack (17th Century?)	British Door Knob (18th Century?)	American Screwdriver Ferrule (19th Century)	British Auger Cover Plate (19th Century)	Laboratory-cast Ingot	Laboratory-cast Ingot	Dutch East India Company Coin (1754)	Brammer C934 (RM)	CITF B32 (CRM)	MBH 31X B27 A (CRM)	BNF C71.34-3 (CRM)	Minimum	Maximum
Fe	0.55	0.22	<0.17	<0.17	0.41	0.82	0.41	<0.17	0.01	0.1	0.31	0.29	0.01	0.82
Ni	<0.35	0.35	<0.35	<0.35	<0.35	0.96	1.1	<0.35	0.49	1.49	0.042	-	0.04	1.5
Cu	71	82	75	85	70	53	72	98	82.64	74.85	78.2	87.23	53	98
Zn	<0.79	9.3	22	3.6	28	34	3.0	<0.79	0.17	1.15	19.9	1.55	0.17	34
As	0.47	<0.25	<0.25	<0.25	0.29	2.52	0.93	0.25	-	0.0056	0.03	0.18	0.01	2.5
Ag	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	0.17	<0.15	-	-	-	0.025	0.03	0.17
Sn	4.1	4.6	<0.27	8.5	0.53	2.8	16	<0.27	8.1	5.9	0.92	8.2	0.53	16
Sb	0.22	0.12	<0.12	0.13	<0.12	3.0	1.9	0.87	0.14	0.13	0.04	0.071	0.04	3.0
Pb	24	3.3	1.9	2.3	<1.22	1.4	3.9	<1.22	8.45	16.1	0.24	2.47	0.24	24
Bi	<0.12	<0.12	<0.12	<0.12	<0.12	0.32	0.18	<0.12	-	-	0.055	0.029	0.03	0.32

Table 2. Compositions and descriptions of the 12 samples (A-L) used in the study. For samples A-H, values are based on the overall group median; for samples I-J, values are as certified by the manufacturer. Lower limits for samples A-H were defined as described in METHODS.

Iron - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
I	7	0.023	0.083	353	Calculated Lower Limit (L)
H	11	0.029	0.062	216	
J	17	0.126	0.192	153	0.165
C	18	0.135	0.156	115	
D	19	0.151	0.213	141	
B	19	0.236	0.303	128	
L	19	0.283	0.356	126	
K	19	0.363	0.412	113	
E	19	0.420	0.459	109	Mean $R_{rel\%}$ for $\bar{X}>L$
G	18	0.427	0.569	133	
A	19	0.592	0.696	118	121%
F	19	0.902	1.101	122	

Arsenic - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
K	10	0.041	0.074	179	Calculated Lower Limit (L)
I	5	0.054	0.142	262	
J	4	0.067	0.280	417	0.246
D	11	0.144	0.573	399	
C	14	0.146	0.231	159	
B	7	0.176	0.764	435	
L	13	0.213	0.746	350	
H	16	0.247	0.249	101	
E	16	0.291	0.337	116	Mean $R_{rel\%}$ for $\bar{X}>L$
A	10	0.444	0.489	110	
G	15	0.908	0.873	96	110%
F	16	2.558	3.261	127	

Nickel - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
K	12	0.074	0.177	238	Calculated Lower Limit (L)
C	10	0.082	0.240	292	
E	15	0.092	0.174	189	0.354
D	7	0.100	0.281	281	
A	12	0.145	0.211	146	
L	4	0.164	0.584	356	
H	14	0.197	0.267	136	
B	18	0.378	0.273	72	
I	17	0.462	0.242	52	Mean $R_{rel\%}$ for $\bar{X}>L$
G	17	1.040	0.582	56	
F	18	1.066	0.732	69	61%
J	18	1.475	0.820	56	

Tin - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
H	5	0.053	0.136	255	Calculated Lower Limit (L)
C	13	0.112	0.132	118	
E	19	0.529	0.235	44	0.271
K	19	0.866	0.315	36	
F	18	3.092	2.176	70	
A	18	4.320	1.660	38	
B	19	4.687	1.295	28	
J	19	5.951	2.330	39	
D	19	8.543	1.804	21	Mean $R_{rel\%}$ for $\bar{X}>L$
I	19	8.554	2.225	26	
L	19	8.608	3.953	46	40%
G	18	17.166	9.082	53	

Copper - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
F	19	53.249	10.289	19	Calculated Lower Limit (L)
E	19	69.855	3.031	4	
A	19	70.508	13.163	19	n/a (see note a)
G	18	71.481	8.980	13	
J	19	73.935	7.083	10	
C	19	75.236	3.123	4	
K	19	78.234	2.590	3	
I	19	81.758	2.701	3	
B	19	81.795	3.930	5	Mean $R_{rel\%}$ for $\bar{X}>L$
D	19	85.266	2.493	3	
L	19	86.209	6.725	8	8%
H	19	98.130	2.694	3	

Antimony - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
E	5	0.026	0.064	247	Calculated Lower Limit (L)
C	6	0.029	0.064	220	
K	8	0.030	0.060	199	0.120
I	13	0.126	0.252	200	
B	13	0.156	0.400	257	
D	12	0.157	0.259	165	
J	13	0.171	0.418	244	
L	11	0.177	0.932	528	
A	14	0.211	0.277	131	Mean $R_{rel\%}$ for $\bar{X}>L$
H	16	0.882	0.473	54	
G	16	1.857	0.738	40	185%
F	17	3.020	1.450	48	

Zinc - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
A	6	0.209	0.710	340	Calculated Lower Limit (L)
H	9	0.240	0.396	165	
I	12	0.315	0.401	127	0.792
J	19	1.132	1.016	90	
L	19	1.653	0.927	56	
G	18	3.005	1.127	38	
D	19	3.669	1.121	31	
B	19	9.376	1.799	19	
K	19	19.873	1.762	9	Mean $R_{rel\%}$ for $\bar{X}>L$
C	19	22.312	2.003	9	
E	19	27.733	1.968	7	31%
F	19	33.600	6.026	18	

Lead - Statistical Summary

Test Material	Number of laboratories (n)	Overall Mean ($\bar{X}$)	Reproducibility Index (R)	Percent Relative Reproducibility Index ($R_{rel\%}$)	
H	17	0.178	0.609	343	Calculated Lower Limit (L)
K	19	0.269	0.397	148	
E	19	1.033	0.693	67	1.217
C	19	1.939	0.670	35	
F	19	2.234	6.701	300	
D	19	2.283	0.659	29	
L	19	2.860	1.909	67	
B	19	3.247	1.210	37	
G	18	3.816	3.084	81	Mean $R_{rel\%}$ for $\bar{X}>L$
I	19	8.650	2.642	31	
J	19	17.346	10.256	59	77%
A	19	24.628	13.570	55	

a. Lower limits are only calculated where the element is to be analyzed near the lower end of its effective concentration range

Table 3. Statistical summaries; for each element, the samples are sorted by overall mean weight percent.

Ranking of Laboratories

Laboratories S_{major} and S_{minor} scores are shown in Table 5, ranked in order of highest to lowest accuracy.

Correlations with Performance

Quantification Method

Clearly, the strongest correlation between laboratory characteristics and accuracy was based on the type of method employed to convert raw elemental intensities into a quantitative result (see Figures 1a, 1b and Table 5).

Three major categories of method were reported by the participating laboratories: standardless fundamental parameter (FP); fundamental parameter calibrated with standards (FP w/standards); and algorithms using empirical coefficients (empirical).

FP methods are based on mathematical models that predict the intensity of fluorescent radiation from a sample of known composition. The models incorporate knowledge of many instrument parameters, such as incidence and take-off angles (for both anode and sample), anode material, detector area and thickness, voltage, attenuators (such as windows, filters and air path), etc. FP models generally account for matrix effects, such as absorption and secondary fluorescence (in which some portion of the characteristic photons

Sample I (C934)	# of Labs (p)	Reference Value	Overall Median ($\bar{\chi}$)	% error
Fe	7	0.01	0.01	*
Ni	17	0.49	0.46	-7%
Cu	19	82.64	81.91	-1%
Zn	12	0.17	0.29	*
Sn	19	8.07	8.46	5%
Sb	13	0.14	0.10	-27%
Pb	19	8.45	8.82	4%

Sample J (CITF B32)	# of Labs (p)	Certified Value	Overall Median ($\bar{\chi}$)	% error
Fe	17	0.10	0.11	*
Ni	18	1.49	1.50	1%
Cu	19	74.85	74.53	-0.4%
Zn	19	1.15	1.10	-4%
As	4	0.0056	0.0328	*
Sn	19	5.92	5.78	-2%
Sb	13	0.13	0.12	-5%
Pb	19	16.10	16.76	4%

Sample K (MBH 31X B27 A)	# of Labs (p)	Certified Value	Overall Median ($\bar{\chi}$)	% error
Mn	11	0.045	0.046	2%
Fe	19	0.31	0.33	7%
Ni	12	0.042	0.054	*
Cu	19	78.2	78.4	0.3%
Zn	19	19.9	19.78	-1%
As	10	0.03	0.04	*
Sn	19	0.92	0.84	-9%
Sb	8	0.04	0.03	*
Pb	19	0.24	0.24	*
Bi	8	0.055	0.046	*

Sample L (BNF C71.34-3)	# of Labs (p)	Certified Value	Overall Median ($\bar{\chi}$)	% error
Mn	12	0.05	0.05	0.0%
Fe	19	0.29	0.25	-13%
Cu	19	87.230	86.592	-1%
Zn	19	1.55	1.62	5%
As	13	0.18	0.17	-6%
Ag	10	0.025	0.038	*
Sn	19	8.20	8.43	3%
Sb	11	0.071	0.119	*
Pb	19	2.47	2.76	12%
Bi	4	0.029	0.025	*

Mean error (median > L) 5%

* certified value below L

Table 4. Comparison of certified values to group medians.

Ranking (major elements)	SCORE (S_{major})	Lab #	Quant Method
1	0.2	13	FP w/stds
2	0.6	24	FP w/stds
3	0.7	6	FP w/stds
4	0.9	19	FP w/stds
5	0.9	3	FP w/stds
6	1.2	8	FP w/stds
7	1.5	2	FP
8	1.8	23	Empirical
9	2.2	15	Empirical
10	3.2	14	Empirical
11	3.3	10	FP w/stds
12	3.7	28	Empirical
13	4.7	27	Empirical
14	5.7	1	Empirical
15	5.7	18	Empirical
16	9.1	12	Empirical
17	10.1	7	FP
18	11.1	22	Empirical
19	14.6	9	FP

Ranking (minor elements)	SCORE (S_{minor})	Lab #	Quant Method
1	0.3	19	FP w/stds
2	0.7	3	FP w/stds
3	0.8	13	FP w/stds
4	0.8	6	FP w/stds
5	1.9	8	FP w/stds
6	2.7	15	Empirical
7	2.8	1	Empirical
8	2.9	28	Empirical
9	3.3	23	Empirical
10	3.9	14	Empirical
11	3.9	2	FP
12	4.5	18	Empirical
13	5.2	22	Empirical
14	8.4	9	FP
15	14.1	7	FP

Table 5. Laboratories' S_{major} and S_{minor} scores, ranked in order of highest to lowest accuracy.

excited by incident x-rays cause enhanced fluorescence in the sample) through theoretically-derived mathematical equations. The complex calculations involved in this method rely on knowledge of many physical constants, such as mass-attenuation coefficients, fluorescence yields, absorption jump ratios, relative line intensities, absorption edges, etc. (de Vries and Vrebos 2002). Some FP applications allow for the use of pure element standards to help model the spectral distribution of the tube output (de Viguerie et al. 2009) or to model transmission efficiency by polycapillary lenses (Karydas et al. 2008). The use of pure element standards in this manner is still considered 'standardless' FP for the purposes of this study, as the standards are not used directly to generate scaling coefficients for analytes.

FP w/standards methods can take several forms. As the name implies, they are based on mathematical predictions of fluorescent intensity and provide a theoretical accounting for matrix effects as discussed above. However, these methods also perform corrections to the model, using spectra generated by the instrument in question, from reference standards of composition similar to that of the analyte. The corrections can be performed in a variety of ways (discussion of which is beyond the scope of this paper), but by and large they attempt to account for instrument-related factors (de Vries and Vrebos 2002).

Empirical calibrations are derived through the measurement of standards that are similar to the unknown. Ideally, the compositional standards have the same elements as the unknown, although the composition may be different. Comparing each elemental fluorescence intensity in the standard to the corresponding composition and fitting a regression between known points, analysts can interpolate between known values. The fluorescence intensity of the unknown is then compared to the calibrated regression, and the composition is derived. Empirical models typically account for absorption, secondary fluorescence and other matrix effects using empirically derived correction coefficients based on regression analysis (de Vries and Vrebos 2002).

For both major and minor elements, it is very clear that laboratories using fundamental parameters software calibrated with standards (labs #3, 6, 8, 10, 13, 19, 24), performed consistently more accurately than laboratories using other methods. Remarkably, of these seven laboratories, no two used the same type of instrument or the same brand of software.

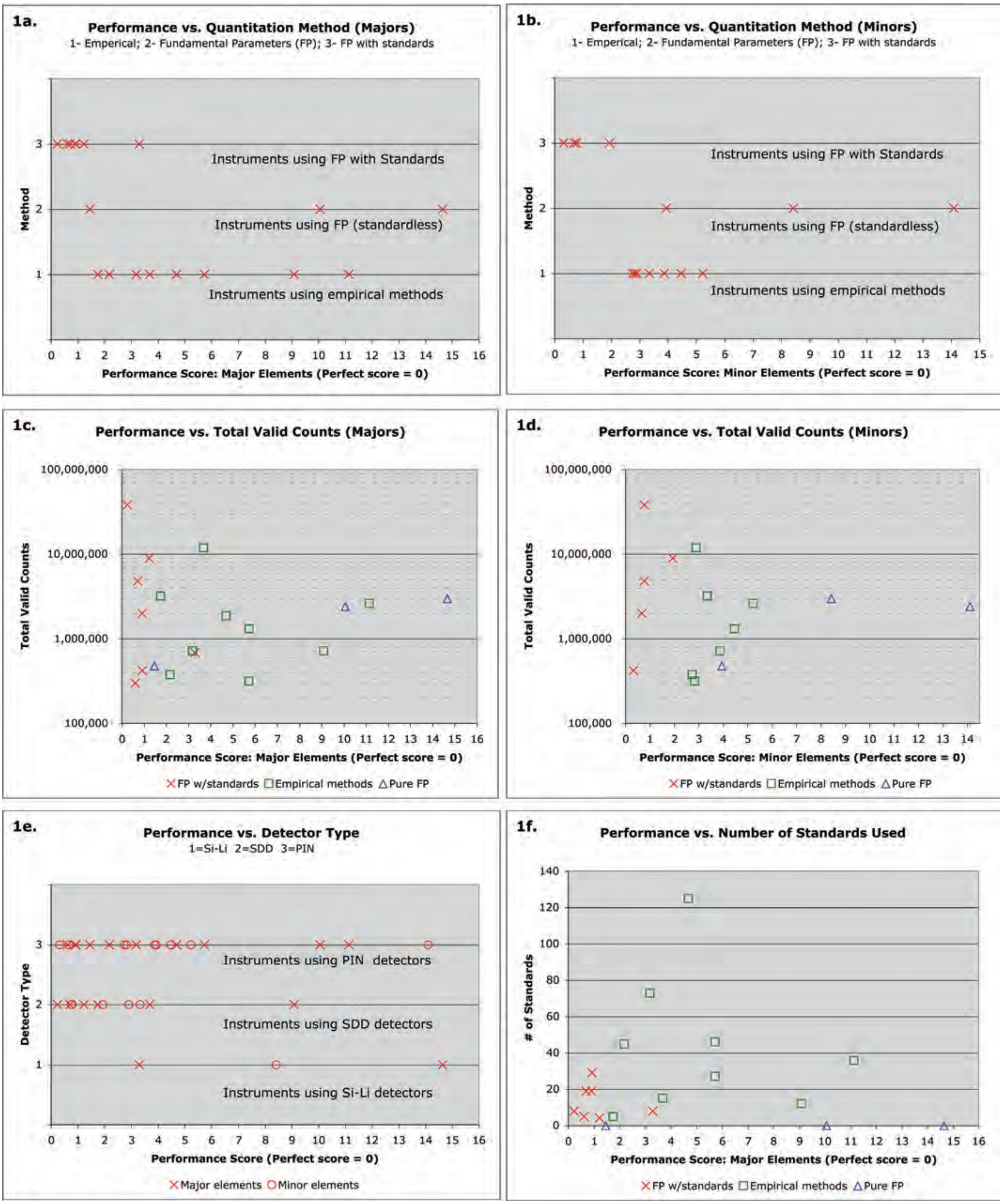

Figure 1. Performance scores (S_{major} and S_{minor}) are plotted against selected laboratory characteristics. High performance is reflected by a score close to zero (i.e. on the left side of the charts).

Among the laboratories using FP with standards, the majority had S_{major} and S_{minor} scores that were tightly clustered near the perfect score of zero. One of these laboratories (#10), however, appears to have performed noticeably less well than the others in the group (though their scores were still better than almost all other laboratories using empirical or standardless FP methods). In their data reporting form, the analysts for this instrument noted that 'While we did the analysis on this instrument, the stability of the instrument is doubtful and we would be cautious about reporting numbers from this instrument at the present time'. They also reported that the last full calibration of the instrument had been performed on the instrument more than four years ago. These observations may explain the difference in performance.

Only seven of the 19 data sets in the study (2, 3, 6, 7, 8, 13, 19) were able to consistently report quantitative results for the four major elements, plus six minor elements (Fe, Ni, As, Ag, Sb and Bi). Of these seven, all used FP or FP w/standards methodology.

Detector Type
Another laboratory characteristic that was evaluated for correlation with performance was detector type. The vast majority of laboratories in this study (84%) used silicon drift detectors (SDD) or silicon-PiN diode detectors (PIN). These are clearly the two dominant types of detectors on the market today. Only three instruments in the study used lithium drifted silicon detectors (Si-Li). Figure 1e plots S_{major} and S_{minor} against the three detector types in the study. While more of the poorly performing laboratories seemed to use PIN or Si-Li detectors than SDDs, it is perhaps more significant to note that the six top ranked laboratories (#3, 6, 8, 13, 19, 24) were equally divided between PIN and SDD detectors. It would appear then that very strong performance can be achieved with either of these detector types. Si-Li detectors did not appear to perform as well as the other types, but with only two laboratories using these detectors, the results should not be given too much weight.

Valid Counts per Analysis
A surprising result of the study is that, within the range employed in this study, the total number of valid counts per analysis (vca) was not positively correlated with performance, either for major or minor elements. The vca is given here as the product of the typical valid count rate per second (as reported by each laboratory and accounting for detector deadtime) and the number of seconds that the analysis was allowed to run. For both major and minor elements (Figure 1c and 1d), there appears to be no correlation between vca and performance. It is interesting and perhaps instructive to note that if the laboratories are grouped by software/analytical method, many of the best results for each group were attained with relatively low total counts, on the order of 300,000.

Number of Standards
The data also suggest that increasing the number of standards used for quantification does not necessarily improve the accuracy of results (Figure 1f). In fact, the vast majority of the best performing laboratories used 20 standards or fewer, and most used fewer than 10. Even among the labs using empirical methods, increasing the number of standards was not a guarantee of improved results, and the best performing laboratory of this group (for major elements) used only five standards per analysis.

Conclusions
This study evaluates the current state of inter-laboratory reproducibility of quantitative XRF analysis of historic copper alloys based upon a representative group drawn from the art and archaeology community, primarily in the United States. Nine members of the working group met for two days of intensive meetings to evaluate the results of the inter-laboratory study. The conclusions and recommendations of this sub-group were reviewed and commented on by the wider group. What follows is a summary of the overall findings of the working group.

Reproducibility
The overall reproducibility of the group's results is relatively poor. Even if one considers only results where the median result is above the calculated lower limits (*L*), the average percent relative reproducibility ($R_{rel\%}$) is greater than 50% for all elements except Cu, Zn, and Sn. The ASTM standard practice stipulates that the working group may determine the degree of precision that may be considered acceptable for a given method, based on the context within which the results are to be used. However, an upper threshold for $R_{rel\%}$ is set at 50% above which the methods reproducibility must be considered unacceptable. While not bound by ASTM guidelines, it was the consensus of the working group that the current reproducibility of XRF analysis of historic copper alloys within the art and archaeology community is, in general, *not* sufficient for any but the most broad comparisons to be made between laboratories.

Two examples drawn directly from table 3 may help serve to illustrate the point. Assume that a laboratory arrives at a result of 8.6% tin in a bronze alloy. Based of the current state of affairs, there is a 95% chance that another laboratory, measuring the same bronze, would arrive at a result somewhere between 4.6% and 12.6%. Similarly, for a result of 33% zinc in brass, the 95% confidence interval ranges from 27% to 39%. Also, considering that tin and zinc are among the elements with the best reproducibility in the study, the group agreed that concerted efforts should be made to improve the situation.

The reproducibility results reported here should evoke a strong sense of caution in those who might wish to publish data, compare their own data with that generated by other laboratories, or pursue meta-studies based on the work of multiple laboratories.

The group also found that the lower limits determined by this study (below which reproducibility rapidly deteriorates) are considerably higher than could be wished for. It was agreed that analyte concentrations below the lower limits are frequently of interest and significance to scientists engaged in the study of historic copper alloys.

Quantification Method

Through this study, one common characteristic of higher-performing laboratories has become clear: the use of fundamental parameters software, calibrated with standards. In comparison, all other factors examined in this study appear to be relatively poorly correlated with laboratory accuracy. The consensus of the group is that options should be explored for ways in which existing instruments that currently use empirical or standardless FP methods could be upgraded to use FP with standards.

A sense of the magnitude of improvement that such a change, if widely adopted, might bring about can be gleaned from Table 6. This presents the method's lower limits (*L*) and the percent relative reproducibility ($R_{rel\%}$) for all participating laboratories compared to the same statistics calculated based only on six laboratories using FP with standards (laboratory 10 was excluded from the group based on their self-described instrumental irregularities). On average, the sub group using FP with standards[5] had a reduction in lower limits of 65% from the overall group limits, reflecting a substantial improvement in their ability to compare results when element concentrations are low. Similarly, the subgroup's $R_{rel\%}$ values were, on average, 55% less than those of the group as a whole. While these levels may still leave something to be desired, it seems apparent that as a first step, movement toward the wider adoption of quantification methods utilizing FP with standards offers the possibility of significant improvements in interlaboratory reproducibility.

		All Participants	Participants using FP with Standards
Iron	Calculated Lower Limit (*L*)	0.165	0.063
	Mean $R_{rel\%}$ for $\bar{X}>L$	121%	41%
Nickel	Calculated Lower Limit (*L*)	0.354	0.057
	Mean $R_{rel\%}$ for $\bar{X}>L$	61%	47%
Copper	Calculated Lower Limit (*L*)	n/a	n/a
	Mean $R_{rel\%}$ for $\bar{X}>L$	8%	2%
Zinc	Calculated Lower Limit (*L*)	0.792	0.147
	Mean $R_{rel\%}$ for $\bar{X}>L$	31%	15%
Arsenic	Calculated Lower Limit (*L*)	0.246	0.193
	Mean $R_{rel\%}$ for $\bar{X}>L$	110%	64%
Tin	Calculated Lower Limit (*L*)	0.271	0.121
	Mean $R_{rel\%}$ for $\bar{X}>L$	40%	14%
Antimony	Calculated Lower Limit (*L*)	0.120	0.037
	Mean $R_{rel\%}$ for $\bar{X}>L$	185%	83%
Lead	Calculated Lower Limit (*L*)	1.217	0.226
	Mean $R_{rel\%}$ for $\bar{X}>L$	77%	27%

Table 6. 'Method's Lower Limits' and 'Percent Relative Reproducibility Indices' as calculated for all 19 data sets compared with the same statistics calculated for the six top performing data sets, all using FP with standards software.

It was suggested by some members of the working group that the use of a common, open source FP software package[6] used in conjunction with a common and readily available set of reference materials could further improve the reproducibility of results within the group.

Many participants expressed a desire to have a set of certified reference materials, replicated for the various institutions that wish to share data, which includes a range of major and trace elements appropriate for historic alloys. Although a selection of available standards might fill a portion of this range, such a set would certainly require some standards to be newly manufactured.

Error and Detection Limits

Reporting of error and detection limits was inconsistent among the participating laboratories. Several laboratories did not report errors or detection limits at all. Many laboratories reported errors calculated from their software based on counting statistics. While these values have meaning, they generally reflect the error associated with repeated analyses by the same instrument (or instrumental precision) rather than expected error with respect to the true value (instrumental accuracy).

The laboratories that produced the most meaningful and reliable error values relative to true values did so by analyzing multiple reference materials and conducting a regression analysis of certified vs. calculated values. These laboratories used the 'standard error' associated with the regression to define meaningful confidence intervals relative to the estimated true value. This strategy was employed both by laboratories using both FP w/standards and empirical methods.

Detection limits were, if anything, less consistently reported than errors. Some laboratories did not report detection limits while others estimated them for selected elements based on experience with standards. Several participants derived their detection limits based on analysis of multiple reference materials with certified values at or near zero. A regression analysis was performed and a value of two or three times the standard error was used to estimate the nominal detection limit. The consensus of the group was that this empirical approach provides useful results in a relatively straightforward manner though other means are possible (Ziebold 1967, Long and Winefordner 1983).

Other Suggestions

The working group suggests that, in instances where data are to be published or shared between laboratories, standard practice should include publication (perhaps separately) of a detailed and comprehensive reporting of the laboratory method along with the presentation of empirically derived error and detection limit values. In addition, it was suggested that publication of data include results for one or two control samples (e.g., reference materials analyzed during the analysis, but which are not part of the calibration).

In some areas, the raw data generated in this study has only been superficially evaluated and many more conclusions may be possible with further data analysis. A number of significant subjects possibly could be addressed using the data already collected. For instance, the relative advantages and disadvantages of different variants of the FP w/standards method; the factors affecting detection limits; factors affecting within-laboratory precision; the effects of filtration; and the importance of careful manual inspection of spectra.

Clearly, much work remains on the issue of inter-laboratory reproducibility of XRF data generated for historical metals. As we have shown above, results among laboratories vary widely, not only for minor elements, but also for major elements. These differences highlight the problems associated with trying to compare data from multiple laboratories and the need for common standards and quantification approaches. Future research in this area should focus on addressing these issues.

Endnotes

[1] The results from this instrument are designated with laboratory numbers 3, 7, and 22.

[2] Three of the reference materials were certified (so-called CRMs) based on analysis by multiple laboratories (samples J, K, and L); one, (sample I) has no certificate of analysis.

[3]A complete explanation of this calculation is given in the ASTM E1601 sections 10.4.5 to 10.4.8. The validity of the formula is contingent upon the result being larger than the method's minimum standard deviation, which was true in every instance in this study.

[4]Using the square of ha has the dual advantages of making all values positive and of emphasizing the negative impact of occasional poor scores. It would be equally valid to rank based on the absolute value of ha; in practice, the rank order changes very little.

[5] Six is the minimum number of participating laboratories required by ASTM E1601. The results calculated for this subgroup may therefore be considered as 'valid' based on the standard procedure.

[6] Several such software packages are available, such as PyMCA (European Synchrotron Radiation Facility) and AXIL-QXAS (International Atomic Energy Agency).

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Author

Arlen Heginbotham received his B.A. in East Asian Studies from Stanford University and his M.A. in Art Conservation from Buffalo State College. He is currently Associate Conservator of Decorative Arts and Sculpture at the Getty Museum where he is currently writing technical essays for catalogs of the Museum's collections of French furniture. Arlen's research interests include the history and analysis of 17th century East Asian export lacquer, the history of metallurgy, the use of X-ray fluorescence spectroscopy as a tool for authenticating and interpreting gilded bronzes, microscopic and chemical wood identification, immunochemical analysis, and the history of wood dyes.

Q & A SESSION

Tim Foecke: This is probably the only opportunity I get to put on my NIST hat. It was a great introduction of a very important topic to the crew here. When I see the analytical techniques being thrown up in the talks I see EDS an awful lot as well. XRF is so useful because you don't have to stuff whatever you are looking at into a vacuum chamber – but anybody doing EDS and trying to do standard-less measurements and trying to report them – please stop. The EDX corporation put out software that says they can do standard-less things and all these other corporations have followed suit. It is virtually worthless. You have to do the standards. It is a pain, it takes time, but it absolutely has to be done and I'm basically channeling Dale Newbury here – Dale Newbury is a fellow at NIST who basically wrote the book on this sort of stuff. He wrote the book, I learned it from certainly. And he has promised anyone at NIST if he has heard anybody publishing stuff on standard-less work at NIST he would personally garrote them.

Shelley Sturman: I just think we all have to applaud Arlen one more time. We just put an idea out there and he ran with it like no-one can believe and that work that you saw just now was just a tiny bit of what he had to do to get all of these labs to cooperate, to send the material in, it took hours and days and months to put all that data together. We really thank you Arlen.

Bruce Kaiser: I'm semi-retired but I work with Bruker. Your data that you posted on the internet – did you post the raw spectra as well?

Arlen Heginbotham: No I haven't but your proposal was suggested to me part way through the collection. Actually I think it would be a great idea so I would be willing to try and collect all the spectra and have everybody send them to me.

Bruce Kaiser: The physics of what goes on here is really very simple. The raw spectrum contains all of the information. Every bit of analysis that you folks did is dependent on a man-made algorithm. The answers are different because the algorithms are different. But in the raw-spectrum is a gold mine of information – you said about mining the information and getting more and more into what is causing these differences. It is all in the raw spectra and in the relative comparison of the raw spectra you can see immediately all of the information. For those that have any Bruker systems there is a set of software called Artax that allows you to analyze just net area under peaks – no algorithms. With that, another 5 papers could be written with the raw data and if you make that raw data available I would be pleased to teach you a little more of that fundamental physics that is in there along with the statistics. I mean that in a very positive sense not in any vendor related [way]. I actually have almost all of those instruments you used except for the older systems; but the raw data is really important, those raw spectra.

Arlen Heginbotham: Great, I'll try to follow up on that.

THE APPLICATION OF ALLOY ANALYSIS TO QUESTIONS OF ATTRIBUTION: GIOVANNI FRANCESCO SUSINI AND THE WORKSHOP OF GIAMBOLOGNA

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Abstract

This study considers the application of alloy analysis using X-ray fluorescence (XRF) spectroscopy to the attribution of small 'bronzes' by the 17th century Florentine artist Giovanni Francesco Susini. Documented works by this artist were analyzed and compared to reference works by the closely related artists Giovanni Bologna and Antonio Susini. Analyses were primarily performed on a handheld portable Bruker Tracer III-V XRF spectrometer for which a custom calibration has been developed for accurate quantification of historic copper alloys. Prior analyses performed on a laboratory-based Kevex 0750A XRF on a number of relevant objects are also considered. Quantified results from the two instruments are compared and integrated. Examination of the combined data reveals that certain alloys can be associated with production by Gianfrancesco, providing an additional means of determining attribution.

Keywords: X-ray fluorescence, calibration, copper alloys, bronze, renaissance, attribution, Giovanni Francesco Susini, Giambologna

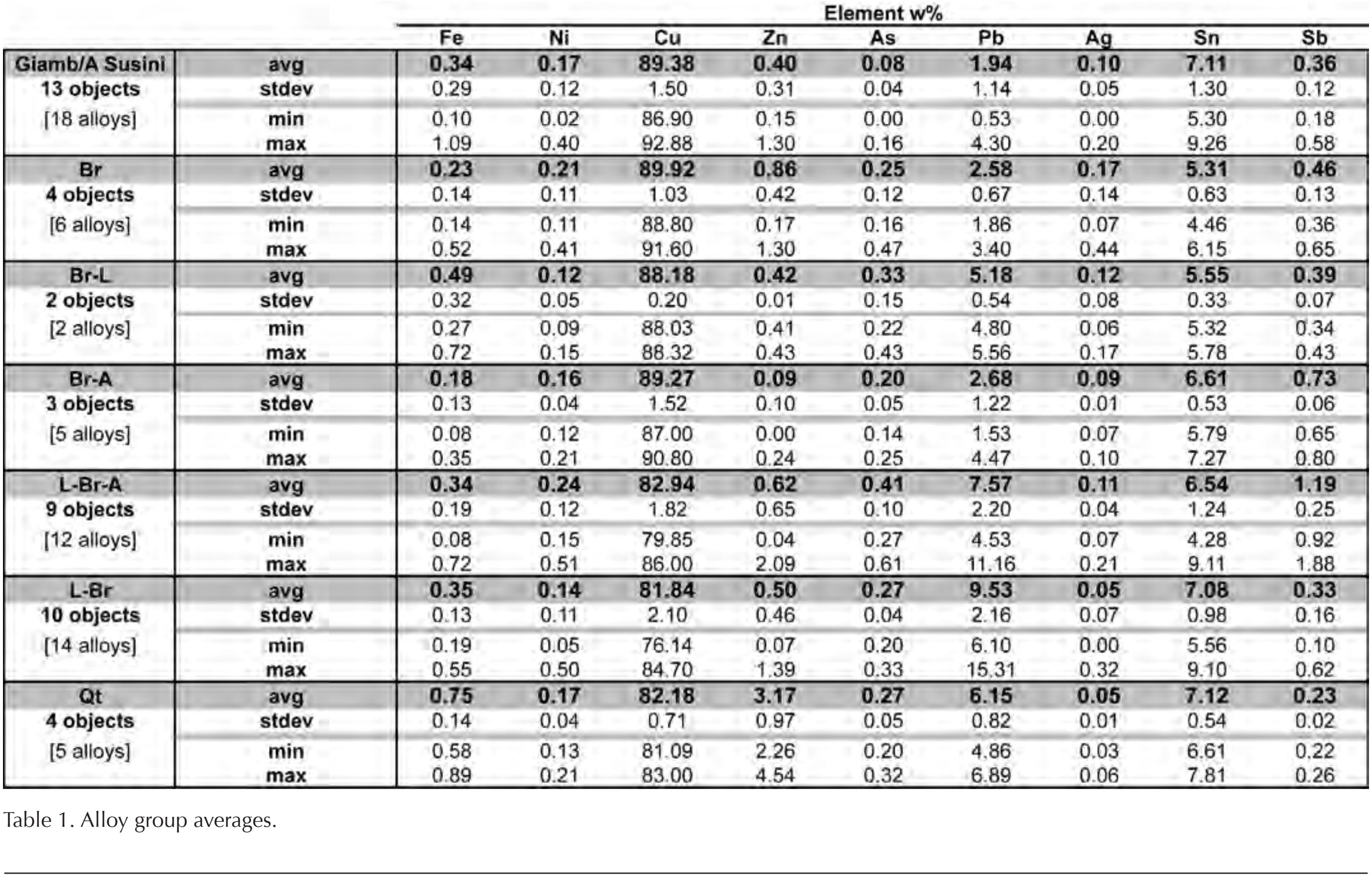
Introduction

Despite extensive art historical investigation by traditional means, many questions of attribution remain for the small 'bronzes' associated with the Renaissance sculptor, Giovanni Bologna (b. 1529 – d. 1608), known as Giambologna (Watson and Avery 1973)[1]. Giambologna established a large and influential sculpture workshop in Florence during the latter part of the 16th century, which produced large-scale masterpieces in marble and bronze, as well as highly refined small bronze sculpture (Avery and Radcliffe 1978). These bronzes (see Figure 1) were reproduced extensively using the indirect casting method by a number of skilled assistants (Sturman 2001). Foremost among these was Antonio Susini (a. 1577 – d. 1624), who joined Giambologna's workshop in 1580. When Antonio established his own workshop in 1600, he received many of his master's molds and models and continued to cast new bronzes from them (Avery 1987). Antonio also produced original models, very much in Giambologna's style (see Figure 2). Giovanni Francesco (Gianfrancesco) Susini (b. 1585 - d. c. 1653) inherited his uncle's workshop after Antonio's death and cast bronzes from Giambologna's and Antonio's models (Brook 1986). Gianfrancesco also created new models including copies after ancient sculpture and original inventions that demonstrate a variety of artistic influences (see Figure 3). Similarities in style and production methods among these artists make attribution of undocumented casts difficult by visual examination and even by X-radiography, especially those after Giambologna's models.

Figure 1. *Mars*, model by Giambologna, cast, att. to G.F. Susini, Robert H. Smith collection. h. 39.3 cm

Figure 2. *Farnese Hercules*, model by A. Susini, cast, attr. to G.F. Susini, Robert H. Smith Collection. h. 31.3 cm

Figure 3. *David and Goliath*, attr. to G.F. Susini, Robert H. Smith Collection. h. 29.5 cm



		Element w%								
		Fe	Ni	Cu	Zn	As	Pb	Ag	Sn	Sb
Giamb/A Susini	**avg**	**0.34**	**0.17**	**89.38**	**0.40**	**0.08**	**1.94**	**0.10**	**7.11**	**0.36**
13 objects	**stdev**	0.29	0.12	1.50	0.31	0.04	1.14	0.05	1.30	0.12
[18 alloys]	**min**	0.10	0.02	86.90	0.15	0.00	0.53	0.00	5.30	0.18
	max	1.09	0.40	92.88	1.30	0.16	4.30	0.20	9.26	0.58
Br	**avg**	**0.23**	**0.21**	**89.92**	**0.86**	**0.25**	**2.58**	**0.17**	**5.31**	**0.46**
4 objects	**stdev**	0.14	0.11	1.03	0.42	0.12	0.67	0.14	0.63	0.13
[6 alloys]	**min**	0.14	0.11	88.80	0.17	0.16	1.86	0.07	4.46	0.36
	max	0.52	0.41	91.60	1.30	0.47	3.40	0.44	6.15	0.65
Br-L	**avg**	**0.49**	**0.12**	**88.18**	**0.42**	**0.33**	**5.18**	**0.12**	**5.55**	**0.39**
2 objects	**stdev**	0.32	0.05	0.20	0.01	0.15	0.54	0.08	0.33	0.07
[2 alloys]	**min**	0.27	0.09	88.03	0.41	0.22	4.80	0.06	5.32	0.34
	max	0.72	0.15	88.32	0.43	0.43	5.56	0.17	5.78	0.43
Br-A	**avg**	**0.18**	**0.16**	**89.27**	**0.09**	**0.20**	**2.68**	**0.09**	**6.61**	**0.73**
3 objects	**stdev**	0.13	0.04	1.52	0.10	0.05	1.22	0.01	0.53	0.06
[5 alloys]	**min**	0.08	0.12	87.00	0.00	0.14	1.53	0.07	5.79	0.65
	max	0.35	0.21	90.80	0.24	0.25	4.47	0.10	7.27	0.80
L-Br-A	**avg**	**0.34**	**0.24**	**82.94**	**0.62**	**0.41**	**7.57**	**0.11**	**6.54**	**1.19**
9 objects	**stdev**	0.19	0.12	1.82	0.65	0.10	2.20	0.04	1.24	0.25
[12 alloys]	**min**	0.08	0.15	79.85	0.04	0.27	4.53	0.07	4.28	0.92
	max	0.72	0.51	86.00	2.09	0.61	11.16	0.21	9.11	1.88
L-Br	**avg**	**0.35**	**0.14**	**81.84**	**0.50**	**0.27**	**9.53**	**0.05**	**7.08**	**0.33**
10 objects	**stdev**	0.13	0.11	2.10	0.46	0.04	2.16	0.07	0.98	0.16
[14 alloys]	**min**	0.19	0.05	76.14	0.07	0.20	6.10	0.00	5.56	0.10
	max	0.55	0.50	84.70	1.39	0.33	15.31	0.32	9.10	0.62
Qt	**avg**	**0.75**	**0.17**	**82.18**	**3.17**	**0.27**	**6.15**	**0.05**	**7.12**	**0.23**
4 objects	**stdev**	0.14	0.04	0.71	0.97	0.05	0.82	0.01	0.54	0.02
[5 alloys]	**min**	0.58	0.13	81.09	2.26	0.20	4.86	0.03	6.61	0.22
	max	0.89	0.21	83.00	4.54	0.32	6.89	0.06	7.81	0.26

Table 1. Alloy group averages.

Figure 4. *Kneeling Bather* (small), model by Giambologna, attr. to G.F. Susini, Robert H. Smith Collection. h. 9.6 cm

This paper will discuss the application of X-ray fluorescence spectroscopy (XRF) to one aspect of this complex historical problem, the identification of bronzes by Gianfrancesco Susini. For this study, a group of documented works by Gianfrancesco were analyzed using a portable handheld XRF analyzer, the Bruker Tracer III-V. Accurate quantification of historic copper alloys with the Tracer has required refinement of the Bruker empirical software method. Additional results are also considered that were obtained with a laboratory-based Kevex 0750A XRF and quantified using fundamental parameters with standards. A group of study objects tested with both instruments were compared and used to integrate the results.

The combined data reveal that many alloys in documented works by Gianfrancesco can be distinguished from those in documented works by Giambologna and Antonio Susini. Although some variations in alloy result from metallurgical factors, such as source ores and processing, the relatively narrow ranges of alloys identified in the study objects suggest a highly controlled and intentional use of materials (see Table 1, particularly group 'Giamb/A Susini'). These characteristics support that alloy analysis, alongside traditional historical methods and connoisseurship, can provide a means for determining authorship of bronzes associated with Giambologna's workshop, notably works by Gianfrancesco Susini (see Figure 4).

Instrumental methods

XRF analysis of forty-five study objects was performed using either a hand-held portable Bruker Tracer III-V or a laboratory-based Kevex 0750A. XRF is an established technique for the analysis of copper alloys and Renaissance small bronzes are generally well suited to this type of examination (Glinsman 1990). These highly valued objects typically remained in protected environments, unaltered by weathering or burial. Original chemical patinations are rare; color was instead imparted by the application of organic coatings (Stone 1990, Pittard 2007). Such films can interfere with analysis of the underlying substrate. Therefore, spots were selected where coatings were thin or absent.

Analyses with the Bruker Tracer III-V XRF spectrometer were run with a rhodium tube, 6 mm spot size, 40 kV anode voltage and 1.8 μA anode current with a sandwiched filter of 25.4 micrometer titanium and 304.8 micrometer aluminum. Most objects were tested for a live time of approximately 36 seconds (60 seconds actual time); some early tests were performed for approximately 18 seconds of live time (30 seconds actual time). Spectra were quantified using PXRF software to calculate weight percentages (w%) for the elements of interest using a customized empirical method for copper alloys. The copper content was normalized to 100%.

Analyses with the Kevex 0750A XRF spectrometer were run with a $BaCl_2$ secondary target, 6 mm collimators, 60 kV anode voltage and 0.4 mA anode current for a live time of 200 seconds. Spectra were quantified using EXACT fundamental parameters software with standards. Data were normalized to 100% across all elements (Glinsman Reports 1987, 1993, 2003, 2004).

Typically, three spots were analyzed on each object to produce an average result; if separately cast parts were present, each component was tested.

Study Objects

Thirteen bronzes are included as reference alloys for production by Giambologna and Antonio Susini. These data are presented only in summary and will be considered in detail in future publications. Nine bronzes from the Kunsthistorisches Museum in Vienna can be dated to 1611 by inventories (Leithe-Jasper 1986). Four bronzes from the Museo del Bargello in Florence originated in old Medici collections, one is signed and two have documented dates (Avery 1978). Seven of these objects were analyzed with the Kevex while on exhibition at the National Gallery of Art, Washington, D.C. in 1986 and 1993. Eleven, including three evaluated with the Kevex, were analyzed with the Tracer at the Kunsthistorisches Museum in 2006 and 2008.

Five documented casts by Antonio Susini, one signed and dated, were analyzed at the Galleria Colonna, Rome, in 2010 (see Table 2). Two of these bronzes previously were attributed to Gianfrancesco; alloy analysis helped to clarify the interpretation of the historical documents (Keutner 1990, Wengraf 2006, see discussion below).

Figure 5. *Venus Burning Cupid's Arrows*, G.F. Susini, Liechtenstein Museum. h. 56 cm

Documented bronzes by Gianfrancesco Susini were tested in three collections: the Liechtenstein Museum, Vienna; the Galleria Colonna, Rome; and the Metropolitan Museum of Art, New York (Draper 1985, Brook 1986, Keutner 1990) (see Table 2). Three of the objects examined are signed and dated (see Figure 5); one has a stamped signature and a documented date. Three works from the Galleria Colonna collection are dated and attributed by documentation; six from the Liechtenstein Museum have documented dates provided by 17th century inventories and are models Gianfrancesco is known to have cast. These objects were analyzed at their respective collections between 2008 and 2010. Among these bronzes are casts after models designed by Gianfrancesco, Giambologna and Antonio Susini. Several of Gianfrancesco's original designs were created through a sequence of cast-on parts.

Published data for three bronzes from the Getty Museum, Los Angeles, analyzed by inductively coupled plasma mass spectroscopy, also are included (see Table 2). *Abduction of Helen* is the earliest signed and dated bronze included in the study; core samples from *Lion Attacking a Horse* and *Lion Attacking a Bull* have been dated by thermoluminescence to after 1637, supporting attribution to Gianfrancesco (Fogelman and Fusco 2003).

Ten undocumented bronzes attributed to Gianfrancesco were analyzed (see Table 2). Seven works in the Robert H. Smith Collection, a private collection in Arlington, Virginia, were analyzed with the Tracer (see Figures 1 - 4); three previously were tested with the Kevex (Radcliffe and Penny 2004). *Lion Attacking a Horse* and *Leopard*

								Element w%									
Group	Artist	Object	Component	Collection	Sign	Date	Design	Fe	Ni	Cu	Zn	As	Pb	Ag	Sn	Sb	Instr
Br	GF Susini	*Venus Chastising Cupid*	Cupid	Liechtenstein	Y	1638	GF Susini	0.52	0.17	88.80	0.70	0.24	3.40	0.07	5.45	0.65	Tracer
Br	GF Susini	*David and Goliath*		Liechtenstein	Y	by 1658	GF Susini	0.18	0.11	90.30	0.75	0.16	1.86	0.11	6.15	0.40	Tracer
Br	GF Susini	*Saccomazzoni*	upper figure	Liechtenstein		by 1658	GF Susini [aft. Mochi]	0.16	0.17	89.00	1.16	0.29	3.33	0.18	5.31	0.37	Tracer
Br	GF Susini	*Saccomazzoni*	rock	Liechtenstein		by 1658	GF Susini [aft. Mochi]	0.20	0.41	91.60	0.17	0.16	2.20	0.12	4.74	0.38	Tracer
Br	GF Susini	*Saccomazzoni*	lower figure	Liechtenstein		by 1658	GF Susini [aft. Mochi]	0.14	0.26	89.60	1.30	0.47	2.71	0.44	4.46	0.59	Tracer
Br	GF Susini	*David and Goliath*		Smith			GF Susini	0.19	0.12	90.23	1.10	0.16	2.02	0.08	5.75	0.36	Tracer
Br-L	GF Susini	*Arria and Peto*	Peto	Colonna		1632	GF Susini	0.27	0.15	88.32	0.41	0.43	5.56	0.17	5.78	0.43	Tracer
Br-L	GF Susini	*Bagpiper*		Colonna		1632	Giambologna	0.72	0.09	88.03	0.43	0.22	4.80	0.06	5.32	0.34	Tracer
Br-A	GF Susini	*Venus Burning Cupid's Arrows*	Cupid	Liechtenstein	Y	1638	GF Susini	0.31	0.21	89.10	0.24	0.25	3.31	0.08	5.79	0.75	Tracer
Br-A	GF Susini	*Venus Chastising Cupid*	Venus	Liechtenstein	Y	1638	GF Susini	0.35	0.17	87.00	0.14	0.20	4.47	0.10	6.76	0.80	Tracer
Br-A	GF Susini	*Hermaphrodite*	base, side 1	Metropolitan	Y	1639	GF Susini	0.08	0.13	90.80	0.00	0.14	1.53	0.10	6.54	0.68	Tracer
Br-A	GF Susini	*Hermaphrodite*	base, side 2	Metropolitan	Y	1639	GF Susini	0.08	0.12	90.52	0.00	0.17	1.68	0.09	6.69	0.65	Tracer
Br-A	GF Susini	*Hermaphrodite*	figure	Metropolitan	Y	1639	GF Susini	0.10	0.17	88.92	0.05	0.24	2.40	0.07	7.27	0.78	Tracer
L-Br-A	GF Susini	*Abduction of Helen*	base	Getty	Y	1627	GF Susini	0.14	0.20	81.08	1.23	0.34	9.27	0.09	6.67	1.11	ICP/MS
L-Br-A	GF Susini	*Small Bather*		Colonna		1632	Giambologna	0.38	0.23	82.93	2.09	0.61	7.49	0.10	4.28	1.88	Tracer
L-Br-A	GF Susini	*Arria and Peto*	base	Colonna		1632	GF Susini	0.49	0.17	82.92	0.31	0.40	5.13	0.21	9.11	1.12	Tracer
L-Br-A	GF Susini	*Arria and Peto*	Arria	Colonna		1632	GF Susini	0.39	0.24	84.46	0.77	0.49	4.83	0.19	7.33	0.92	Tracer
L-Br-A	GF Susini	*Venus Burning Cupid's Arrows*	Venus	Liechtenstein	Y	1638	GF Susini	0.35	0.17	86.00	0.18	0.27	4.53	0.10	7.36	1.00	Tracer
L-Br-A	GF Susini	*Venus Burning Cupid's Arrows*	base	Liechtenstein	Y	1638	GF Susini	0.72	0.16	83.10	0.04	0.33	7.18	0.12	7.29	1.07	Tracer
L-Br-A	GF Susini	*Crouching Bather*		Liechtenstein		by 1658	Giambologna	0.18	0.16	84.30	1.19	0.35	6.62	0.11	5.72	1.32	Tracer
L-Br-A	GF Susini	*Hercules and Nessus*		Liechtenstein		by 1658	Giambologna	0.23	0.48	82.80	0.10	0.47	8.37	0.07	6.30	1.15	Tracer
L-Br-A	GF Susini	*Hercules and Antaeus*		Liechtenstein		by 1658	Giambologna	0.08	0.51	85.10	0.05	0.40	6.36	0.12	6.28	1.12	Tracer
L-Br-A	GF Susini	*Lion Attacking a Horse*	horse's neck	Frick			Giambologna	0.37	0.17	80.92	0.15	0.31	11.16	0.08	5.85	0.98	Tracer
L-Br-A	GF Susini	*Lion Attacking a Horse*	main section	Frick			Giambologna	0.53	0.15	81.86	0.31	0.40	10.20	0.10	5.20	1.24	Tracer
L-Br-A	GF Susini	*Kneeling Bather*		Smith			Giambologna	0.18	0.23	79.85	1.08	0.49	9.67	0.07	7.12	1.32	Tracer
L-Br	A Susini	*Farnese Bull*	bull	Colonna	Y	1616	A Susini	0.44	0.05	82.51	0.07	0.30	9.07	0.00	7.35	0.21	Tracer
L-Br	A Susini	*Farnese Bull*	base	Colonna	Y	1616	A Susini	0.54	0.05	83.37	0.08	0.33	7.17	0.04	8.16	0.26	Tracer
L-Br	A Susini	*Farnese Bull*	back female	Colonna	Y	1616	A Susini	0.52	0.07	82.00	0.10	0.29	9.50	0.05	7.16	0.32	Tracer
L-Br	A Susini	*Farnese Bull*	PL male	Colonna	Y	1616	A Susini	0.19	0.11	82.44	0.35	0.27	9.81	0.01	6.61	0.22	Tracer
L-Br	A Susini	*Farnese Bull*	PR male	Colonna	Y	1616	A Susini	0.40	0.09	81.72	0.43	0.31	11.24	0.02	5.56	0.24	Tracer
L-Br	GF Susini	*Lion Attacking a Stallion*	main section	Getty		1646-1682	Giambologna	nd	0.10	83.40	0.10	nd	7.30	0.00	9.10	0.10	ICP/MS
L-Br	GF Susini	*Lion Attacking a Stallion*	horse's head	Getty		1646-1682	Giambologna	nd	0.11	78.00	0.30	nd	12.00	0.03	8.90	0.19	ICP/MS
L-Br	GF Susini	*Lion Attacking a Bull*	bull	Getty		1637-1673	Giambologna	nd	0.50	83.40	0.10	nd	7.90	0.00	8.00	0.20	ICP/MS
L-Br	GF Susini	*Striding Horse*		Liechtenstein		by 1696	A Susini	0.20	0.09	82.50	0.30	0.31	9.42	0.04	6.86	0.24	Tracer
L-Br	GF Susini	*Farnese Hercules*		Smith			A Susini	0.41	0.13	81.70	0.85	0.24	10.25	0.02	6.09	0.32	Tracer
L-Br	GF Susini	*Pacing Lion*		Smith			Giambologna	0.22	0.15	80.56	0.88	0.23	10.35	0.32	6.74	0.56	Tracer
L-Br	GF Susini	*Bagpiper*		Smith			Giambologna?	0.34	0.18	82.01	1.32	0.31	9.17	0.08	6.08	0.50	Tracer
L-Br	GF Susini	*Mars*		Smith			Giambologna	0.55	0.15	83.91	1.39	0.26	7.29	0.04	6.13	0.28	Tracer
L-Br	GF Susini	*Leopard Attacking a Bull*	leopard	Frick			GF Susini?	0.27	0.10	81.10	0.31	0.28	10.37	0.06	6.90	0.62	Tracer
L-Br	GF Susini	*Leopard Attacking a Bull*	bull	Frick			GF Susini?	0.30	0.09	81.91	0.35	0.20	9.84	0.05	6.69	0.56	Tracer
L-Br	GF Susini	*Leopard Attacking a Bull*	base	Frick			GF Susini?	0.32	0.10	76.14	0.28	0.24	15.31	0.06	6.97	0.58	Tracer
L-Br	GF Susini	*Cesarini Venus*		Quentin			Giambologna	0.20	0.30	84.70	1.30	bdl	8.10	0.00	7.10	0.23	Kevex
Qt	A Susini	*Striding Horse*		Colonna		by 1609	A Susini	0.89	0.21	81.09	4.54	0.20	6.08	0.06	6.66	0.26	Tracer
Qt	A Susini	*Striding Bull*		Colonna		by 1609	A Susini	0.63	0.17	82.18	3.83	0.24	4.86	0.06	7.81	0.22	Tracer
Qt	A Susini	*Nessus and Deianira (Type A)*		Colonna		by 1609	Giambologna	0.75	0.13	82.58	2.48	0.27	6.89	0.04	6.61	0.24	Tracer
Qt	A Susini	*Hercules and Nessus*	Nessus	Colonna		by 1609	Giambologna	0.58	0.19	83.00	2.26	0.32	6.85	0.03	6.94	0.23	Tracer
Qt	A Susini	*Hercules and Nessus*	Hercules	Colonna		by 1609	Giambologna	0.87	0.13	82.03	2.76	0.32	6.09	0.05	7.56	0.22	Tracer
Trt	GF Susini	*Striding Bull*		Liechtenstein		by 1696	A Susini	0.61	0.39	79.80	6.71	0.35	7.07	bdl	4.52	0.52	Tracer
Trt	GF Susini	*Venus and Adonis*	Adonis	Smith			GF Susini?	0.36	0.09	85.30	8.71	0.15	2.67	0.09	2.37	0.25	Tracer
Trt	GF Susini	*Venus and Adonis*	Venus	Smith			GF Susini?	0.37	0.11	86.10	7.88	0.15	2.66	0.12	2.41	0.22	Tracer

Table 2. Result of alloy analysis of study objects.

		standards					difference from actual						linear regression fit to actual					
		factory		custom			factory			custom			factory			custom		
	Element	max	> 0	max	> 0	avg	avg	%	max	avg	%	max	slope	intercept	R^2	slope	intercept	R^2
Major	Cu	99.9	33	99.9	46	80.53	1.38	2	14.53	0.36	0	1.38	0.97	1.46	0.95	0.99	0.75	1.00
	Zn	39.8	32	39.8	46	10.46	0.25	2	1.30	0.12	1	0.93	0.99	-0.13	1.00	1.00	0.00	1.00
	Pb	9.5	29	12.9	43	3.04	0.89	29	20.44	0.24	8	1.34	1.47	-0.60	0.81	0.99	0.04	0.99
	Sn	9.8	22	11.6	42	3.89	0.20	5	2.12	0.10	2	0.52	0.98	-0.07	0.99	1.00	0.01	1.00
Minor	Sb	0.6	11	4.8	33	0.24	0.07	30	1.73	0.02	7	0.09	0.65	0.02	1.00	1.00	0.01	1.00
	Fe	4.0	33	1.8	43	0.20	0.05	24	0.43	0.02	9	0.16	0.81	0.03	0.96	1.00	0.00	0.99
	Ni	29.6	33	29.6	42	1.25	0.06	5	0.46	0.03	2	0.32	1.00	0.04	1.00	1.00	0.01	1.00
	As	0.3	7	4.6	26	0.15	0.16	101	1.69	0.02	16	0.09	1.37	0.09	0.94	0.99	0.01	1.00
	Ag	3.5	6	3.0	19	0.08	0.02	31	0.15	0.01	12	0.11	0.94	0.02	1.00	1.00	0.01	1.00

max = maximum standard value for element in calibration
> 0 = number of standards with value for element > 0
avg = avg value in custom calibration & test set

avg = avg of absolute difference from actual value
% = avg difference from actual/avg value of standards * 100
max = maximum absolute difference from actual value

Table 3. Comparison of factory and custom empirical calibrations for Bruker Tracer III-V.

Attacking a Bull from The Frick Collection, New York, were analyzed in New York in 2009. *'Cesarini' Venus* in the Quentin Collection, a private collection in New York, was analyzed with the Kevex in 2003; Antonio Susini has also been proposed as its author (Leithe-Jasper and Wengraf 2004, Luchs and Smith 2007).

Calibration of the Tracer

Forty of the forty-five objects included in this study were analyzed using the Bruker Tracer. Confidence in the accuracy of these results is based on improvements made to acquisition procedures and quantification methods. Most crucial has been the replacement of the factory empirical calibration with a custom calibration for historic copper alloys. A 'calibration' describes the settings and standards used by the Bruker PXRF software to translate spectral data into numerical results for a particular material. For each instrument, representative standards must be analyzed at particular settings for kV, μA, and geometry; over time the standard set may need to be re-analyzed.

The calibration also indicates elements of interest and which peaks are assessed. In the custom calibration, the elements chosen are those most relevant for Renaissance bronzes — iron, nickel, copper, zinc, arsenic, lead, silver, tin and antimony. For arsenic, the As K-β peak has been selected instead of the As K-α peak to reduce the effect of the overlap with the Pb L-α peak. Available corrections within the PXRF software for peak overlaps and matrix effects were adjusted to improve accuracy.

The most significant difference in the custom calibration is the set of copper alloy standards. Ten factory standards were removed that contained significant manganese, silicon, or aluminum. Twenty-two certified and reference copper alloy standards have been added; a few were purchased to fill gaps in the calibration[2]. The custom calibration also includes a Renaissance medal, previously tested with the Kevex, with high levels of lead and antimony; no standards are available at present for this unusual alloy type. The change in standards has increased the maximum values in the calibration for four elements and the number of reported values for every element (see Table 3).

Errors in the actual values reported in the factory calibration also were identified. The trace levels of silver in four standards (Cu 7131-7134) and a trace level of lead in another standard (CuB10) were over-reported by a factor of 10. The negative influence of these errors was particularly pronounced for quantification of silver because of the general lack of standards with trace levels.

The accuracy of quantification for the custom calibration was then compared to the original factory calibration (see Table 3). For copper, zinc, and tin, the custom calibration reduced the average difference from the actual values, as well as the maximum difference reported. The factory calibration reported very large differences for lead contents above 9%; the new calibration calculated these values more accurately. Differences between the calibrations were more pronounced for the minor elements, with the exception of nickel. The factory calibration also demonstrated systematic errors for some elements, deviating consistently across all values. Comparing the regression fit of the factory calibration to actual values identifies some of these errors; the custom calibration demonstrates none of these defects and quantifies minor elements more accurately (see Figure 6).

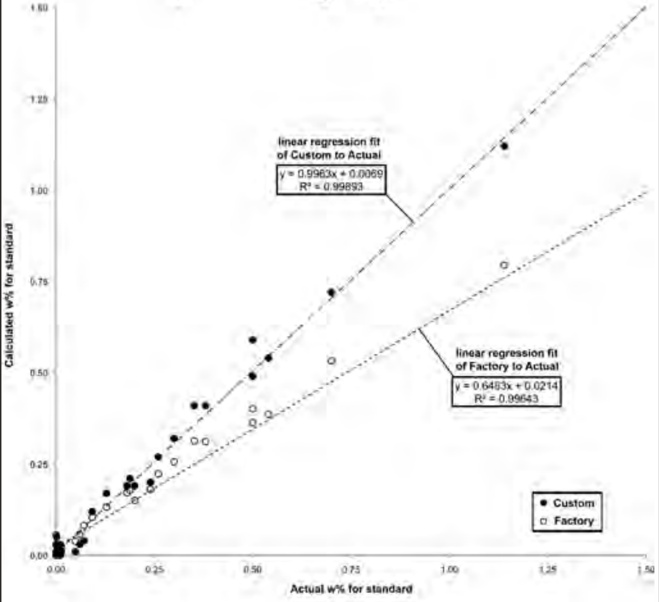


Figure 6. Comparison of antimony quantification using factory and custom calibrations.

Comparison of Tracer and Kevex Results

Quantification performed by the Tracer and the Kevex was also evaluated to determine whether data from the two instruments can be confidently integrated. For this purpose, results were compared for eleven of the study bronzes (representing thirteen distinct alloys) (see Table 4). Based on the deviation between spots analyzed on an individual bronze, an average expected 'intra-object' variation was calculated for each instrument. Overall,

		comparative values (13)			intra-object variation				inter-instrument difference				linear regression fit		
					Tracer		Kevex								
	Element	avg w%	min w%	max w%	+/- w%	+/- %	+/- w%	+/- %	avg	%	max	diff > var	slope	intercept	R^2
Major	Cu	86.73	80.63	91.81	0.86	1	1.27	1	0.75	1	2.34	4	0.80	16.60	0.98
	Zn	2.17	0.11	8.53	0.30	14	0.25	11	0.16	8	0.29	0	0.95	0.19	1.00
	Pb	3.97	0.98	10.03	0.83	21	2.06	52	0.22	6	0.53	0	0.99	0.02	0.99
	Sn	6.08	2.45	9.47	0.68	11	0.63	10	0.52	9	1.38	3	0.96	0.61	0.92
Minor	Sb	0.34	0.16	0.69	0.08	23	0.13	40	0.18	55	0.29	9	1.18	0.12	0.83
	Ni	0.16	0.10	0.25	0.06	39	0.10	62	0.11	72	0.20	10	0.69	0.17	0.57
	Ag	0.09	0.03	0.19	0.04	43	0.01	12	0.03	29	0.06	4	0.60	0.02	0.70
	As	0.20	0.14	0.34	0.09	47	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	Fe	0.27	0.09	0.55	0.11	41	0.13	50	0.14	54	0.38	9	0.18	0.20	0.04

intra-object variation = 2*average SD among spots for individual object = ~ 95% confidence interval
% variation = average variation/average value of element *100

avg difference = avg absolute difference of Tracer and Kevex
% difference = avg difference/average value of element*100
max = maximum absolute difference in tested objects
diff > var = number of values where difference exceeds intra-object variation

Table 4. Comparison of Tracer and Kevex quantification.

this variation was similar, approximately 10% of the average value for major elements and 50% for minor elements. The intra-object variation for lead reported for the Kevex was considerably higher than the Tracer. For silver, variation values for the Tracer were higher, likely the result of insufficient trace silver standards in the calibration combined with the interference of the Rh K lines.

For the major elements, the average inter-instrument difference between the Tracer and Kevex was found to be less than the intra-object variation for the Tracer (see Table 4). Therefore, on average, a test performed on an object with the Kevex should fall within the range of values that might be obtained using the Tracer, allowing results to be successfully combined. Some individual inter-instrument differences exceeded the expected intra-object variation, including the four highest values for copper and the tin values associated with three of the same objects. This appears to be an effect of normalization, which is applied across all elements for the Kevex and is most pronounced in the highest values, in this instance, copper and tin.

For trace values, the inter-instrument differences were slightly higher than the expected intra-object variation. Nickel values reported by the Kevex were consistently higher than those on the Tracer. However, a nickel artifact of approximately 0.1% was previously was identified for the Kevex, close to the offset observed. A systematic difference was also observed for antimony, the cause of which has not been determined (see Figure 7). The Tracer custom calibration contains antimony standards in the range evaluated and calculates values for those standards accurately. Because of the particular importance of antimony in the present study, the Kevex values were adjusted to conform to the Tracer values using the linear regression least squares fit.

Results and Discussion

The vast majority of the study group objects are tin bronze alloys (see Figure 8). Within the tin bronzes, discriminant analysis identified five distinct groups differentiated primarily by lead and antimony content. (see Tables 1, 2; Figure 9) The significant variations in lead represent deliberate modification of the alloy; antimony is most likely introduced incidentally with one or more of the raw materials.

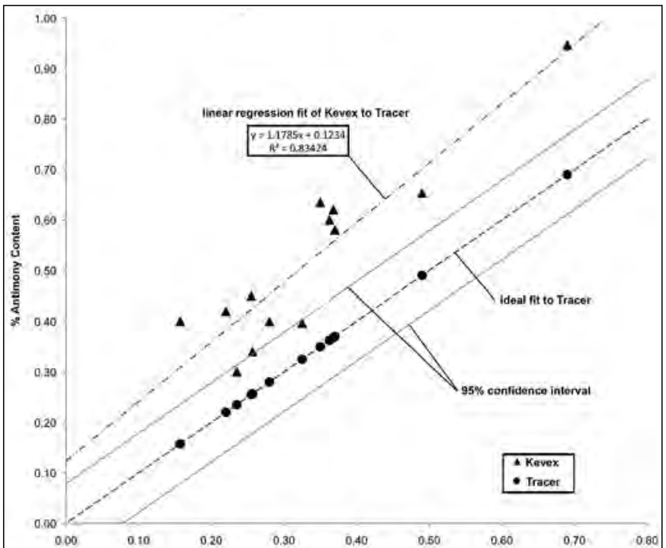


Figure 7. Comparison of antimony quantification on Tracer and Kevex.

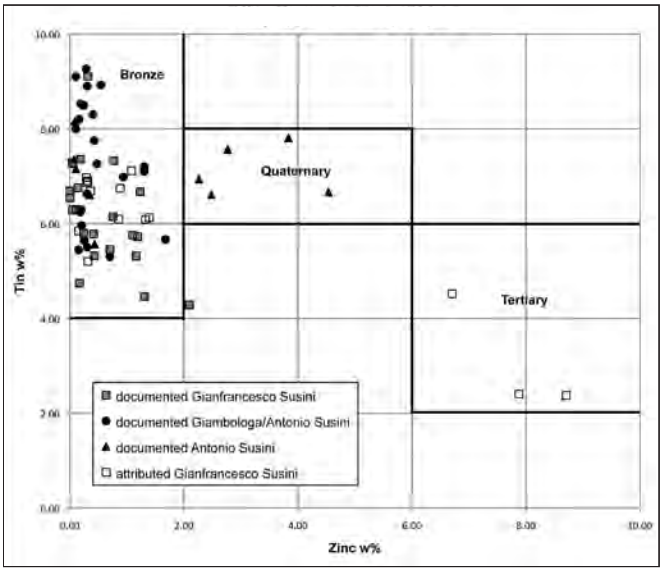


Figure 8. Alloy types in study objects.

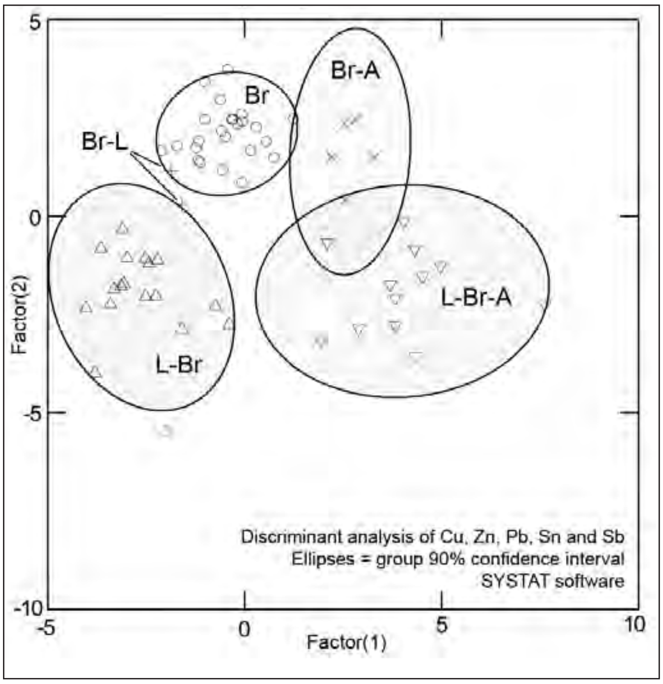


Figure 9. Alloy groups in study objects.

All thirteen reference objects for Giambologna and Antonio Susini belong to group (Br), which has low levels of lead and antimony. Three of the reference works by Gianfrancesco also belong in this category and therefore would not be differentiated by alloy analysis. However, these three are models of Gianfrancesco's own design, clearly identifiable by style and subject. One of the undocumented objects, *David and Goliath* (see Figure 3), also fell into this group. Gianfrancesco's authorship is confirmed by the nearly identical alloy of the stamped and documented cast of this subject in the Liechtenstein Museum.

Two of the reference objects by Gianfrancesco fell close to the (Br) group, but are distinguished by additional lead (> 4 w%). These are designated (Br-L). One of these was a model by Gianfrancesco, the other a model attributed to Giambologna.

The (Br-A) group includes three documented works by Gianfrancesco, all from his own models. This group is distinguished from the (Br) group by a small increase in antimony (0.73 w% vs. 0.45 w%).

The (L-Br-A) group contains additional lead and elevated antimony (> 0.9 w%). Parts of three models of Gianfrancesco's design belong to this cluster, including three bases. The group also includes four documented casts by Gianfrancesco after the designs of Giambologna. Two unattributed objects fall into this category, confirming their connection to Gianfrancesco: a small *Kneeling Bather* from the Smith Collection (see Figure 4) and *Lion Attacking a Stallion* from The Frick Collection.

The (L-Br) group has added lead but without the elevated antimony content of (L-Br-A). Two animal groups and a *Pacing Stallion* belong to this alloy group. These are after models by Giambologna or Antonio Susini, but with documented dates that suggest production by Gianfrancesco. Six of the undocumented works fall into the (L-Br) category. Five of these casts are after models by Giambologna or Antonio Susini (see Figures 1, 2). The design of *Leopard Attacking a Bull* has been attributed to Gianfrancesco. However, a documented model by Giambologna may also correspond to this group (Draper 1985).

The (L-Br) group also includes a bronze with the signature of Antonio Susini, *Farnese Bull* from the Galleria Colonna. Although the cast itself is dated 1616, its purchase from Gianfrancesco is documented to 1628 (Keutner 1990). It is difficult to imagine that this large and expensive bronze sat in the workshop for more than a decade. Perhaps it was cast by Gianfrancesco for his uncle or at a later date using his uncle's model? Alternatively, this leaded alloy could represent a practice introduced late in Antonio's career and continued by Gianfrancesco.

At present, the different alloys found in works by Gianfrancesco do not appear to be associated with the date of production. However, there may be a relationship to the author of the model. The objects found in groups (Br), (Br-A), and (Br-L) are all Gianfrancesco's casts of his own designs. Most of the objects in groups (L-Br) and (L-Br-A) are casts after models by Giambologna or Antonio Susini. The high levels of lead included may suggest a desire to reduce the cost of raw materials in works not of his own design. The leaded alloys found in models by Gianfrancesco are all components of multi-part casts that also include non-leaded components. In these objects, the addition of lead may reflect modification of the alloy for distinct stages of casting. Further investigation of the casting sequence of Gianfrancesco's bronzes may lead to a better understanding of these alloy differences.

In addition to the bronze groups, four of the tested objects were quaternary alloys (Qt). These four objects originate from the Salviati family collection and are now in the Galleria Colonna. All can be documented to Antonio Susini (Watson and Avery 1973, Keutner 1990). Two of these, *Pacing Horse* and *Pacing Bull*, have been considered documented works by Gianfrancesco, however, the Salviati collection also had casts of these models by Antonio. When considered with the documentary evidence, the similar alloys of *Horse*, *Bull*, and the two *Hercules* groups supports the theory that Antonio Susini was their creator. Quaternary alloys are not typically associated with works by Antonio Susini. This discovery provides a new point of reference for attribution to be explored in future studies.

Two objects attributed to Gianfrancesco, the Liechtenstein *Striding Bull* and the Smith Collection *Venus and Adonis*, were found to be tertiary alloys (Trt) containing more than 6% zinc, clearly distinguishing them from any of the reference objects. These do not represent a coherent group, therefore an average is not reported. These bronzes may have been produced by other successors to Giambologna's workshop, such as Pietro Tacca (b. before 1577 – d. 1640) and his son Ferdinando (b. 1619 - d. 1686).

Conclusion

Results of this study demonstrate that the handheld Bruker Tracer XRF can successfully analyze historic copper alloys, if the instrument has been calibrated properly for this purpose. Analysis of a comparative set of bronzes on the Tracer and the laboratory-based Kevex XRF indicate that results can be integrated, although some corrections may be necessary for the minor elements.

Using data obtained with the Tracer and Kevex instruments, this study has determined that alloy analysis can assist in the attribution of small bronzes by Gianfrancesco Susini, distinguishing them from casts by Giambologna and Antonio Susini. Two groups of antimonial alloys, one with added lead, appear to be specifically associated with Gianfrancesco Susini. A third group of leaded bronzes also appears to be associated with Gianfrancesco, although certain historical questions remain to be resolved. A group of quaternary alloys identified in documented works by Antonio Susini may also provide a basis for future attributions.

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Endnotes

[1] 'Bronze' here refers to any copper alloy sculpture; 'tin bronze' indicates the technical definition.

[2] European Commission, Institute for Reference Materials and Measurements, reference set for historic copper alloys, BCR-691; one with 4.6 w% arsenic.

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Q & A SESSION

Bruce Kaiser: When you did the analysis on the small objects at the different locations – those last objects we saw, did you do several locations, did you determine the average? Is that how you got the lead content or the antimony content so close?

Dylan Smith: Yes, I think generally there would be at least 3 points, not only on every object, but since some of these objects are made of multiple parts there would be 3 or more points on each part to generate an average.

Bruce Kaiser: And that plus or minus, was how much those points varied in composition? So when I see a 0.4 ± 0.3, that's actually the difference in the location, it's not the difference in the instrument itself. Is that correct?

Dylan Smith: Yes that's two standard deviations based on the measurements made on the object.

Bruce Kaiser: Ok, and if I was looking at that bull on the screen there, what were your typical locations on the "pacing bull"?

Dylan Smith: Flat places.

Bruce Kaiser: Flat places – ok that's fair.

Dylan Smith: This is an interesting question that we can get into in the discussion – spot selection, which when you are running samples is not a big deal but when you're looking at actual objects [it is]. But usually I'd try to look at spots that are clean and also not overly worn. This is something that has come up in discussion at the Gallery. All of these objects – and this is something I didn't get into here, have original coatings on them – typically drying oils. And there is somewhat of a debate about whether it is better to analyze through that film, recognizing the film will have some impact, but that the metal under it will be well-preserved. This is as opposed to say, a spot that is very worn, which might be perfectly clean but that wear is going to have its own impact on the analysis. But a general comment I would make is that I am actually surprised in doing these at how consistent you can get results on various locations on these objects. I think a lot of that has to do with the fact they've lived very happy lives in these beautiful Renaissance and Baroque interiors and in various museum collections.

Bruce Kaiser: So if you are looking at lead it says 1.9 ± 2.3

Dylan Smith: I'm sorry, that is for the entire group. So basically the objects in that group maintain a level that is below about 4 per cent, and it is likely that the lead is not deliberately added to those.

Bruce Kaiser: Ok, thank you.

Mark Erdmann: Not being an experienced user of XRF and maybe you just answered this, but could you elaborate a bit further on the effect of surface patina and whether there is any need for preparation before doing your analysis?

Dylan Smith: Yes. That's a great question and I think there is the problem that for the most part you cannot do preparation. So really the main thing you can do is to try and select optimal spots. For these objects, and even objects in your own collection, it is not going to be desirable or in many cases possible to do anything like polishing. An issue that I didn't address here is that because a number of these objects are made in parts you really have to test locations. Like with the '*Hercules killing a Centaur*' the top part of that and the bottom part of that were actually separate parts. To test those, there wouldn't be anywhere convenient, you could test the bottom by polishing it maybe but on that upper part you couldn't possibly test it by polishing so what you do is just try and pick a spot that seems to be the cleanest and the best preserved. One issue that I've certainly run into on some projects is - a lot of dust can accumulate over the centuries as some of these objects have sat out [in the gallery]. Sometimes it's appropriate to do a little dusting but other times, if it is someone else's object they may not be ok with you dusting it. So you just try and pick the cleanest possible spot. Of course that introduces other sources of error but you just have to take that into account when you're thinking about what that data really means.

Mark Erdmann: And are you getting any results to indicate the chemistry of the patina that is on the surface?

Dylan Smith: There is some interesting work that has mainly been done by Richard Stone and the Metropolitan Museum and just a little [plug] for his work – he has been collaborating with some of the scientists at the Kunst Historisches Museum in Vienna and he has an article that is about to come out on the organic patinas that are on Renaissance bronzes, that is going to come out in December, in the *Metropolitan Bulletin*. But for the most, the most common material is drying oils – linseed oils – they are baked, a lot of these were probably transparent. They didn't have any pigments in them, and with a little bit of coloration caused by using stand oils or by heating the oil. Sometimes they do have pigments in them, the most common one is carbon black which is just lucky as that doesn't really interfere with XRF analysis, but you could have other pigments added to that. Which again, then you have to when you're doing the analysis, analyze a spot that doesn't have the patina and analyze one that does, so you get a sense of what is really going on there and that is going to affect your XRF analysis.

BRINGING CONTEXT TO THE SMITHSONIAN COLLECTIONS OF PRE-COLUMBIAN GOLD FROM PANAMA THROUGH TECHNICAL EXAMINATION AND ANALYSIS

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Abstract

The study of pre-Columbian gold in Panama has been slow to progress due to the relative scarcity of well-contextualized materials. While the original contexts of many museum objects have been lost, the Smithsonian collections of Panamanian gold were re-evaluated for their potential to answer key questions about gold working in the region. Over 300 objects underwent technical examination and calibrated X-ray fluorescence (XRF) analysis to provide information on fabrication techniques and composition. The results have already begun to contribute to our understanding of gold working in the Isthmian region.

Keywords: Gold, copper, tumbaga, archaeology, Panama, XRF

Introduction

Pre-Columbian goldwork from Panama has been widely collected and admired, but unlike the metalwork of Mexico, Costa Rica, Colombia and the Andes, Panamanian objects have been the focus of relatively few technical studies. Since Lothrop published his comprehensive monograph on the excavations at Sitio Conte (1937), which included analysis of metal objects by W.C. Root, only a handful of researchers have undertaken technical studies specifically addressing Panamanian gold and *tumbaga* (gold-copper alloy) objects (Root 1950, Howe 1986, Fleming 1992, and Scott 1995).

A significant stumbling block is that most Panamanian gold objects housed in museum collections were excavated by grave robbers (*huaqueros*) and amateur archaeologists who rarely recorded location or context. Without contextual information, these objects are of limited scientific value, allowing only broad technological generalizations to be made. Institutional regulations discouraging destructive analysis have also presented another obstacle to the scientific study of this material. The question then remains: Is it possible to gain useful information about the development and regional variations of gold working in Panama from the objects in museum collections?

Researchers at the Smithsonian's Museum Conservation Institute (MCI) have attempted to do so through a large-scale technical study of Panamanian gold and *tumbaga* objects. Begun in 2007, it incorporated technical examination and XRF analysis of several collections in Panama (Beaubien 2008). The second phase of the project, which is the focus of this paper, applies the same analytical and data recording methods to the collections of two Smithsonian museums, comprising 231 catalogued objects from the National Museum of the American Indian (NMAI) and 78 objects from the National Museum of Natural History (NMNH). These objects, which include beads, pendants, bands, plaques, sheathing, bells, rings and tools, were selected based on their Panamanian origin and identification as gold, copper, or an alloy (see Figure 1).

Methodology

The project design comprised three major components: research into object provenience, technical examination and non-destructive instrumental analysis, described briefly below. In order to organize the varied sources of information for each object, a FileMaker Pro database was designed, which allowed active recording during examination, as well as import of data, images and related documents.

Archival Research

As the museum records often contained little

Figure 1. Panamanian gold and *tumbaga* objects in the NMAI collection packed for study at MCI (Courtesy, National Museum of the American Indian, Smithsonian Institution, Photo by A.Harrison)

provenience information, such as the excavation site, research was conducted in the collection archives at NMAI and NMNH, as well as holdings in the University of Pennsylvania Museum of Archaeology and Anthropology, and the American Philosophical Society. From the resulting letters, customs documents and field notebooks, it was possible to more closely assign provenience and site locations to a substantial number of objects, and confirm the reliability of the site and province attributions already in the museum records.

Technical Examination

Visual examination and optical microscopy were carried out on each object included in this study. Description, condition information and notes on fabrication techniques were recorded, including evidence of tool marks, casting traces, joinery, corrosion types, and surface enrichment. The primary production technique (e.g. hammered or cast) was also identified for each object at this time.

XRF Analysis

Every object in this study was analyzed at one or more locations using a portable bench-top ElvaX XRF. The instrument measures elements present at and just below the surface within the beam area (~1cm diam.). The heavy element mode was used for this study, which allows detection of elements from Cl (17) to U (92). Analyses were conducted at 45 keV in count rate stabilization mode, which varies the tube current to achieve a per-sample count rate of 6000-6200 counts per second for 100 seconds live time.

For this study, a set of approximately 35 matrix-matched gold reference standards (Royal Canadian Mint BCR 8079) were analyzed to create a material-specific calibration in the ElvaX software, reporting results in wt%. A selection of these standards was analyzed periodically during testing to adjust the calibration and monitor instrumental precision and accuracy. The limits of detection for each element vary according to the matrix in which they are present. For copper and silver in a gold matrix, they are approximately 0.1-0.2% and ~0.25%, respectively, and for gold in a copper matrix, ~0.25-0.5%.

One or more analyses were made of each object, with condition features recorded and photographs taken of each analysis spot. By noting the presence of bulky corrosion crusts, surface enrichment and variations in surface coloration, it was possible to better evaluate the reliability of the data as representative of original composition.

Results and Discussion

The data set of objects used for further interpretation was refined in two steps. First, only those with reliable provenience information, determined during the archival research phase of the study, were selected; this step reduced the number of objects from 309 to 218. Second, objects with XRF data considered to be unreliable were removed: this further refined the group to 189 objects. Compositional data were eliminated in instances of extensive copper corrosion at the analysis spots or of obvious depletion gilding exhibited by thin gold surface layers on copper-rich (typically heavily corroded) interiors. In general, copper-rich objects are assumed to have undergone some degree of corrosion of those alloy phases in the burial environment, so XRF measurements can only be considered approximations of the original composition. The presence of extensive corrosion signaled that data were even less likely to be representative.

Surface-matrix differences present another issue, as surface enrichment is known to occur frequently on Panamanian objects either as a consequence of annealing and further working or from intentional depletion gilding (Scott 1995, La Niece 1998). Techniques such as surface abrasion and cross-sectional sampling are generally used to increase confidence in results; however, only non-destructive methods were permitted on the Smithsonian objects. Scott (1995) had found experimentally that the elemental variation between surface and substrate was only a few percentage points difference. In addition, depletion gilded layers generally contain some percentage of lower density elements (Ag and Cu), are porous, and typically under 20μm thick. This is well within the characteristic X-ray attenuation depth for Au, calculated to be 49μm using the mass absorption coefficient of Au at 43KeV (from Roy et al. 1997). Our assumption, therefore, is that in cases where surface enrichment is present, the compositional data would be most representative of the matrix. Nonetheless, those objects with obvious depletion gilding were eliminated in this study. Variation in elemental concentration due to segregation was not considered a problem, as the beam diameter of the ElvaX is relatively large (1cm). Despite the issues involved with surface analysis of heterogeneous metal objects, it is believed that many of these problems have been mitigated by the experimental parameters used and removal of potentially misleading data, although the resulting data set under-represents objects with higher copper levels.

The compositional data indicate that all the museum objects contained Au and Ag, with a majority also containing Cu. Many had trace amounts of Fe, noted as an impurity in similar materials (Lothrop 1937) and likely due to traces of soil. No other elements were detected. For interpretation, the Fe data were removed from the compositional calculations, and the Au, Cu, and Ag measurements were normalized to 100% (see Figure 2).

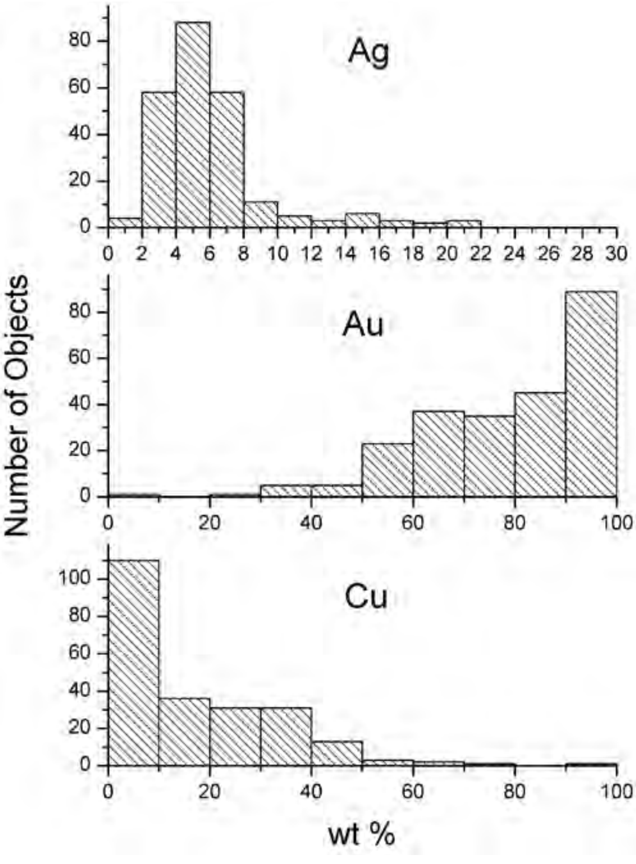


Figure 2. Relative frequency plots of XRF data from Panamanian objects in the NMAI and NMNH collections showing Ag, Au, and Cu content

The Ag content for a majority of objects was 4%- 6%, with the occasional outlier ranging up to 22% (see Figure 2). The plot of Ag to Au content demonstrates two major compositional groupings (see Figure 3). The first group is distinguished by the linear trend extending from near 0 to around 5% (±3%) Ag. The majority of objects fall within this group, which comprises Au and Au-Cu objects with Ag present entirely as an impurity in the Au. The other linear trend with the negative slope from 20% to 0% Ag indicates objects with no Cu component at all. A silver content of more than 8%, which was measured in a relatively small number of objects, was determined to be beyond the typical Ag content found as an impurity in Panamanian gold.

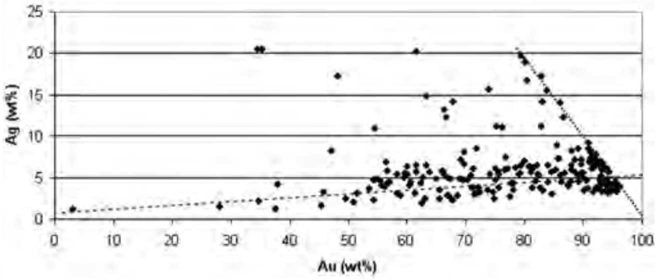
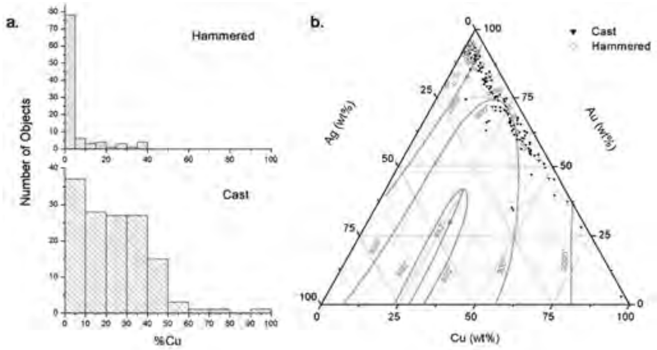


Figure 3. Plot of Ag vs. Au concentration in wt% of Panamanian objects in NMAI and NMNH collections

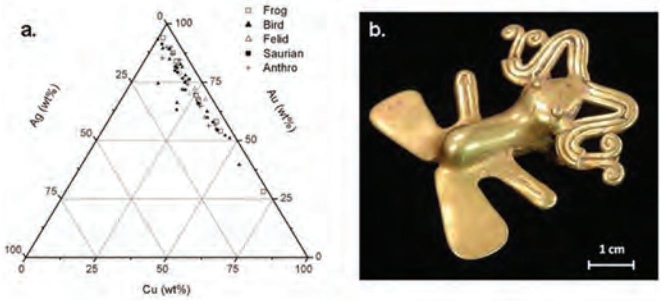
There is a clear correlation in our results between the cast objects and a higher Cu content (see Figures 4a, 4b). From a practical standpoint, the addition of copper to gold lowers the melting point and increases hardness, which in turn improves the ease of casting. In addition, gold-copper alloys can be depletion gilded, which produces a gold colored surface on a copper-rich substrate. Symbolic meanings of imagery, certain colors, construction methods, tastes and smells have also been suggested as factors in technological choice (Reichel-Dolmatoff 1990, Lechtman 1996). However, the review of the data plotted by object type (pendant, sheathing, bell, bead, etc.) revealed no visible compositional patterns other than that expected from differences in basic fabrication technique.



Figures 4. a) Comparison of Cu content between hammered and cast objects from Panama in the NMAI and NMNH collections. b) Ternary diagram of cast and hammered objects with superimposed Au-Ag-Cu phase diagram

Within the group of cast pendants, which represent a wide range of animal types, some distinctions are suggested. Researchers have proposed a connection between the smell of high-copper alloys and that associated with frogs (Reichel-Dolmatoff 1990), and in a study of Panamanian and Costa Rican pendants, Scott (1995) found a higher copper content in those representing frogs compared with other animal types. Our data reveal only a slight difference between the compositions of frog, saurian, avian, felid and anthropomorphic pendant types (see Figures 5a, b).

This finding should be considered in context, however, as data generated from 50% of the frog pendants were removed from consideration – the largest group of pendants eliminated – due to excessive corrosion. This statistic points to a higher overall copper content of the frog pendants.



Figures 5. a) Ternary diagram showing compositional differences by pendant type. b) Frog pendant, from La Vuelta, Panama, A396672 (NMNH, Dept. of Anthropology)

When comparing data from the Panamanian material with adjacent regions, a clear compositional trend emerges (see Figure 6). The data used here for comparison is taken from the published results of SEM-EDS analyses by Rovira (1994) of objects produced by the Calima, Muisca, Quimbaya, Sinú, and Tairona, all pre-Columbian cultures in Colombia. While other elements were reported in minor and trace amounts, only Au, Ag and Cu were used here, normalized to 100%. In addition, several XRF and SEM-EDS analyses reported by La Niece (1998) were included. While the Colombian material has a similar range of Au content to that of the Panamanian objects, there clearly is a higher average Ag content. A greater percentage of the Panamanian material has a lower Cu content and the gap between 5 and 25% Cu in the Colombian material is not at all present in our data. This compositional distinction between Panamanian objects and those produced in neighboring regions provides strong evidence that the vast majority of gold objects were produced locally. While some scholars have suggested that long distance trade was a primary source of the skillfully crafted gold ornaments found in Panama (Helms 1979), the current data contradict these claims.

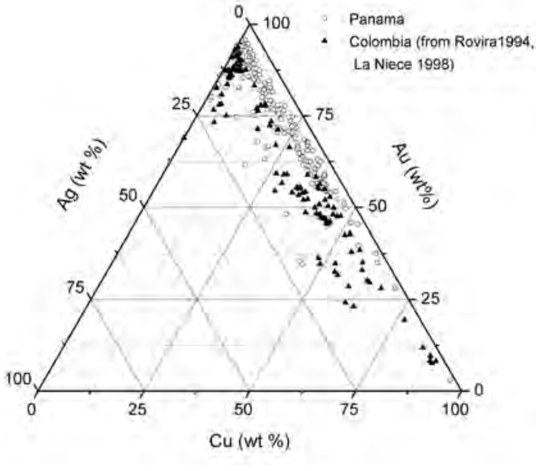


Figure 6. Ternary plot of Cu, Au, and Ag comparing composition of Panamanian and Colombian gold and *tumbaga* objects

Sorting the data by archaeological zones within Panama reveals a slight inter-regional variation in composition (see Figures 7, 8). The group from Veraguas Gran-Chiriquí (VGC) in western Panama includes objects with up to 22% Ag, a trend noted by others (Root 1950, Fleming 1992). Similarly high levels of Ag occur in the group from Panama/Colón, named after the modern provinces in the east. Objects from Gran-Coclé, which includes most of the Azuero Peninsula in central Panama, exhibit a lower average Ag content and no objects with over 9% Ag. A greater percentage of Gran-Coclé objects are also made of very high purity gold. The high Ag content of VGC and Panama/Colón objects may indicate imported objects and materials, or local sources of high-Ag gold ores. This regional pattern may not be so straightforward, however, as Cooke et al. (2003) have presented evidence of high Ag ore sources in central Panama, and elsewhere.

Figure 7. Map showing the three archeological regions discussed in this paper (after Cooke et al. 2003)

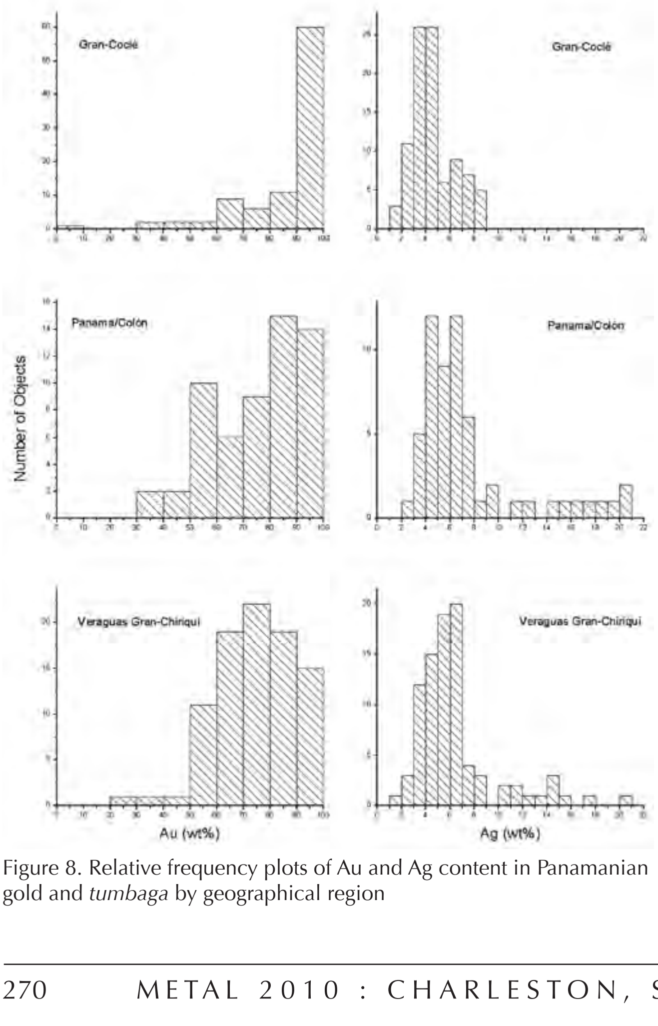


Figure 8. Relative frequency plots of Au and Ag content in Panamanian gold and *tumbaga* by geographical region

Conclusion

Results from this investigation suggest that archaeological metals from museum collections may be fruitfully studied, despite their often limited provenience information and necessity of using only non-destructive analytical techniques. Archival research was found to be useful for refining the final XRF data set to objects with reliable provenience information, and it is also believed that errors in the XRF data were minimized by removing potentially misleading data due to corrosion and enrichment.

The findings to date suggest that the compositions of a majority of the objects used in the final data are the product of using gold ores with impurities, rather than deliberate alloying. The overall percentage of Ag was found to be within a naturally occurring range and characteristically low compared to that of neighboring regions, providing evidence of local production centers in Panama. A large number of objects were also found to have Cu in relatively low quantities, which we believe could have been introduced as an impurity in the ore. However, it is also clear that deliberate alloys with much higher levels of Cu were also being produced, particularly for cast objects, although many of these were eliminated from the data set on the basis of excessive copper corrosion.

This project has added significantly to a growing body of information about an understudied gold working region. Detailed documentation of fabrication techniques, composition and condition, and additional contextual information retrieved from archival sources, are available for each of the 309 objects in the study, which will be of benefit to those researching and conserving the NMAI and NMNH collections. Results also underscore the need for more detailed metallographic study of individual objects, further analytical investigation of ore sources and placer deposits, in addition to well-contextualized scientifically excavated materials to better understand the development and history of gold working in ancient Panama.

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Q & A SESSION

Karl Knauer: This is really phenomenal Ainslie, I think this is going to have a lot of implications for other conservators working on comparable collections. I was just wondering, do you have plans to go further with trace element analysis or work on other collections that do have well-documented materials with good provenience?

Ainslie Harrison: Ok, the first part of the question: Yes we have samples from a site in Panama that we've been working at, that we are allowed to do destructive analysis on. So we are going to do analysis – ICP-MS on that material. As far as doing trace element analysis on the collections, it's a bit more difficult with sampling requests.

Karl Knauer: Thank you.

Bruce Kaiser: This is Aaron Shugar's question/answer: You said when you probed with 45 KeV you could go to what depth?

Ainslie Harrison: We calculated 55 microns.

Bruce Kaiser: Here's a bit of physics for everyone: what's important is, if you are going to excite gold, yes you have to use an energy higher than the binding energy of gold – no question. The bad news is: that's always the case. The depth that you can actually analyze to is the depth that the gold X-ray coming out can go through so while it's 55 microns for 45 KeV, the actual depth that you can measure gold in gold is ¼ of that. So in XRF you always have to send in energy that is higher in energy than the binding energy. Otherwise you cannot excite the atom. But the depth you actually measure to is what that atom can emit back out and in gold it is actually ¼ of that distance.

Ainslie Harrison: We imagined that the depth would be greater or not greater than that. But hopefully the porosity of the matrices that we were analyzing would compensate for that difference.

Bruce Kaiser: Ok, now I have some other bad news: it matters not whether it is a powder or a solid. Porosity has absolutely no effect.

Ainslie Harrison: Also, we did some empirical testing where we layered gold foil on the analyzer with a copper penny on top and we were able to measure the copper, we got copper peaks.

Bruce Kaiser: By the way that's an excellent way to determine how deep you can measure copper.

Aaron Shugar: I can ask my own questions or answer my own questions but when I was looking at that I was asking Bruce about the potentials to focus exclusively on the gold. Because tumbaga is mainly copper and silver and has a small amount of gold which is brought to the surface through the process you described. So my question was more, how can you adjust your settings to focus on a thinner gold layer and exclusively get the information back from the gold rather than collecting information of the copper-gold-silver 'Tumbaga' alloy?

Tim Foecke: Please excuse my number of times to the microphone here but this is my first introduction to this particular community and I'm having a really good time. One of the things, as you mentioned, you can change the composition through alloying and obviously the ring was cast so it is possible there are co-mingling sources. One of the ways that you could identify the source of gold is an extension of a technique we've developed for analyzing locations where coal came from. By doing sulfur-isotope geochemistry, where we just look at the isotope make-up of sulfur out of various samples, it'll vary depending on where it came from in the world. I would imagine with gold it would be even easier because of the number of isotopes available that you'd be able to get some sort of a pretty good fingerprint from 6 or 7 isotope ratios depending on where it physically came from. That brings in the question: you have to put it into a vacuum chamber and what is non-destructive – you have to sputter off 1 or 2 atom layers in a little spot - you'll probably never see it, but that is splitting hairs again.

Ainslie Harrison: Yes you also have to have access to the gold ore sources in Panama to do any provenance studies. I've tried contacting all the mining companies because there is a great deal of mining going on in Panama and it is almost impossible to get data or samples from them.

Tim Foecke: Yes it took me 6 years to get a rivet from the Panama Canal – so I can empathize…

THE EFFECT OF SURFACE CHANGES IN HEAT TREATED BRONZE SAMPLES ANALYZED BY X-RAY FLUORESCENCE SPECTROMETRY

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Abstract

X-ray fluorescence spectrometry (XRF) is often used to determine the composition of bronze sculpture. The limitations of XRF are well known: patinas, platings or other surface treatments can potentially interfere with the accuracy of results. However, the influence that previous restorations involving the use of heat may have on surface analysis has not been studied. In this study, XRF was used to examine the effect of heat treatment on 37 copper alloy samples of varying composition, following a simulated restoration treatment with temperatures above 680°C. Cross sections were studied by reflective microscopy and SEM-EDS. Results indicate that restoration treatment using heat causes a difference in the surface composition of many alloys. In particular, lead-containing alloys are highly influenced by heat treatment; both zinc and tin-containing alloys change to a lesser extent, and the use of acid pickling also plays an important role.

Keywords: XRF, XRD, copper alloys, reconstructed production techniques, surface changes, restoration treatment, acid pickle

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Introduction

The composition of a Renaissance bronze directly relates to the appearance of the object and has been the subject of increasing interest over past decades (Bewer 1996, Scholten et al. 2003, Scholten et al. 2005). Various studies have tried to correlate alloy composition to a sculptor's workshop (Cristanetti et al. 2007, Bassett et al. 2008). X-ray fluorescence spectrometry is frequently used for the compositional analysis of bronze objects (Lutz and Pernicka 1996, Ferretti and Moioli 1998, Glinsman 2004). A major advantage of XRF is that it is non-destructive and provides results quickly. XRF has been shown to provide information to a depth of 20-30 µm on bronze alloys (Glinsman 2004). Careful choice of sample location on exposed metal surfaces, multiple analyses and large spot size can be used to obtain the most representative result. However, another factor that appears to be significant has not yet been studied: changes due to restoration treatments involving heat. Since visual changes can often be seen on the surface of bronze objects during and after heat is applied, it is likely that compositional changes are also occurring. Therefore, an XRF result obtained from a sculpture that has been heat treated may not be representative of the original alloy of the sculpture.

The aim of this research is to give more insight into the surface changes that take place on 37 different copper alloys after a simulated restoration using heat has taken place. The simulated restoration treatment employed is the common historical restoration technique of brazing, including the application of flux and its subsequent removal with an acid pickle. The alloys were chosen based on information found in different recipes from Renaissance literature sources (Cellini 1967, Gauricus 1969, Dodwell 1986, Smith 1990, Kee 1992, Bewer 1996, Brepohl 1999, Cristanetti et al. 2007) and were chosen to reflect a wide range of alloys in use from this period onwards.

The research focused on binary, tertiary and quaternary copper alloys, with varying amounts of tin, lead and/or zinc. This research aims to investigate if restoration treatment involving the application of heat, flux and pickle influences the surface composition measured by XRF.

Experimental

A Bruker Artax x-ray fluorescence spectrometer with a tungsten tube with a 2x3mm spot size and a silicon drift detector with a resolution < 145 eV for Mn-Kα was used. Analyses were performed with a tube voltage of 50 kV and a tube current of 300 µA for 120 seconds. A

25 µm nickel filter was inserted in the primary beam. Results were quantified using the Artax software (version 5.3) with a standards based quantification method. To study the process of compositional surface changes, polished cross sections of the samples (embedded in Epo Fix) were examined by reflective microscopy (Leica D8 with a 420 Digital camera using Leica LM1000 software) and energy dispersive X-ray spectroscopy (EDS, Ultra dry silicon drift detector, Noran System 7 software, Thermo Fisher Scientific) coupled to a scanning electron microscope (SEM, JSM5910LV). The X-ray micro diffraction instrument used for identification of the dark layer on the metal after treatment was a Bruker D8 DISCOVER with GADDS (Bruker, Karlsruhe, Germany). The instrument was equipped with a two-dimensional detector (HI-STAR, Bruker, Karlsruhe, Germany) and operated with Cu-Kα radiation working at 40 kV and 30 mA.

Sample preparation

Pure metals of technical grade (technical grade means that the metals are 99.9% pure) were obtained and analysed using XRF, weighed and melted together. One rectangular plate measuring 60 x 20 x 5mm was cast from each alloy. Plates were cast in sand molds according to traditional casting methods based on Campbell (2007). Each plate was subjected to the same procedure, as follows: the plate was air cooled and then sanded with 220 grit sandpaper. Two spots (numbered spot 1 and spot 2) were stamped with circular marks so that analyses could be done in the same locations throughout the process. XRF measurements were taken on spot 1 and spot 2, to quantify the components of the alloy before heat treatment. The metal plate was sawn into two pieces and borax flux (sodium tetraborate) to enable the brazing was applied to the cut edges and to a portion of the surrounding surfaces, covering spot 2. The cut pieces were then brazed back together using standard restoration techniques, using a silver solder with a melting point of 680°C. The heating time was approximately 60-90 seconds, depending on the length of time required for brazing. After brazing the plate was air cooled and spot 1, not covered with borax, was analyzed with XRF before the plate was dipped in a 5% heated (50°C) sulfuric acid solution (pickle) to remove oxides and borax. The plate remained in the pickle until the flux was removed. Spot 1 and 2 were analyzed again with XRF. The results are recorded in Tables 1-4. Three cross sections were taken:

1. after casting and sanding, at one end of the sample
2. after brazing and before pickling, at the end not covered with borax
3. after pickling, in the middle of the sample including the brazing seam, overlapping the borax-protected and unprotected areas

Results and discussion

Binary copper lead alloys

Visual examination of alloys containing less than 3% lead revealed that the copper color of the surface does not change after heat treatment and pickling. Alloys containing more than 3% lead have a black surface that remains after the pickle treatment in areas that were not covered by borax. Areas that were covered by borax are still copper colored after the pickle treatment. The black surface that remained on the sample was analyzed by XRD, and consists of a mixture of lead(II) oxide (PbO) and lead sulphate.

XRF measurements (Table 1) show two major results:

Alloy type	Cu99.5 Pb0.5		Cu99 Pb1		Cu97 Pb3		Cu95 Pb5		Cu93 Pb7		Cu90 Pb10		Cu85 Pb15	
Element	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
Before brazing spot 1	99.5	0.5	99.1	0.9	97.1	2.9	95.1	4.9	92.7	7.3	89.8	10.2	86.5	13.5
Before brazing spot 2	99.5	0.5	99.0	1.0	97.0	3.0	95.3	4.7	92.7	7.3	90.7	9.3	85.3	14.7
After brazing spot 1 no borax	98.4	1.6	97.5	2.5	74.0	26.0	40.0	60.0	29.1	70.9	12.2	87.8	3.3	96.7
After pickling spot 1 no borax	99.7	0.3	99.6	0.4	93.1	6.9	60.6	39.4	38.6	61.4	12.0	88.0	3.1	96.9
After pickling spot 2 borax	99.8	0.2	99.7	0.3	94.3	5.7	98.7	1.3	75.6	24.4	72.8	27.2	22.7	77.3

Table 1. Composition of copper lead alloys before and after brazing, analyzed by XRF.

Alloy type	Cu99Sn1		Cu97Sn3		Cu95Sn5		Cu93Sn7		Cu90Sn10		Cu85Sn15		Cu80Sn20		Cu75Sn25		Cu70Sn30	
Element	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn	Cu	Sn
Before brazing spot 1	99.1	0.9	96.8	3.2	94.5	5.5	92.4	7.6	88.7	11.3	82.7	17.3	76.4	23.6	69.9	30.1	63.9	36.1
Before brazing spot 2	99.1	0.9	96.8	3.2	94.3	5.7	92.5	7.5	89.3	10.7	82.7	17.3	76.3	23.7	70	30	63.9	36.1
After brazing spot 1 no borax	99.1	0.9	96.8	3.2	94.5	5.5	92.4	7.6	88.6	11.4	82.6	17.4	76.3	23.7	69.8	30.2	63.7	36.3
After pickling spot 1 no borax	99.8	0.2	99.3	0.7	98.7	1.3	98.2	1.8	97.4	2.6	83.9	16.1	95.0	5.0	93.5	6.5	90.7	9.3
After pickling spot 2 borax	99.8	0.2	99.3	0.7	98.7	1.3	98.4	1.6	97.6	2.4	83.2	16.8	94.9	5.1	94.5	5.5	90.6	9.4

Table 2. Composition of copper tin alloys before and after brazing, analyzed by XRF.

the first result indicates that before pickling, the lead concentration increases following heat treatment. A second result showed that, after pickling, the lead concentration in alloys above 3% is still much higher than the original lead concentration.

The difference in measured lead concentrations can be explained as follows. Lead is only slightly soluble in copper alloys (Scott 2002), and therefore unalloyed lead segregates and migrates towards the surface during heat treatment. However, in alloys above 3% lead, not all corrosion products are dissolved from the surface by the pickle. The lead(II)oxide (PbO) and lead sulphate most probably accounts for the higher lead concentration detected by XRF.

Binary copper-tin alloys

Visual examination revealed that after the restoration treatment using heat, the alloy turns red; however, when the tin composition approaches 30%, this phenomenon no longer occurs.

XRF measurements (see Table 2) show two major results: the first result indicates that almost no change in tin concentration takes place after heating. The second result shows that after the pickle treatment, all measurements of tin have decreased in comparison to the original concentration. There is no influence of borax on these analyses as can be seen in Table 2.
The tin in the alloy is clearly not affected by the heat treatment; however the pickle removes the tin from the surface and seems to have a considerable effect on the alloy composition.

Binary copper-zinc alloys

Visual examination revealed that after the restoration treatment using heat, the alloy turns red; however, as the Zn composition approaches 25-30% this effect is less noticeable.

XRF measurements (see Table 3) show two major results. The first result indicates a similar pattern to that of the copper-tin alloys: heat treatment has no effect on the XRF results. The second result shows that a pickle treatment removes zinc from the alloy, but the effect is not as strong as that observed with tin. There seems to be no influence of borax on the measured spots.

Tertiary copper-tin-lead alloys

Visual examination revealed that after the restoration treatment using heat, all of the alloys turned red, whilst a black layer formed on the alloys with a lead content above 10%.

XRF measurements (see Table 4) show three major results: one, the tin concentration is not influenced by the heat treatment. Two, the lead concentration is influenced by the heat treatment as can be seen in the result reported in Table 4 *after brazing spot 1 no borax*. Three, both the tin and lead concentration in all alloys after pickling is still much higher than the original tin and lead concentration (in Table 4, see *after dipping in pickle spot 2 borax* in comparison with *before brazing both spot 1 and 2*). However, there seems to be no influence from the borax as there was with the copper-lead alloys. This phenomenon is illustrated in Figure 2.

Cross sections of samples obtained before brazing, after brazing and after pickling, were prepared from one of the tertiary copper-tin-lead alloys, Cu91Sn4Pb5, a composition often found in sculptures. These samples were analyzed using reflective microscopy and SEM-EDS (see Figure 1 and 2). Figure 1 shows a layered structure at the surface of the sample after the heat treatment (left),

Alloy type	Cu95Zn5		Cu90Zn10		Cu85Zn15		Cu80Zn20		Cu75Zn25		Cu70Zn30	
Element	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
Before brazing spot 1	96.8	3.6	92.3	8.3	88.6	12.2	82.8	18.0	77.3	23.4	72.4	28.4
Before brazing spot 2	96.7	3.6	92.2	8.4	88.5	12.2	82.5	18.0	77.5	23.2	72.5	28.3
After brazing spot 1 no borax	96.2	3.8	91.9	8.4	88.4	12.3	81.5	18.4	76.7	23.8	71.6	28.4
After pickling spot 1 no borax	97.7	2.6	94.4	6.0	92.1	8.1	89.2	11.0	83.0	17.5	78.6	21.8
After pickling spot 2 borax	97.9	2.5	94.4	6.1	91.7	8.5	90.4	9.9	83.8	16.4	80.8	19.5

Table 3. Composition of copper zinc alloys before and after brazing, analyzed by XRF.

Alloy type	Cu95Sn4Pb1			Cu93Sn4Pb3			Cu91Sn4Pb5			Cu86Sn4Pb10			Cu91Sn8Pb1			Cu89Sn8Pb3			Cu87Sn8Pb5			Cu82Sn8Pb10			Cu77Sn8Pb15		
Element	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb	Cu	Sn	Pb
Before brazing spot 1	96.9	3.8	0.9	94.9	3.8	3.0	91.9	4.1	5.6	87.6	3.8	10.3	91.6	8.9	1.3	89.7	8.4	3.7	86.7	8.7	6.4	81.1	8.2	12.6	76.6	7.7	17.7
Before brazing spot 2	96.7	3.9	1.0	94.4	3.9	3.3	92.2	4.0	5.6	87.2	3.8	10.7	91.5	9.0	1.4	89.5	8.5	3.8	86.6	8.6	6.6	80.1	8.0	13.6	76.1	7.6	18.3
After brazing spot 1 no borax	96.7	3.8	1.2	91.9	3.8	6.0	81.1	4.0	16.6	29.7	2.4	69.1	90.9	8.9	1.7	85.3	8.4	8.2	80.7	8.6	12.5	57.2	7.4	36.9	64.4	7.1	30.3
After pickling spot 1 no borax	99.8	0.9	0.4	99.5	0.9	0.7	99.4	0.9	0.7	24.8	0.9	75.5	99.0	1.8	0.3	98.6	1.6	0.9	95.8	1.5	3.7	83.9	2.0	15.3	89.5	1.8	10.0
After pickling spot 2 borax	99.8	0.9	0.2	99.4	0.9	0.7	99.3	0.9	0.8	92.6	1.0	7.5	98.9	1.9	0.3	98.6	1.8	0.8	97.5	1.7	1.8	90.5	1.9	8.8	86.7	1.8	12.7

Table 4. Composition of copper tin lead alloys before and after brazing, analyzed by XRF.

which has disappeared in the cross section after the pickling (right).

In Figure 2, the distribution of different phases in the alloy, marked as copper (Cu, rich in copper), lead (Pb, rich in lead) and tin (CuSn, rich in tin), is represented in the X-ray mappings of cross sections of the samples before brazing, after brazing and finally after pickling. The metal shows the presence of copper and tin-rich phases and un-dissolved lead globules. A layer of tin oxide is present followed by a copper oxide layer. Finally a layer containing lead is visible on top. After the pickling the lead and copper oxide layers disappear and the upper 20 µm of the metal is depleted of lead.

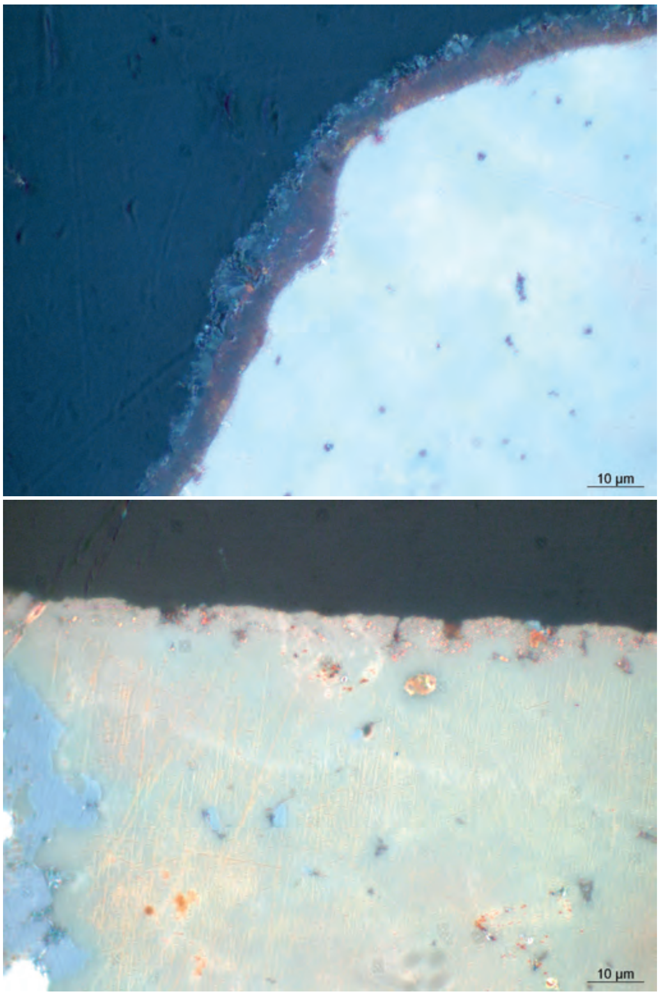

Figure 1. Cross section of Cu91Sn4Pb5, after heat treatment (*top*) and after pickling (*bottom*).

The reason for the removal of both lead and tin is due predominantly to the fact that the alloy consists of various lead and tin-enriched phases, as well as tin-depleted phases, as can be seen in Figure 2. Lead and tin from the richer phases dissolve more rapidly in the pickle causing the values to decrease sharply.

Quaternary copper-zinc-tin-lead alloys

Visual examination revealed that all alloys turned red after the restoration treatment using heat, except for the last alloy given in table 5 which is slightly more yellow. XRF measurements (see Table 5) show three results. One, the zinc content is hardly influenced by the heat treatment and only slightly by the pickle treatment. Two, the tin follows the same pattern as the other tin containing alloys. The third result reveals that lead also follows the pattern of an increase in quantity after heating and a decrease after the pickle treatment. After pickling the lead and tin concentrations are in all cases lower than the original values. The zinc concentration is in some cases lower after pickling, but to a lesser degree than lead and tin. Areas protected by borax seem to have a slightly lower lead value than areas not covered with borax.

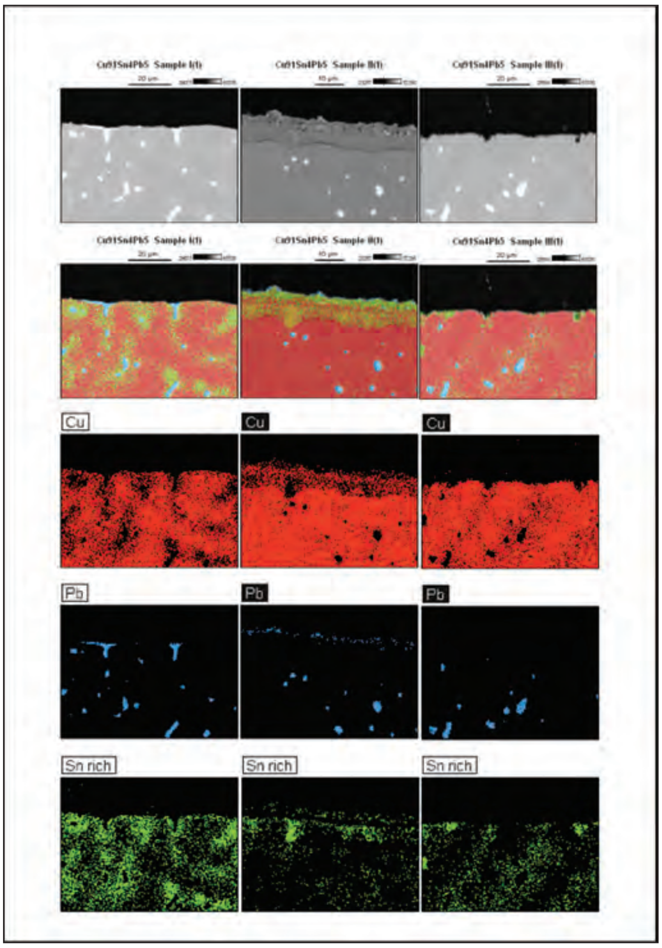

Figure 2. Backscattered electron image and X-ray mappings of the sample.

Alloy type	Cu89Zn5Sn3Pb3				Cu85Zn5Sn5Pb5				Cu80Zn10Sn5Pb5				CU75Zn15Sn5Pb5				Cu82Zn10Sn3Pb5				Cu77Zn15Sn3Pb5			
Element	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb
Before brazing spot 1	92.6	2.9	3.1	3.3	87.8	3	5.3	5.7	80.9	9.2	5.6	6.3	81	9.2	5.7	6	87.4	5.8	3.1	5.6	84.3	9	3.1	5.5
Before brazing spot 2	92.1	2.8	3.3	3.7	87.7	3	5.2	5.8	80.8	9.2	5.7	6.2	81.1	9.2	5.8	5.8	86.7	5.8	3.3	5.9	84.1	9.1	3.1	5.6
After brazing spot 1 no borax	89.4	2.8	3.1	6.5	81	2.8	5.2	12.7	71.9	5.7	5.3	18.9	78.8	9.1	5.7	8.3	79	5.3	3	14.3	75.6	8.4	3	14.6
After pickling spot 1 no borax	97.8	1.8	0.7	0.6	96.1	2.2	1.2	1.6	94.4	4	1.2	1.5	88.7	9	1.3	2.2	94.4	4.6	0.7	1.4	93.1	5.8	0.6	1.5
After pickling spot 2 borax	98	1.9	0.7	0.4	96.9	2.1	1.1	1	96.1	2.9	1.1	1	90.1	7.5	1.3	2.4	96.1	3.7	0.7	0.6	94.3	5.7	0.6	0.5

Table 5. Composition of copper zinc tin lead alloys before and after brazing, analyzed by XRF.

Conclusions

This research has focused on the effects of heat treatment, with temperatures above 680C, on 37 copper alloy samples using XRF analyses. Based on these findings, it is clear that XRF analyses should be carefully interpreted for heat-treated alloys containing copper, lead, tin and zinc in either binary, tertiary or quaternary compositions. The impact of a heat treatment is clearly demonstrated when lead is present in the alloy, more clearly in alloys with 3% or more lead. Both zinc and tin-containing copper compositions are strongly affected by a restoration treatment when pickle (5% sulfuric acid) is used for the removal of oxides and when borax is applied. Careful examination of the object by a conservator is necessary in the process of choosing sample spots which are presumed to be representative of an alloy. Further research needs to be done on the extent of changes in the alloy which are commensurate with the size and location of the restored area. In some cases the entire sculpture may be heated during the course of a restoration treatment. The effects of pickle, the influence of patinas on alloys and investigation of corrosion products produced during restoration treatments involving heat also merit further study.

Materials

Metals:

Copper tubing from a hardwear store, XRF detected no impurities.

Zinc from Interchema
Rozenburg, The Netherlands, 99.9%.

Tin and lead from Salomon's Metalen B.V.
The Netherlands, XRF detected no impurities.

Sand mould supplies:

Bindol zand, De Hazelaar Art Supplies
Soest, The Netherlands.
http://www.hazelaar.nl/

Silver solder and flux:

Solder: "625 AgL1"
Schöne Edelmetaal B.V.,
Amsterdam, The Netherlands.
http://www.schone.nl/index.html

Borax cone:

Schöne Edelmetaal B.V.,
Amsterdam, The Netherlands.
http://www.schone.nl/index.html

Pickling acid

Nitric acid: general purpose grade, 70% concentrated

Fisher Scientific
Scheepsbouwersweg 1b
Postbus 4
1120 AA LANDSMEER
http://www.eu.fishersci.com/

Sample molding material

Epoxy
Specifix 20, 2 component epoxy system,.

Struers GmbH Nederland
Elektraweg 5, 3144 CB Maassluis
The Netherlands
http://www.struers.nl

Polishing of samples

Buehler EcoMet with Buehler abrasive paper and polishing cloth.

Buehler GmbH - European and MESA Headquarters
Postfach 160355
40599 Dusseldorf, Germany
http://www.buehler-met.de/unternehmen/buehler-in-deutschland.html

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Authors

Robert van Langh is a gold and silversmith, and began his career in 1995 at the Museum of the Tropics, Amsterdam. In 1995, he began working for the Rijksmuseum Amsterdam as a metals conservator, after graduating from the National Higher Institute of Fine Arts in Antwerp. In 2006 he began a PhD in Materials Science at Delft University of Technology, and became Head of Conservation of the Rijksmuseum Amsterdam.

Arie Pappot graduated as a metals conservator from the Netherlands Institute for Cultural Heritage in 2009. Currently he is employed part-time at the metals conservation department at the Rijksmuseum Amsterdam and is studying towards a MA in Conservation at the University of Amsterdam.
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Sara Creange began her conservation career in 1998, working for the Western Archaeological and Conservation Center and the Arizona State Museum (both located in Tucson, AZ), and then Griswold Conservation Associates (Los Angeles, CA). She graduated in 2004 from the Winterthur/University of Delaware Program in Art Conservation, with a specialty in objects conservation. She subsequently worked at the Philadelphia Museum of Art, and as a conservator in private practice. In 2007 she moved to the Netherlands where she is currently a metals conservator at the Rijksmuseum Amsterdam.
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Q & A SESSION

Peter Northover : One quick point is that the solid solubility of lead in copper and bronze is I think about 80 ppm – so the lead is always going to be dispersed. What matters, I think in relation to what you're doing is the size and distribution of the dispersion. If you have enough alpha-delta-eutectoid there you've got enough tin, the fine dispersion of lead at low levels is probably going to be trapped in the eutectoid, so it is going to behave differently with your heating than when you've got larger particles of lead loose in the matrix. What I was actually going to mention was I've had the good fortune with a number of post-excavation projects to look at the effects of cremation on bronze; in fact being involved in two experimental cremations. I hasten to add that although you can do do-it-yourself burial in Britain you cannot do do-it-yourself cremation so it had to be a sheep that we cremated but it is a very nice contrast. What you could add to the way people are doing brazing is the atmosphere and what you've been looking at is primarily an oxidizing atmosphere. We found metallographically we could identify something of a ritual because the body burns with reducing flame at about 800˚ C and for this particular cemetery, I think it was in Austria, it was published last year, you had some cremations done where just the body was cremated and the grave goods were put cold in the grave. Some were done with the body wearing ornaments, usually brooches, one or two other things – they're on the body, they have just been very thoroughly annealed and so there is virtually no alteration of the surface. If it was a rich burial and they had an excess of grave goods they were put around the body on the pyre so they had been at 1000˚C in an oxidizing atmosphere, so you get a nice contrast in the microstructures. The composition of all these things is the same in cross-section, but the metallography tells you what has been happening. Another thing I'm doing at the moment is actually with silver alloys. There are no issues with brazing or anything but it is possible they have been in a fire – so what has that done to the surface? That is something certainly in the archaeological end of things you've got to think about. It is always easier if you can take a sample.

Robert van Langh: It is true. I think it would be nice during the tea-break that we also come back to that a little bit because I have some questions on that as well.

Peter Northover: The other thing I'm disappointed about is that you weren't analyzing the brazes because that never gets analyzed!

Robert van Langh: I did analyze the brazes of the bull and showing that there was no lead and tin.

Peter Northover: What we do need is a whole chronology for solders and brazes from the ancient world onwards. We just don't have that sort of data to know what might be the original repair or an original assembly and what might be more modern. We just have no idea at the moment. People don't analyze them on the objects.

Melanie Roy: Touching on what Peter was saying about dispersion of lead: you said you sectioned each of your samples before you did the brazing. Have you got micrographs to go along with the data for your analysis and can we see those micrographs?

Robert van Langh: Yes I did, but I don't have them here. But they are accessible.

Arlen Heginbotham: Thank you very much, that was a great talk. I feel like this kind of study is really important to do and I hope that a lot more people do this kind of thing. I had a couple of questions too: I missed, and maybe you said, how you did do the brazing?

Robert van Langh: With a torch.

Arlen Heginbotham: I don't know a lot about a lot of different periods but I do know in the 18th Century in France for instance, that kind of brazing was usually done by putting the two pieces together and putting some solder on it and then putting it in to a coal fire to reduce the environment. And I think it would be really interesting to do the same kind of study, with all your spare time, with an alternative brazing process. That could really add to our information too. Another thing was: I think it would also be interesting, and maybe you know this, and I missed it, is how thick these effects, how deep these effects are? Because a lot of times, of course after brazing, the surface would get reworked to disguise the seam and things. So it would be interesting to know how much they had to rework the surface to start to minimize those effects.

Robert van Langh: I think this already indicates that slightly. But of course what you see here and it's different when you look through a microscope. But this layer [on the screen], this is the layer where it has been affected. That means where the copper and tin alloy, 91% copper, 4% tin, 5% lead , where you have the phase which is being formed and taken away completely at that surface afterwards, then also there is a little bit of depleting of the surface and that is until 10 microns which is effective.

Arlen Heginbotham: Interesting, that's pretty thin. Another question, maybe I should even direct this to Peter - earlier in the conference I heard Peter mention that small amounts of arsenic can minimize dezincification? But that would not apply to something like this?

Peter Northover: In response to Arlen's question, arsenic inhibits dezincification in corrosion in aqueous media. Arsenic does other things in copper alloys at high temperature. One of which is, it restricts grain growth. I think it does help resist oxidation which is why in those parts of the world, which persisted with copper fire boxes on steel locomotives, they're arsenical copper. Which is why we wanted some experiments on arsenical copper. I actually went to a locomotive preservation group and bought part of the engine so I drilled out the fire box, because that was free arsenical copper.

Dylan Smith: Really great talk Robert, really a lot to think about. One thing I was wondering is for the group of objects after they've been heated. That seemed to be the moment at which it had the most exaggerated effects of mainly additional lead on the surface. This would be something – you would visually see this layer. What I'm thinking about is whether you would actually find a finished object that would ever have had that layer.

Robert van Langh: The *Charging Bull* has that.

Dylan Smith: I guess what I'm thinking of is the original sequence of production, as opposed to a repair. Because of course on a repaired object, I guess you could still strip the entire thing. But hopefully they won't do that. I'm just thinking about what classes of change we might find in an actual object in the course of its original production. So that enhanced lead layer would presumably always be removed?

Robert van Langh: A good point of course. I'm realizing as well that after each treatment, whether it is a repair or from the beginning, that something has been made and brazed together and put together because we know that these surfaces, whether it is on Renaissance bronzes or other objects, that this exists. I realize that this is the case and that people have after-worked it in order to get everything even because you don't always get an even surface, and so you would have to grind it down. But I'm not thinking only of bronzes. If you think of the quaternary alloys and the copper-zinc alloys then you're thinking of brasses as well.

Dylan Smith: I'm sorry I was using 'bronze' in the dreaded art historical sense there.

Robert van Langh: But for instance copper and zinc up until 40% of zinc, that is really a binary alloy that you can use for that and looking at the effects. Seeing here, the chandeliers - if you start analyzing chandeliers using this technique – many chandeliers have been broken in the past and been repaired. The only purpose, so to say, is to be aware that these techniques are not made for that specific purpose and if you start using them and thinking that this is the alloy composition that you can derive using the XRF, that might be a pitfall. So let me come back to really answering your question: yes I understand that traditional techniques might have had some after-working from the very beginning when they cast and then mounted the object together in comparison to something that was a repair… that most likely also had some after-working – it is just that these are the things that can occur and we saw that they did occur and for instance with the *Charging Bull*, and we have many other objects as well, where we see differences. And I've always been wondering no matter what kind of XRF and the talk of Arlen, it doesn't matter which XRF that you're using, suggests that we are all using the exact right one. Still I think that the machine, calibrated in the right manner would still give different results. Which result is correct?

Dylan Smith: A sort of a follow up on the *Charging Bull* – the repaired hoof that was on that, was that an original part of it?

Robert van Langh: Yes. As far as we know yes.

Dylan Smith: I was thinking this would be an interesting [project] – this is where it would really present a problem, if say, you analyzed that hoof and you found it to be so different that maybe you convinced yourself that it was actually a replacement. I can't remember now from the beginning how different that hoof ended up being.

Robert van Langh: Relatively the same, I would say. Same kind of elements, different composition. And of course Bruce has something to say about that…

Bruce Kaiser: I was just wondering what the spot size for that was?

Robert van Langh: Spot size for this was also a relatively large area so roughly 2 mm square.

Dylan Smith: Thank you.

X-Ray Fluorescence Analysis

Chair: Tom Chase
Panelists: Arlen Heginbotham, Dylan Smith, Ainslie Harrison, Robert van Langh

Tom Chase: At the Freer Gallery of Art we did a lot of Chinese bronze analyses and when the idea of using lead isotopes to differentiate bronzes to try to find out workshops came along, we jumped on that and it actually proved to be fairly successful. Ernst Pernicka has now begun to do tin isotopes and that may be even more interesting although it's an even more difficult analytical problem. Mr Foecke brought up the idea of gold isotope analysis, does anyone know if anybody has done this? I mean a lot of us know about Eugster and Kossolapov's work with gold dating, but does anybody know about gold isotope analysis?

Peter Northover: Ernst Pernicka a few years ago had a PhD student not on gold isotopes in particular – I think he thought that was not promising – what he was looking at was osmium isotopes, dealing with I think a group of materials where osmium was there in platinum group element inclusions, and I think if I recall rightly is that it didn't contribute very much. The tin isotope analysis has got to the stage where basically tin has 10 stable isotopes, and let's say the natural variation is about 11% in the abundance, and the detection limit of the apparatus is down to about 9% so there are peaks beginning to appear above sea level so that broadly you can distinguish Nigeria and Cornwall and Malaya. But what we want to for a particular late Bronze Age shipwreck, which started disgorging tin ingots off the Devon coast last year and this year, is it would be extremely useful to distinguish between Cornwall and Brittany, but as they are geologically of similar ages, I think the technique has a long way to go for that. That does seem to be next best thing. I have wondered myself about sulfur isotopes but again, I don't think for most of our questions it's a lot of help; there may be questions where it is.

Robert van Langh: I know that Gary Davis from the Free University in Amsterdam it looking at lead isotopes as well. We are starting to look into that in regard to silver, but also in regard to paintings and paintings analysis.

Tom Chase: We would welcome somebody working on gold isotopes but it is not going to be me!

Aaron Shugar: All your papers were excellent and I enjoyed listening to them. I am interested in your ideas of limits of detection and limits of quantification of XRF and the published information that is coming out. I am really concerned about the publications with SEM-EDS and detection being reported at parts per thousand, when in reality the machine is not capable of reporting less than half a percent accurately, and what are you feelings? XRF is much more sensitive to this but I am curious what you've found with your individual projects and the limit of quantification and the limit of detection.

Dylan Smith: This is the perfect question for Aaron to ask because this is something that I've been looking into for a paper on portable XRF which I think will be a really great publication that Aaron and Jennifer Mass are putting together and this was looking at the levels of detection and quantification. I am not going to be able to rattle off the numbers off the top of my head, but I think by analyzing standards with a range of trace values that can be a problem for finding certain elements, because there aren't necessarily so many standards that have those, you can start to calculate where it really starts to fall apart. What's been interesting is that I have had the opportunity not only to do that with the older Tracer, but we have one of the newer Tracer's also so this gave us the opportunity to look at those two together. There is definitely an improvement also, this is not a sales pitch, but the new instrument is more sensitive and so you do get lower levels of detection and quantification with that; but you'll have to wait for that publication.

Robert van Langh: I also wanted to comment on that. I've always been kind of reluctant in the case with XRF analysis, I really also clearly see, and that is something that Dylan has indicated in his research, that yes, it is very obvious that there are some clear observations that we can see. I must say though, that because it is a surface analysis technique that I have started a kind of belief that we have to take a different approach. What we have done now is neutron diffraction to look at different phases and can we distinguish the different phases using diffraction and that seems to be possible. Also we can combine that with tomographic techniques so you can go into depth as to combining neutron tomography with neutron diffraction and you can do analysis of the composition. So I think we have to look at combinations of these kinds of materials and there is a lot more research especially on diffraction that needs to take place but don't bet your money on one horse, that's what I am thinking.

Arlen Heginbotham: It seems like a really important issue [detection limits] and one that in our study was not handled consistently well. I am not an expert on this but there seem to be a lot of different ways to calculate the detection limit. I experimented with a couple of different ways in my work because I am particularly interested in silver and so I am trying to figure out what is my detection limit for silver. I tried taking my background and calculating the standard deviation and the noise and then saying well, is my silver peak greater than three times the standard deviation of my background, and that's a really robust method for doing it. The problem is reporting your data because for every spectra you collect, your detection limit is different. So, it makes it a little cumbersome to report but it's pretty robust. Another way of doing it that's the American Chemical Society, or someone's way, is to say measure a lot of reference samples that are at or near zero, plot a regression line, calculate your standard error and determine your detection limit from that. So, that is also a pretty robust way if you have a good sample set. Regardless of the method that is chosen, it seems like it is a good idea for us as a group to spend a little more time saying what method we are using, using one of the methods carefully and saying what it is that we are reporting and making sure that that is presented in your publication. The other thing is then error reporting, which is associated, because as you get closer to zero the relative percent error goes up. So then it is a question of how do you report your error, over your entire range you are looking at? Because it is going to be different for different ranges and there are different ways of modeling that and there are a lot of established ways of modeling that. If at the beginning you are setting up your instrument, you can pay attention to it and we can maybe develop some common ideas on how to do this, then you can say ok, my error is following this model. At lower concentrations it is at this relative percent and then it changes through here or it's very linear in this range but its different down here etc. If that is incorporated into your published data, I think that data becomes much more valuable.

Jean-Bernard Memet: I am an end-user, I have never used XRF. As far as I know XRF is a semi-quantitative method, I mean it gives you the quality, the composition – or it gives you some indication of the composition, and all of you have used it as if it was a real composition technique. I wanted to know, as an end-user, and we have seen how difficult the reproducibility of the tests were, first, how can I trust the result, and second what advice can you give us to better understand it?

Robert van Langh: You gave the answer yourself - it's a semi-quantitative way, that's the way to go with it.

Jean-Bernard Memet: What I mean is that we can see in many labs people who give you the results and say, well you have 55% copper, 25% of zinc and so on, but they don't give you the advice to better understand it and you have to read these results. The precautions regarding all that you have said before means that we have to be very careful with these results.

Robert van Langh: That was exactly the point that I wanted to make with that, is that now I looked at high temperature, but with low temperature definitely you will also get differences, not as obvious perhaps as the ones we have seen here, but that is exactly the point – be aware.

Dylan Smith: I might add just a little bit to that. First of all one thing that's very important is that there is this interaction between the person that is looking at the object and the person that is doing the analysis. Say, looking at that bowl, if the questions aren't clear as to which spots to look at and what that information is really going to mean, that's where you really run into problems. There needs to be this intimate communication between all of the various parties involved in order to actually get a meaningful answer. The other thing I would say about the semi-quantitative part – basically for me, I have a large set of standards, the instrument is able to reproduce the value of those standards very closely, so if the objects I am looking at are in the range of those standards, I should be able to get a quantitative result. I think the thing is that you see a lot of variation within the results and it is partially due to very exaggerated effects like some of the ones that Robert identified, which is a cautionary tale, but there are also just a lot of inherent variation within the production methods that were used in the particular periods. Something that I was trying to get at in my paper was that you shouldn't get upset with the XRF because every single spot on the object isn't exactly the same, that's never going to be true. What you need to do is be precise enough so that the variation you are seeing is due to the object, and that you can interpret to mean something, as opposed to be due to the instrument.

Aaron Shugar: I think Dylan you are correct with that. I just want to make one clarification everyone, there is no such thing as semi-quantitative! It is quantitative or not quantitative, its either poorly quantified or well quantified, there is no such thing as semi-quantitative, so we should avoid using that terminology. The other thing is that XRF is so dependent on how homogeneous your material is, and was designed to look at homogenous materials with well-prepared surfaces. If you go to a class now on XRF analysis the techniques to produce materials for analysis are extreme – fusion, high temperature processes producing very flat surfaces to get accurate results. We don't have that luxury and in some cases we are looking at such diverse materials we're stretching to get quantitative analysis and we probably can't. You've all given great examples of how you can look at your material, understand it before you come to the XRF analysis, adjust the machine to suit your particular needs and then extract the information, and that was impressive, so thank you all for that.

Arlen Heginbotham: If I can make one comment about this whole topic too – thank you for saying that about semi-quantitative analysis, too - it seems like a semantic game, either you can try to quantify something and either you can be very precise or very imprecise, right, but if you measure your precision then you understand what the result means. The other thing - one of the things we are talking about too is the different between reproducibility and accuracy, which is a big distinction too because there are so many surface effects and patina effects that we don't really understand yet and hopefully we will begin too, depletion gilding effects and all kinds of things that are very complicated, but the good place to start is to say ok, Renaissance bronze may have effects that means that when you have to take an XRF analysis you are not getting something that represents the true bulk alloy of the metal, which is a sort of conceit anyway, because if you wanted to know that you would melt down the whole object because it's heterogeneous to begin with. So, I think the idea that if you can be reproducible then you can start to get information that shows patterns that are real regardless of what the real meaning of that number is. The other thing is to say that when we talk about that this is a semi-quantitative technique and it gives you an idea of what you are doing I think that's probably right and based on the results of the study, if you don't know anything about the lab that you are getting the results from and you don't know what kind of technique they are using to do their work, well, hopefully one of the things that we have been able to do is say, well, look at this, this is the kind of range of precision that you should expect from those results.

Robert van Langh: I am reading Campbell and Castings [John Campbell, *Castings*, Butterworth Heinemann, 2003], really a very nice book and because of that I went into thin wall castings and then seeing where the flaws actually occur and especially in regard to heterogeneity of these metals and you have it in many more cases than you can imagine, so it's the thickness of the metal, it's the shape, the geometry of the object, all these things have to be taken into account in order to explain why you can have differences which is not purely based on, let's say, the differences that we've shown with this work with the heat treatment. XRF is designed, as Aaron said, for a different purpose and as long as everybody understands that and see what the drawbacks are it doesn't mean that you cannot use it, and Dylan is actually proving that.

Peter Northover: I thought it might be useful to share some of the experience we had with XRF in our project in the 1990's. I'll start with a more recent experience matching analyses, which was the publication project on the big Iron Age treasure from Norfolk, the Snettisham Treasure. A student of mine analyzed everything that had been found up to 1987 using electron microprobe wavelength dispersive spectrometry and the ZAF correction routine. The British Museum have been analyzing the material from their excavations in the early 1990's and this is actually on cut samples and their doing their SEM with EDX and I think the software is essentially Phi-Rho-Z. I took some of my samples along for comparison and we were getting identical results except for small systematic errors which are certainly down to the algorithm as we've mentioned before. What it means is that we will publish the data in two separate tables and the differences are so small, they are smaller than the size of a dot on a graph, so we can put everything on one graph which is a start.

With the project with my late and much missed friend Valentine Rychner it started off because a lab doing I think atomic absorption did a wrong dissolution and precipitated out of it all of the silver, and so he was trying to get analyses done quickly in two or three different labs and everything was coming out fine except silver. So, that's how the comparative project grew. When it came to XRF, and this is mainly on cut samples, sometimes on the surface of real archaeological bronzes with nice quantities of arsenic, antimony, silver and nickel, so not just the tin. Brian Gilmour at the Royal Armouries then did a lot of work on the polished samples, so running the same spectra past all his alloy standards so the publication had a nice graphic of the effects of alloy standards. We're taking for various reasons the British Museum's atomic absorption data as the gold standard and comparing everything with that. By putting the AAS data for one of the bronzes in as the standard for running the others, it came out as exact as you could like, it can be done. I am glad that people have mentioned spot size a bit, because these are objects some of which retain their dendritic segregation and some of it might be quite coarse and some of these elements are highly correlated so that antimony and nickel go with the tin. So, if you were doing a relatively small spot size you might get some odd answers. If you are finding with your analyses that you're not getting that correlation, then something is wrong. The literature, if you are going to look for published comparative analyses, is a mess - a lot of stuff is in museum archives and is not in the literature. Then you have the issue of is it XRF, is it sample based, so I hope this collaboration, in at least getting some agreement on how to do XRF, will lead to the sort of luxury we have of tens of thousands of compatible analyses for prehistoric metalwork. Essentially you can take different published databases, mix them together for you own purposes, and for the sort of material for which the XRF comparison was devised, I really look forward to that.

Michael Drews: It has limitations, it's not the do everything for everybody, but as least as far as the handheld goes, I can take it in the field, I can take it to any spot on a large object, and it can help me understand why that object is behaving the way it is. We always have to keep in mind it's so easy to get the data - it's what we do with the data that's the critical point.

Molly Carlson: As a person who does not operate any of these machines or have access to them unless I hire an operator to do this, I would be very interested to have a check list of things that I should ask my hired person to put into their reports. I have had reports back that don't even identify the machine that they used. So I'm not sure I have a big enough picture of what I should be collecting from my researchers in order to make sure that I have the information that I need in 3 years to go ahead and publish something. So, I wonder if there might be a way to have a suggestion like the XRF standards could there be a little checklist made that you collect the spot size…all the different parameters and what those might be.

Arlen Heginbotham: It might not be the best list in the world, but a place to start would be the data recording form that we sent around for the workshop, and that's available on the website.

Shelley Sturman: At the National Gallery we have started something called the Renaissance bronze database and that's how we got into this in the first place where we had that small roundtable and then Arlen took off on this whole idea so that we could start putting together analyses that were made by other people. If we know that we are all collecting similar types of data and then it will all be meaningful because we have had a lot of success in the kinds of projects that Dylan just reported on, we've been very lucky in that many other institutions have permitted us to come in and do analyses on their objects, so we are building up a big database and our hope is that when the Getty makes a series of analyses or Philadelphia or the British Museum or the Victoria and Albert, that we will all be comparing apples to apples and not apples to oranges. That's what we are hoping to be able to move forward in that we will have the thousands of analyses the way you do have for ancient bronzes right now.

Someone asked about patinas earlier and with Renaissance bronzes for the most part they are patinated with resins baked on but we've had some success looking at some late 19th century/early 20th century bronzes and many of them have been chemically patinated, and when we look at them with XRF, again, one has to be very careful, know what you're looking at, take many, many spots, you have to make notes about color, take pictures but we have been able to compare unpatinated areas with areas that, for example, are very red, and we can tell that the iron is elevated in there and we know that there is an actual chemical patination going on based on iron. There are a few published treatises from the 19th century from the very foundries in Paris and it was unusual, but we stumbled upon the fact that chromium is being used in a certain number of patinating solutions and it seems to be associated perhaps with a particular foundry and then we are able to move forward with these patinas that have chromium in them to wonder if we can use it for authentication if an object was supposed to be cast by one foundry and its got chromium in it and it had to have been cast by another foundry. So XRF does have some benefit that way, but again, as Molly was saying you have to know what you are looking at, what you're asking for, what you spot size is and know how you're operating it.

TECHNICAL STUDIES

Session Chair: Tom Chase

BLISTERS IN FIRE GILDINGS ON SILVER: AN INVESTIGATION INTO BLISTER FORMATION AND THE EFFECT OF CONSERVATION TREATMENTS

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Abstract

Blisters in the gilding layer were noted on a number of fire-gilt objects at the Rijksmuseum, Amsterdam, particularly on objects that had been subjected in the past to restoration treatments involving heat. In many cases, blistering was accompanied by delamination and losses within the gilding layer. Research was undertaken to examine the mechanism of blistering and to determine the effect of current conservation treatments on a blistered gilding layer. Fire-gilt and partially burnished sample coupons were heated to simulate soldering. It was found that blistering only occurred in burnished areas. SEM-EDS analysis showed that mercury was present in these areas, whereas in the unburnished areas it had evaporated. In addition, electroplated samples treated the same way did not blister. This suggests that mercury plays an active role in blister formation. Simulated conservation treatments show that the use of a steam cleaner, ultrasonic cleaner, silver dip and polishing with precipitated calcium carbonate can all damage blistered fire-gilt surfaces to a certain extent, so it is important to be aware of the presence of blisters before choosing a treatment.

Keywords: fire-gilding, blisters, burnishing, silver, mercury, polishing, steam cleaner, ultrasonic cleaner

Introduction

During conservation treatment of fire-gilt silver objects at the Rijksmuseum, Amsterdam, blisters and small delaminating areas in the gilding layer were often noted (see Figure 1). To gain insight into the extent of this problem, 40 fire-gilt objects were visually examined (with the naked eye) for blisters. Twelve were found to have blisters in the gilding; it is possible that more objects have blisters that are only visible under magnification. Five of the 12 blistered objects showed clear signs of soldered repairs. Closer examination is needed to determine if the other blistered objects were heat treated, since a good silversmith can hide evidence of repair.

Blister formation has been linked to the Kirkendall effect, which is a form of vacancy diffusion where (in the case of gilt silver) silver atoms have a faster diffusion rate into the gold atoms than vice versa, which leads to porosity in the top layer of silver at the silver/gold interface (van Langh 2000, Callister 2003, Paul 2004), (see Figure 2). The Kirkendall effect does not appear to occur in gilt silver at room temperature, but has been shown to result from excessive heating, either during the fire-gilding process itself, or during later restoration treatments involving heat. Delamination and blister formation was observed in van Langh's experiments on fire-gilt silver samples after heating to 750ºC for two minutes (van Langh 2000, van Langh 2010). It is known that fire gilding was usually carried out at low temperatures of between 250-350ºC (Northover and Anheuser 2000), just below the boiling temperature of mercury (357ºC) (Weast 1975-1976).

The current research, undertaken as a final thesis in the metals conservation course at the Netherlands Institute for Cultural Heritage (ICN), has two main goals. The first goal is to examine the mechanism of blister formation, since it is not certain how a porous underlayer of silver (likely a result of the Kirkendall effect) leads to the observed raised blister formations. Factors such as burnishing, the presence of residual mercury, and various heating times and temperatures were examined. The second aim of the research is to determine the effects of commonly used conservation treatments on blistered fire-gilt objects. Since a significant proportion (over one in four) of the fire-gilt objects surveyed at the Rijksmuseum exhibit blistering, it seems advisable for conservators to examine fire-gilt objects closely and to carefully consider all options before treating these objects.

Figure 1. Blisters in fire gilding (magnification 20x). Detail of the foot of the chalice of Jan Berewout, Rijksmuseum Amsterdam, BK-1958-72, height 54.2 cm. © Rijksmuseum, Amsterdam.

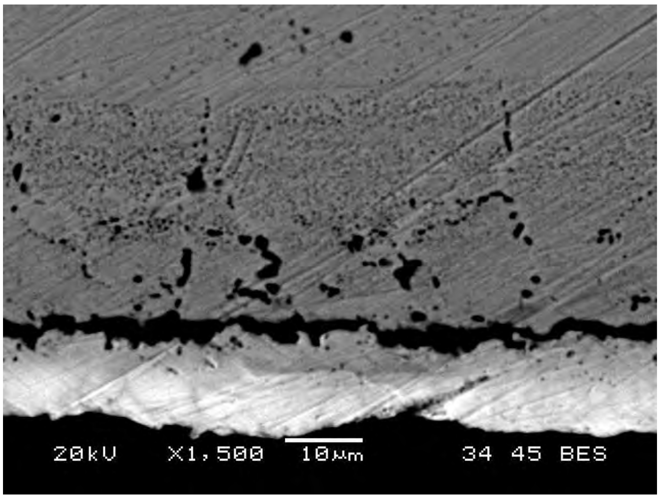

Figure 2. Porosities at the silver gold interface after heating a fire gilt sample at 680 °C for 120 seconds. © Rijksmuseum, Amsterdam.

Experimental

Reproduction of the blisters

Fire-gilt silver samples were subjected to conditions simulating soldering treatments. The goal was to heat the metal enough to produce blistering but not hot enough to change the colour of the gilding by (excessive heat-induced) diffusion of the silver into the gold since most of the surveyed Rijksmuseum objects still had a deep yellow color in restored/blistered areas. A 10 x 10 x 0.1 cm Sterling silver sheet was sent to a laboratory equipped to safely fire-gild in the traditional manner[1]. The preparation of the sheet was performed according to a recipe from the book *'Weg-wyzer voor aankomend goud en zilversmeden'* (Guide for prospective gold- and silversmiths) (van Laer 1786)[2]. The completed gilding, measured in cross-section on an optical light stereomicroscope[3] had an average thickness of 3 µm.

For comparison, a sheet of sterling silver was gilt without mercury: the gold was applied by electroplating[4]. The electroplated gilding had an average thickness of 14 µm. All the gilt samples were cut into 1 x 1 cm pieces. Half of each piece was burnished with an agate stone and saliva as described in van Laer and the other half was left unburnished. The final color of the fire gilt samples and the electroplated samples was deep yellow.

The samples were heated in an oven[5]; temperatures and heating times were chosen to approximate soldering treatments with hard (melting point 760°C), medium (mp 720°C), and soft solder (mp 680°C) (see Table 1). One electroplated sample was heated to 800 °C. The surface of each sample was examined with an optical light stereomicroscope[3] at 50-times magnification to determine the amount of blistering and the colour of the metal. Samples were embedded in SpeciFix-20 polyester resin and polished. The distribution of chemical elements was studied on three fire-gilt samples by energy dispersive X-ray spectrometry (EDS, Ultra dry silicon drift detector, Noran System 7 software, Thermo Fisher Scientific) coupled to a scanning electron microscope (SEM, JSM 5910 LV). It was possible to create a standard set of blistered coupons by heating fire-gilt samples at 680 °C for two minutes (see Table 1).

Temp(°C)	Time (sec.)	Burnished	Blisters	Colour
450	90 180	Y	After 90 sec several blisters. When heated for 180 s no increase in blisters.	Lightly faded
620	120	Y	Yes, spread across the surface	Lightly faded
620	120	N	No	Lightly faded
680	60 120	Y	After 60 sec no blisters. When heated for 120 sec blisters across the surface.	Lightly faded
680	120	N	No	Lightly faded
680	180	Y	Yes, spread across the surface	Strongly faded
680	180	N	No	Strongly faded
760	60	Y	Yes, spread across the surface	Strongly faded
760	60	N	No	Strongly faded
820	20 60	Y	After 20 sec several blisters. When heated for 60 sec no increase in blister, but more fading of the colour.	Strongly faded

Table 1. Results of the soldering simulation describing the amount of blistered and the visual colour changes

Part II Conservation treatments

Blistered fire-gilt silver samples were artificially tarnished by placing them in a sealed glass container for 14 days with 0.5 grams of barium sulphide. Four techniques commonly used during conservation of silver objects were examined in order to evaluate their effect on blistered gilding: removal of silver tarnish with precipitated calcium carbonate and silver dip, removal of lacquer with a steam cleaner, and cleaning in a ultrasonic tank.

Removal of tarnish with precipitated calcium carbonate

Artificially tarnished blistered samples were polished with a dilute slurry of precipitated calcium carbonate Socal N2R® in demineralised water[6]. The slurry was applied to a cotton wool swab and was rubbed over the surface of the coupons, as would normally be done to remove tarnish. The polishing strokes were observed under 50-times magnification (see Figure 3).

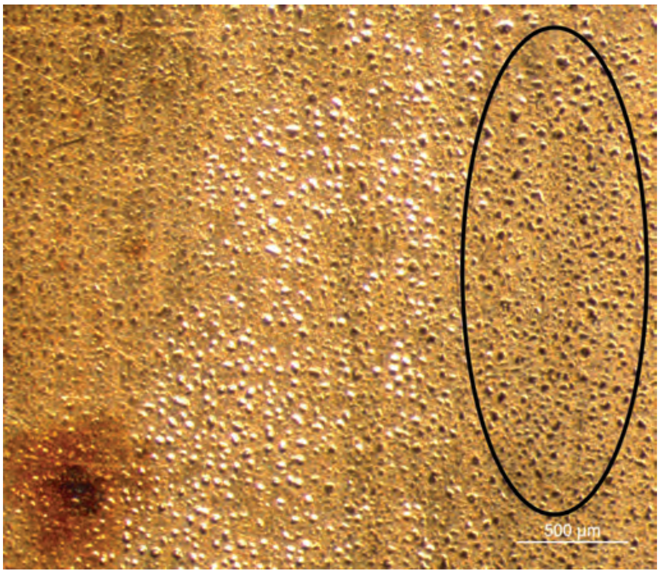

Figure 3. A blistered sample after rubbing over the surface 160x with a cotton wool swab and a slurry of precipitated chalk (*treated area circled*). © Rijksmuseum, Amsterdam.

Removal of tarnish with Silverdip, Ecorr measurement

Silverdips consist of an acid (often sulphuric acid (H_2SO_4) and a complexing agent (often thiourea $SC(NH_2)_2$ (Selwyn 1997)[7]. Two ways of removing tarnish from silver (gilt) objects can be applied; by immersing a cotton wool swab in the silverdip and rubbing over the surface or by immersing the object, followed by thorough rinsing. Silverdip dissolves tarnish faster than silver, but must be completely removed to avoid attack on the silver. If all the silverdip is not removed there may be further reactions with the silver.

To determine how quickly the corrosion of silver occurs the corrosion potential, Ecorr, was measured. By measuring Ecorr versus SHE (standard hydrogen electrode) the half reaction (anodic and cathodic) at the metal surface can be determined. This can provide information as to whether a metal is passivating, corroding or not reacting with the solution. An artificially tarnished blistered sample was degreased with acetone and attached to the Volt-exit of a multi-meter. A reference electrode (Ag/AgCl, +0.203 V/SHE) was placed close to the sample and attached to the COM-exit of the multi-meter (see Figure 4)[8,9]. From the moment the sample was placed in the silverdip the Ecorr values were recorded every 10 seconds and the results were plotted on a diagram (see Figure 5).

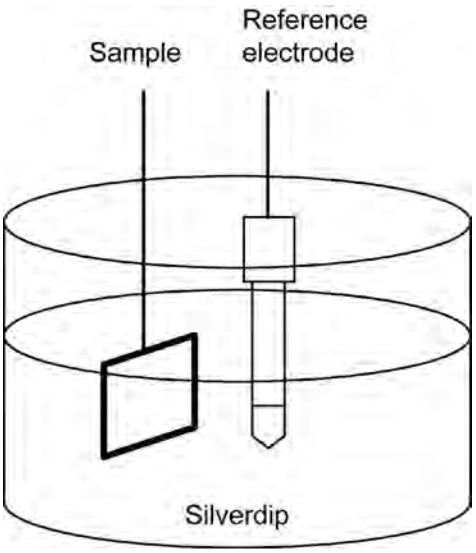

Figure 4. A schematic representation of the setup. © Rijksmuseum, Amsterdam.

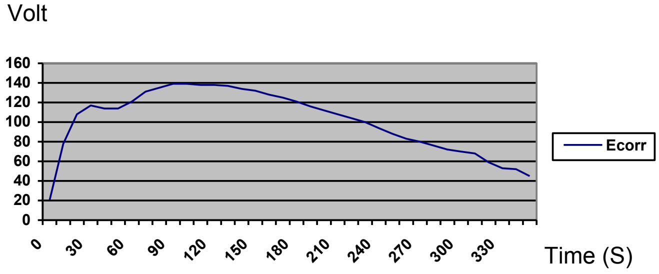

Figure 5. Ecorr versus time. Ecorr first rises, showing that the surface is passivating, but after 150 seconds Ecorr goes down meaning that the surface is corroding.

Simulated lacquer removal with steam cleaner

Nitrocellulose lacquer (commonly called Frigilene®) is often used to protect silver objects from corrosion, and since it has a limited useful lifespan it is often necessary to remove it, usually with solvents and/or a steam cleaner. For this experiment, a steam cleaner operating at approximately 3 bars of pressure was filled with demineralised water and the nozzle was set in position with a clamp[10]. The samples were fixed on a wooden board to hold them in position. Fourteen burnished unheated samples and 14 samples with blisters were tested in this experiment. It is advisable not to keep the nozzle closer to the object than 2 cm (Ankersmit et al 1997). In practise it is sometimes used slightly closer when the lacquer is hard to remove. Therefore, the samples were placed at a distance of 1.5 cm and 2 cm from the nozzle. Since the time necessary to remove a lacquer varies, the steam cleaner was switched on and the samples were inspected every 10 seconds under 50-times magnification (see Figure 6). The results were recorded in a table (see Table 2).

Time (sec.)	Surface change visible	
	Burnished unheated	Burnished heated (Blistered)
Distance 15 mm		
10	N	N
20	N	Y
30	N	Y
40	Y	Y
50	Y	Y
60	Y	Y
70	Y	Y
Distance 20 mm		
10	N	N
20	N	N
30	N	N
40	N	Y
50	N	Y
60	Y	Y
70	Y	Y

Table 2. Results of the experiments with the steamcleaner.

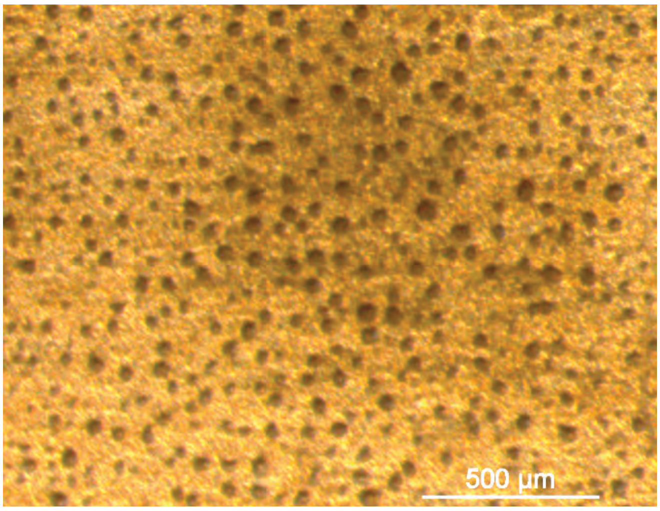

Figure 6. A blistered sample after 60 sec. of steam cleaning at a distance of 1.50 cm at 3 bars. © Rijksmuseum, Amsterdam.

Simulated cleaning in an ultrasonic tank

Samples prepared according to Table 1 were placed in an ultrasonic tank that is often used to remove polish residue and soil from hard to reach places[11]. Ten samples were placed directly in a stainless steel basket that was lowered into the water and 10 samples were placed suspended in the water, not touching the tank or basket. Table 3 shows the results for different cleaning times.

Time (sec.)	Damage	
	In the basket	Suspended in the tank
30	N	N
60	N	N
120	N	N
180	Y	N
240	N	N
300	Y	Y
360	Y	N
420	Y	Y
480	Y	N
540	Y	Y

Table 3. Results of the experiments with the ultrasonic tank

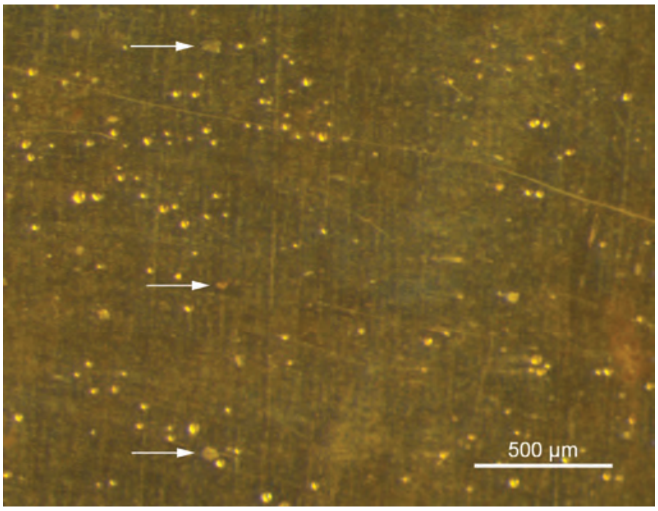

Figure 7. A sample after four minutes in the ultrasonic tank basket with demineralised water at room temperature. The arrows indicate the damaged areas. © Rijksmuseum, Amsterdam.

Results and discussion

In Part 1 of the experiment, blisters were successfully reproduced (see Table 1), with the most comparable results occurring after two minutes of heating at 680ºC, the temperature at which soft solder repairs are applied. This supports the theory that heating plays a role in blister formation. Since all blisters produced in this experiment occurred only on surfaces that were both heated and burnished, burnishing also appears to play a key role in the process. However, this phenomenon should be investigated further by studying if unburnished areas of fire-gilt objects ever exhibit blistering.

The role of mercury may also be linked to the blistering process. It is known that 8%-25% mercury can be left behind after fire-gilding (Anheuser 1999). Interestingly, SEM investigation showed residual mercury in burnished, heat-treated areas and none in the unburnished areas (see Figures 8, 9, and 10). It is possible that burnishing traps mercury that would otherwise escape during excessive heating. The evaporation of the mercury during the process of fire gilding is a solid-state reaction, since it normally occurs below the boiling temperature of mercury (357ºC) (Anheuser 1999). Blistering only occurred on samples heated above the boiling temperature of mercury, suggesting a possible mechanism for blister formation: mercury entrapped by burnishing boils or sublimates, causing stress that is eliminated by pushing the gilding layer upwards, causing the blister (Oddy 2008). And it follows that the porous upper layer of silver (as predicted by the Kirkendall effect) is the point at which the gilding cleaves off. The fact that heated, burnished electroplated samples did not show blistering, even at temperatures up to 800ºC, supports the theory that mercury is a necessary component of blister formation. On fire-gilt samples where gilding averaged 3µm, larger blisters were observed in areas with thicker gilding; this result may be significant and is worth further study. Electroplated samples had a gilded layer measuring 14µm. Therefore, we would expect larger blisters to form, since there were no blisters this supports the theory that mercury has an important part in this process.

Migration of silver atoms into the gold, and not gold into silver, resulting in porosity at the gold/silver interface (the Kirkendall effect) was observed in all fire-gilt samples examined with SEM-EDS. Rapid migration of silver into the gold likely accounts for the lightening in color of the gilding observed on samples heated to higher temperatures or for longer times than required to produce blisters. Since this discolouration was also observed on heated electroplated samples, it is likely that the rapid diffusion, and, by implication the Kirkendall effect/porosity, can occur on heat-treated electroplated silver.

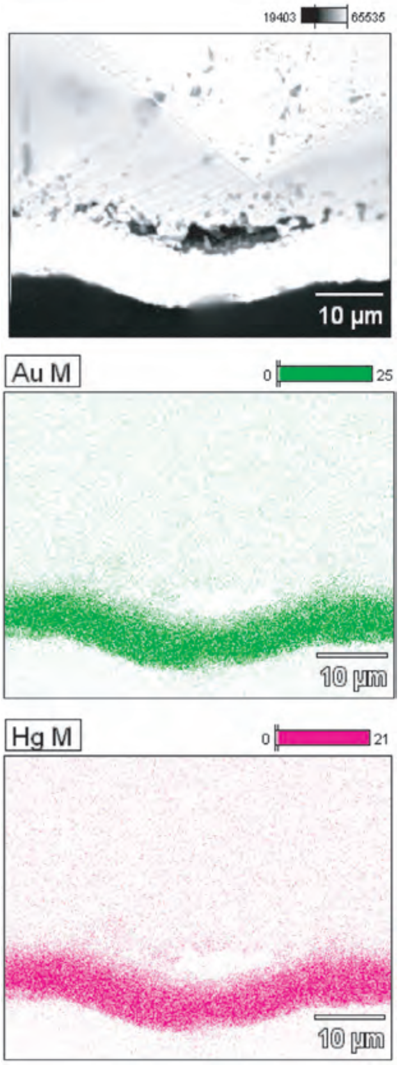

Figure 8. Distribution of gold and mercury (20 Kv) of a blister in a burnished sample after heating for 120 sec. at 680 ºC (magnification 2200x). © Rijksmuseum, Amsterdam.

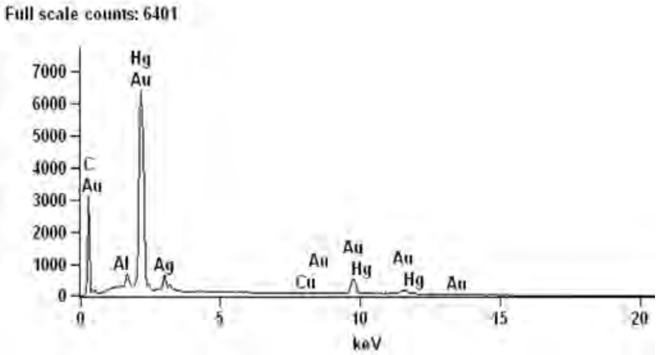

Figure 9. EDS spectrum (20 keV) of a burnished sample after heating for 120 sec. at 680 ºC showing mercury is present in the gilding layer. © Rijksmuseum, Amsterdam.

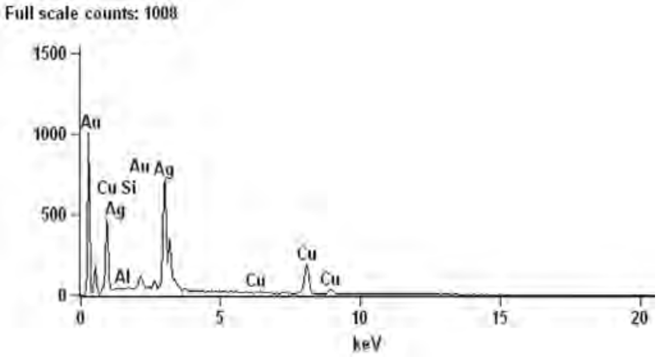

Figure 10. EDS spectrum (20 keV) of an unburnished sample after heating for 120 sec. at 680 ºC showing no mercury is present in the gilding layer. © Rijksmuseum, Amsterdam.

Part 2 of the experiment showed varying levels of damage to blistered gilding caused by conservation treatments normally used on silver. The samples were subjected to extreme conditions in order to determine at which point damage occurs, or to simulate long-term effects of repeated treatments. Observation of tarnish removal with calcium carbonate showed that on average it took 10 rubs to remove the tarnish, at which point the blisters were not visibly changed. After rubbing 160 times, the blisters were pressed in or worn down at the top. Therefore, after 16 such conservation treatments visible damage would appear on the blisters. To put that in perspective, a 400 year-old object polished once every 25 years would have visible damage on blistered areas.

The use of silverdip for tarnish removal is not without risk, either. Measurement of the Ecorr shows that after 120 seconds the silver starts corroding. Depending on the extent of burnishing, the gold on fire-gilt objects can be very porous (Northover and Anheuser 2000). Furthermore, in blistered areas it appears likely that a very porous silver (Kirkendall) layer is present under the gold. Therefore, there is a great risk that silverdip remains in the pores despite thorough rinsing. However, if silver dip is applied in very small amounts on a cotton wool swab, and immediately rinsed off, the chance that the dip seeps into the pores is minimized.

Experiments with a steam cleaner show that the risk of damaging the blistered gilding, and also burnished unheated samples, is very high. If this technique is chosen for cleaning, it is important to use it for short periods (less than 40 seconds), with a working distance of at least 2 cm, and to switch to other methods for difficult areas.

The ultrasonic tank for general cleaning was shown to damage blistered surfaces when used for long periods. After 180 seconds, some of the blisters were removed from samples placed in the basket and after 300 seconds from samples that were suspended in the tank.

Conclusions

Objects with blistered and/or delaminating gilding are extremely vulnerable to loss of gold. To avoid damage during treatment, fire-gilt objects should be carefully examined for blisters, keeping in mind that they can be very small and are often only visible under magnification. The factors of heat, burnishing and the presence of mercury appear to be linked to blister formation. Therefore, blisters can be expected in burnished areas that have visible solder repairs. The fact that mercury was not detected by SEM-EDS in heat-treated unburnished areas should be studied further. However, it could be significant since the detection of mercury by analysis is sometimes used to identify fire-gilding.

All conservation treatments tested appear likely to cause damage, either immediate or visible over the long-term, to blistered fire-gilt objects. Tarnish removal can best be performed with a minimum of abrasion and pressure, keeping in mind that the gilding and underlying silver are likely to be porous. Lacquer removal and other cleaning methods should also be gentle and solvent cleaning with poultices or immersion (to minimize abrasion) may be good options. The best option is to prevent tarnishing of these objects by optimising storage and display conditions to maintain a low relative humidity and provide protection from airborne pollutants.

Acknowledgements

The author would like to thank Joosje van Bennekom, Robert van Langh, Arie Pappot, Marilyn Hockey, Fleur Shearman, Thibaut Devièse and Craig Williams for their help and support.

Endnotes

[1] The fire gilding was executed by G. Eiblmeier of *Atelier Eiblmeier*, Lenggries, Germany, 0049-8042111, mail@atelier-eiblmeier.com

[2] The silver was heated to cherry-red and pickled in 10% sulphuric acid three times, air-cooled, scratched with a brass brush, and painted with mercury salts (1 part mercury to 4 parts nitric acid). A gold-mercury amalgam was prepared (5 parts mercury to 1 part gold, squeezed in a leather bag and then rinsed), and was applied in five layers using a rabbit's foot (Eiblmeier 2008). The completed gilding had an average thickness of 3 µm (measured under magnification with Leica software). The fire-gilt sheet was sawn into 1 x1 cm pieces with a jewellers saw of which one half was left unfinished and the other half burnished with an agate stone and saliva as described in van Laer.

[3] The microscope used was a Leica MZ8 optical light stereomicroscope.

[4] The sheet of sterling silver was degreased with acetone and placed in the galvanic gold tank as the cathode (-) opposite a stainless steel anode (+) and connected to a power source. The gold bath contains 4 gr. of 24 carat gold per litre and is cyanide free. The silver was placed in the tank for 4 hours at 2 V and 0.5 m/A and was afterwards rinsed with demineralised water. The power source used is a Power Supply EA-PS 3016-10.

[5] The oven is a Carbolite BWF 12/13.

[6] Socal N2R, particle size 200-300 µm.

[7] A recipe used at the Rijksmuseum is: 40 g thioureum, 9.5 ml H_2SO_4, 2.5 g Synperonic A7 non-ionic soap en 440 ml demineralised water, pH 1.

[8] The multi-meter is a Tektronix DM250, sensitivity 0.1 mV.

[9] The reference electrode is a Metrohm, Ion analysis

[10] Derotor Steam Cleaner GV6

[11] The ultrasonic tank is an Elma® Transsonic 470/H

Materials

Barium sulphide (99,9%)
Aldrich, supplied by Sigma Aldrich Chemie B.V.,
Zwijndrecht, the Netherlands,
+31(0)786205411,
www.sigmaaldrich.com/nederland.html

Precipitated calcium carbonate Socal N2R
Solvay Chemicals GmbH, Xantener Str. 237, 47495
Rheinberg, Germany,
+49(0)2843 732158,
www.solvaychemicals.com

SpeciFix-20 polyester resin
Struers GmBH, Electraweg 5, 3144 CB Maassluis,
the Netherlands,
+31(0)105997209,
www.struers.nl

Synperonic A7
Conservation Resources UK Ltd., Unit 2 Ashville Way,
Off Watlington road, Cowley,Oxfordshire, OX46TU,
United Kingdom,
+44(0)1865747755,
www.conservation-resources.co.uk

Thiourea
Aristoforma-Interchema, Beukenlaan 3, 8536 TK
Oosterzee, the Netherlands
+31(0)514564488

Sterling silver sheet
Schöne edelmetaal, Meeuwenlaan 88, 1021 JK
Amsterdam, the Netherlands,
+31(0)20 4350222,
www.schone.nl

Sulphuric acid (99,9%)
Fluka, supplies by Sigma Aldrich Chemie B.V.,
Zwijndrecht, the Netherlands,
+31(0)78 6205411,
http://www.sigmaaldrich.com/nederland.html

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Authors

Ellen K van Bork graduated as a gold and silversmith from the 'Vakschool' in Schoonhoven, the Netherlands in 2004. After one year of museum studies she specialized in metals conservation at the Netherlands Institute for Cultural Heritage in Amsterdam, from which she graduated in 2009. During her education she worked as a goldsmith at Beaufort jewellery and as a metals conservator at the Rijksmuseum, both in Amsterdam. Currently she is a metals conservator at the British Museum in London.

Sara Creange began her conservation career in 1998, working for the Western Archaeological and Conservation Centre, the Arizona State Museum (Tucson, AZ) and then Griswold Conservation Associates (Los Angeles, CA). She graduated in 2004 from the Winterthur/University of Delaware Program in Art Conservation, with a specialty in objects conservation. She subsequently worked at the Philadelphia Museum of Art, and as a conservator in private practice. In 2007 she moved to the Netherlands where she is currently a metals conservator at the Rijksmuseum Amsterdam. Email: s.creange@rijksmuseum.nl

Dr. Ineke Joosten earned a master in Geochemistry at the University of Utrecht (RUU) in1992, and a Ph.D. in Earth and Life Sciences at the Free University (VU) Amsterdam, the Netherlands (2004). From 1992 she worked at the National Service for Archaeological Heritage (ROB) in the field of archaeometallurgy and conservation of archaeological metal. As a research scientist at the Netherlands Institute for Cultural Heritage (ICN) since 2001, she applies diverse analytical methods but mainly SEM/EDS to the study and conservation of objects such as the conservation of plaster casts, dying techniques of ancient textiles and graffiti on metal objects. Email: Ineke.joosten@icn.nl

Q & A SESSION

Lesley Frame: I have two questions: did you consider looking, or trying to test for volatile mercury while doing the heat treatments to see if you were actually getting mercury leaving the samples?

Ellen van Bork: I thought of that but I didn't have the means to actually do that but that would indeed be very interesting.

Lesley Frame: Another thing - you said that after 10 rubs you didn't see any damage but I'm wondering what kind of pressure you used for each rub?

Ellen van Bork: Yes, that was one of the problems I had, so I tried to simulate what I normally do in practice. But I'm sure there is a better way in actually determining how much to stabilize the pressure and therefore making it more accurate. But yes, it was one of the problems I had. But I just wanted to see that if I applied a treatment which I used on objects, what that effect would be on the samples I had.

Sara Goidanich: Could you please go back to the graph – the last one you showed about the corrosion potential? Is it volts or millivolts? And can you comment a little bit more about this graph because I know there is a lot of research at the moment about how to use corrosion potential to monitor treatments to understand the state of our surfaces. So you said that from this graph you understand that corrosion starts at a certain point.

Ellen van Bork: What I wanted to do was almost a quick test to visualize when that would happen: we know that because the dip has a low pH that it will corrode if it isn't removed sufficiently. What I could see here on the graph is that it first passivates until about 120 seconds and then it starts dropping and starts corroding the object.

Karen Stemann Peterson: Thank you very much, it is a very interesting subject. I've seen a lot of blisters on gilt silver in Denmark in the Museum and also in churches. You tested the steam treatment – it has been a suggestion from Dutch conservators to clean off lacquers this way – was the time you spent on this realistic? I heard that you could speed up this treatment just by soaking the object first in water.

Ellen van Bork: Yes, it is true. I didn't do that with this test, but it's been proven that it swells up the lacquer, especially if you use warm water and it will take off the lacquer more easily.

Karen Stemann Peterson: And then you should go on and look at different ways of cleaning to avoid the acid.

Ellen van Bork: Yes, that would be very interesting indeed, thank you.

Janneke Nienhuis: Could you go back to your EDS spectra please? My question is about the peak of mercury and gold. It looked like there was no escape peak – so how could you quantify the mercury and say that there was mercury or that there wasn't?

Ellen van Bork: I didn't quantify the mercury. The spectra showed us that there was mercury present in the sample.

Janneke Nienhuis: But are you sure that wasn't gold? Because it looked like it was the same peak.

Ellen van Bork: They are very close to each other…

Janneke Nienhuis: So it was the scale of the picture that was a bit confusing...

Ellen van Bork: Yes

Stéphane Lemoine: Assuming that these blisters formed by evaporating mercury, would it be possible to reduce them under vacuum using a consolidant?

Ellen van Bork: I think the problem with these blisters is that they are extremely thin and very vulnerable. So I think that if you would apply a vacuum, even though you have a coating on it, microcracks would occur around the edges of them, which would in the end possibly lead to complete delamination of the blister.

Jettie van Lanschot: When you were making those E_{corr} measurements I suppose you used the recipe of old Stambolov? So it is not only acid but also a chelating agent?

Ellen van Bork: No I didn't do that.

Jettie van Lanschot: So what is your silver dip consisting of?

Ellen van Bork: It is sulfuric acid, a non-ionic soap [detergent] and thiourea.

Jettie van Lanschot: Because thiourea is also a chelating agent and you should take that into consideration when you look at your measurements.

Ellen van Bork: Yes, thank you very much.

ORGANIC COATINGS FOUND ON TIBETAN BUDDHIST GILT COPPER ALLOY STATUARY AT THE AMERICAN MUSEUM OF NATURAL HISTORY

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Abstract

An investigation was undertaken to characterize surface coatings, residues and accretions found on Tibetan Buddhist gilt copper alloy figures in the collection of the American Museum of Natural History. The purpose of the study was to guide conservation treatment. Pinaceae (pine family) resin, Acacia catechu extract and tung oil, sometimes with urushi, are among the materials found in the coatings, characterized by spectroscopic and chromatographic techniques. Fat and oil residues were also present on some surfaces. Identification of the materials in the coatings was confirmed by comparison with analysis of available reference standards. These findings will inform conservation treatments, provide a basis for future research and comparison, and supplement art historical research.

Keywords: Buddhist sculpture, Tibet, FTIR, GCMS, Py-GCMS, catechu, Pinaceae resin, urushi

Introduction

Vajrayana Buddhism and its arts developed over centuries and involved mutual influence and exchange between Tibet and its neighbors, particularly Nepal, China and Mongolia. The collections at the American Museum of Natural History (AMNH) in New York feature a sizable assembly of nearly 2,600 Tibetan Buddhist objects, including figural gilt copper alloy statuary.

In 1937, New York collector William B. Whitney bequeathed more than 800 Tibetan items to AMNH, half of which were the figural statuary that form the core of this study. Whitney started his collection circa 1924 (Anon. 1936) with purchases made largely from New York-area private dealers.

AMNH research associate Antoinette Gordon organized an exhibition of Whitney's collection in 1936 at the museum. In 1939 she published 'The Iconography of Tibetan Lamaism', an important early source, which discussed many of these figures.

Most of the museum's Tibetan-Buddhist figures originated in eastern Tibet, northwestern China, Inner Mongolia and Nepal. The earliest examples in the collection may date to the 11th century, though most were probably made during and after the 18th century.

The AMNH collection is significant because of its large size, diversity of materials, and its relatively early acquisition and publication. The statuettes were predominantly fabricated from mercury amalgam gilt copper alloys, hollow-cast and with separately cast attributes and bases. Some surfaces were additionally 'cold-gilt', either with foil or locally painted bound metal powders. Other surface decorations include polychromy and stone or metal inlay.

A condition survey of this collection was undertaken in 2008 and 2009. It revealed the presence of several types of coatings on approximately one-third of the figures in the collection. There are localized clear coatings over isolated painted areas and translucent orange coatings covering foil gilt surfaces, both of which appear to have been intentionally applied. Other observed surface applications, usually over entire surfaces — although sometimes only present as residues — are less straightforward. These range in appearance from subtle, translucent red to thick, dark coatings that partially conceal the gilding. Additionally, some accretions on the surfaces resemble degraded coating residues, corrosion products, grime, other deposits, or all of these.

The purpose for these surface-obscuring applications is unclear, although scattered drip, brush, or wipe marks suggest deliberate applications. Microscopic examination revealed that none of these applications contained pigment particles. Examination under long wave ultraviolet radiation induced a yellow-green fluorescence of the clear coatings over paint and an orange-yellow fluorescence of orange coatings over foil. The thick-dark and thin-red layers were non-fluorescent. Solubility and microchemical spot tests were employed, and several of the clear coatings over paint produced positive results in the Raspail test for rosin (Odegaard et al. 2000).

The presence of these coatings, residues, and accretions constituted an impediment to conservation treatment. Although structural treatments could be undertaken, surface cleaning could not proceed without a deeper understanding of these surface materials. Therefore, characterization of the coatings and accretions, and a need for an explanation for their presence on the Tibetan figures, instigated this study. It was hoped that the resultant findings would elucidate whether the coatings originated from use within their original contexts or from a later context, such as the art market, or within the museum.

Figures in this study are grouped by region, as depicted in Illustrations 1-5 below. (Note: all objects appear courtesy of the Division of Anthropology, American Museum of Natural History. Scale bars are in centimeters, and captions use the following convention: sub-image number: AMNH catalog number; subject; origin; estimated date). Some of the regions have consistent coating types; others were found to have a mixture of coating types.

Figure 1. Group 1 – Nepalese; (multiple coating types). 1a: 70.3/ 4958; Siddha; Nepali; 1200s-1500s. 1b: 70.0/ 2048; Syamatara [Green Tara]; Tibetan-Nepali; 1700s-1800s. 1c: 70.0/ 4667; Indra; Nepali; 1600s-1700s

Figure 2. Group 2 – Sino-Tibetan; (mostly catechu containing coatings). 2a: 70.0/ 7081; Boddhisattva?/Offering Goddess?; Sino-Tibetan; 1800s-early 1900s. 2b: 70.0/ 7147; Guanyin; Chinese; 1800s. 2c: 70.0/ 7516; Bardo deity?; Tibet or Mongolia, folk style; 1800s or later


3a 3b 3c 3d

3e 3f 3g 3h

Figure 3. Group 3 – Sino-Mongolian; (most have Pinaceae resin coatings). 3a: 70.0/ 7562; Possibly a Heruka figure (Bardo deity); Tibet or China, folk style, probably Nyingma order; Mid-1800s or later. 3b: 70.0/ 7163; Bardo deity; Tibet; 1800s?. 3c: 70.0/ 7115; Mi Tri Lugs gyi mK'a sPyod?; Tibet, Mongolia, or China?; 1800s. 3d: 70.0/ 7535; Kshetrapala; Tibet; late-1700s or after. 3e: 70.0/ 7432; Hayagriva; Tibet (Inner Mongolia), Dolonnor style; mid-1700s or after. 3f: 70.0/ 7456; Yama and consort Tibet / China; 1700s - 1800s. 3g: 70.0/ 7470; Protector; Mongolia / China; 1800s. 3h: 70.0/ 4688; Lhamo; Sino-Tibetan; mid-1700s or later


4a 4b 4c

Figure 4. Group 4 – China; (all urushi / tung oil lacquer coatings). 4a: 70.0/ 5218; Lokapala; Chinese-made; 1800s? 4b: 70.0/ 5225; Gautama Buddha as baby; China or Korea?; 1800s. 4c: 70.0/ 5249; Samantabhadra; China or Korea; Ming Dynasty style, 1368-1644

Figure 5. Group 5 – Ming and Qing Periods; (multiple coating types). 5a: 70.0/ 5246; Arhat; China; 1400s-1800s. 5b: 70.0/ 7002; Vajradhara; China; Late Ming style, 1600s. 5c: 70.0/ 6994; Vajrasattva OR Vajradhara, and consort; Sino-Tibetan; High Qing style, mid-1700s. 5d: 70.0/ 7053; Bodhisattva; Mongolia; 1800s-1900s. 5e: 70.0/ 7143; Vasudhara; Sino-Tibetan; late Qing, 1800s. 5f: 70.0/ 6975; Gautama Buddha; Sino-Tibetan; 1700s-1900s. 5g: 70.0/ 7049; Achala; Tibet?; possibly Qing revival of Pala style, late 1700s-1900s

Background Literature

Ethnographic accounts, translations of Tibetan texts, collection and exhibition catalogues, and modern technical studies were scrutinized for information on coatings applied to Tibetan statuary, producing scant and varied references (see below). The majority of these relate to patination, rather than to accretions through use.

Several ethnographic accounts from the 1970s and 1980s mention surface treatments to produce color changes. Dagyab (1977), for example, recounted that figures are 'treated to enhance the golden color and give the surface a warm reddish flow much prized by Tibetans' by immersion in an aqueous bark extract or boiling with 'salt', copper and silver. Similarly, in 1979, Mavis Bimson described immersion to obtain a red surface coloration using twigs of the Rubia genus, in a Nepalese Newar workshop (Oddy et al. 1981). In the 1970s, Lo Bue observed Nepalese patination using mustard seed oil and shoe polish (Lo Bue 1981). In 1959, Tucci translated a Tibetan text, which described surface treatment of figures in Tibet as follows: 'they are fire gilded or they are polished with resin or greasy material (byo rtsi) or not polished at all (Tucci 1959)', although Lo Bue retranslated the phrase 'byo rtsi' as 'curds varnish'. Tucci additionally translated the surface treatment of 'New Chinese' Vajrayana Buddhist figures as: 'besmeared with red (Tucci 1959)'.

Reedy provided the most comprehensive account of 19th century Tibetan metalworking with an investigation of the text by Ju Mi-Pham (1846-1912), which included patination recipes made from complex mixtures of vegetal materials, metallic/rock elements, animal fat and salts (Reedy 1991).

Most modern technical studies did not include study of finishing and decorating techniques (Reedy 1991). Among those that did, Hykin analyzed red and black surface residues on a 12th-13th century Tibetan Avalokitesvara figure, characterizing them by Fourier-transform infrared spectroscopy (FTIR) as vermilion/gypsum/wax and calcite/clay/oil/bitumen mixtures, respectively (Hykin et al. 2007). However, the age and lack of gilding on the figures and visual appearance of the residues are dissimilar to the AMNH figures.

Toned surface finishes have also been used to imitate gilding over metals on Tibetan pieces. Price has identified tung oil toned with barberry, turmeric and saffron as well as Pinaceae (pine family) resin with tung oil on a 19th century Tibetan altar and cabinets that typically held figures (Price et al. 2008).

It is clear that available sources in the literature that describe the application of coatings are limited, and little analysis has been done to date. The results of this project will not only aid conservation treatment design, they also will augment existing knowledge on the topic.

Instrumental Analysis

Prior to sampling, counsel was sought regarding ethical considerations, as outlined by Reedy (1992). AMNH scientific assistant Laila Williamson and Lozang Jamspal, a Tibetan monk and lecturer (Williamson and Young 2009), were consulted to insure respectful sampling procedures were performed. Based on visual distinctions, a range of coating types over gilt surfaces was selected for study, and samples from 24 figures were analyzed.

Samples were obtained by gently scraping surface residues with steel scalpel blades, while viewing the surfaces under magnification. Initially, coating residues and accretions were analyzed by FTIR[1]. Pinaceae resin, oil, and plant carbohydrates (gums) were detected. However, interference from corrosion products (atacamite) and metal complexes (copper oxalate and copper fatty acids) prevented an accurate characterization of most organic mixtures (Derrick et al. 1999). Therefore, subsequent analysis was carried out by gas chromatography mass spectrometry (GCMS) and pyrolysis-GCMS (Py-GCMS) to identify the individual chemical components of the observed coatings, residues, and accretions[2, 3]. These results are presented in Table 1.

KEY:
gum = plant carbohydrate
catechu = *Acacia catechu* extract ("cutch")
urushi = *Rhus verniciflua* lacquer

PR = *Pinaceae* resin components
DO = drying oil
TO = tung oil
OF = oil/fat

Ct: catechin derivatives
CS = copper fatty acid soap
Tn = gallotannin derivatives
AC: alkyl and alkenyl components of *Rhus Verniciflua*

CO: copper oxalate
BA = benzoic acid derivatives (often in tannins)

Designation	Coating description	Notes	FTIR	Py-GC-MS	GC-MS	Coating conclusion
Group 1: Nepalese; multiple coating types						
1a	Glossy red-brown, back of arm	---	---	TO, AC	OF	Tung oil, urushi (Rhus verniciflua)
1b	Matte brown black, base	---	---	DO, OF, BA, Tn	DO	Drying oil, gallotannin
1c	Matte brown, PL side of waist	---	---	OF (low), BA, Tn, caffeine	OF	Oil/ fat, gallotannin
Group 2: Sino-Tibet; catechu						
2a	Thick, red-black coating, body	Solubility = 10% NaOH (aqueous) > hot water; Partial solubility = water > dimethylformamide>methanol> toluene=xylene; Insolublility = acetone, ethanol, petroleum benzine, Stoddard's solvent	Catechu	Ct, BA,Tn	Ct, caffeine	Catechu
	Localized, thin, red coating, face	---	Catechu	---	---	Catechu
2b	Crusty black, base	---	---	Ct, BA	Ct	Catechu
	Thin red, face	---	---	Ct, BA,Tn, OF	Lignin product	Catechu, other gallotannin, oil/ fat, lignin
2c	Black patina or residue	---	---	Ct, OF, Tn	Unknown components, DO?	Catechu, oil/ fat, other gallotannin?
Group 3: Bardo, *Pinaceae* resin						
3a	Red-brown, body	Adjacent clear coating (pine resin) probably contaminated the Py-GCMS sample.	Gum, OF, CS, CO, atacamite	OF, PR, BA, Ct	OF, unknowns	Oil/ fat, catechu, corrosion
	Clear, behind ear	---	*Pinaceae* resin	PR	Natural resin	*Pinaceae* resin
3b	Thin red-brown, back of skirt	---	Gum?, OF, CS, CO, atacamite	OF,Ct, Tn	OF, BA	Oil/ fat, catechu, other gallotannin?
	Clear, near paint	Positive for terpenoid resin (Raspail test); Solubility = acetone ethanol; Insolubility =Water, petroleum benzine, xylene.	*Pinaceae* resin	OF, PR, BA	Natural resin	Oil/fat, *Pinaceae* resin
3c	Overall red-brown, reverse (pooled)	Unusual subject.	Gum	OF, Ct, Tn, BA	palmitic acid	Catechu?, corrosion
3d	Thin, light brown, base	---	Gum, OF, CS, atacamite	OF, BA, Ct, PR	OF, nicotinic acid	Catechu, oil/fat, *Pinaceae* resin, corrosion
	Belly	---	---	OF, BA, Tn	OF, nicotinic acid	Oil/fat, gallotannin?
3e	Thin red-brown, back of garment	---	Gum, unknowns	OF , PR, Tn	OF, nicotine	Oil/fat, corrosion, gallotannin?, unknowns
	Corrosion spots?	---	Gum, unknowns	---	---	as above
3f	Black on leg, under animal	---	---	OF,PR, traces Ct, BA	OF, PR	Oil/ fat, *Pinaceae* resin, catechu?
3g	Localized on animal hoof	---	*Pinaceae* resin	---	---	*Pinaceae* resin
3h	Orange over foil	Solubility = acetone, ethanol, xylene; Insolublility = petroleum benzine, water	Oil	TO	TO	Tung oil
Group 4: China, *urush*i						
4a	Thick, translucent red, over skirt	---	---	TO, OF, AC	TO	Tung oil, urushi (Rhus verniciflua)
4b	Thick, translucent red, base	This is not a popular Tibetan form. The figure wears a silk garment. The GCMS sample gave a weak chromatogram.	---	TO, AC	DO	Tung oil, urushi (*Rhus verniciflua*)
4c	Brownish red, PL thigh	---	---	TO, AC	TO	Tung oil, urushi (*Rhus verniciflua*)
Group 5: Ming & Qing; multiple coating types						
5a	Matte brown, base	---	---	OF	OF	Oil/ Fat (possibly animal)
5b	Dark residue, base	---	---	OF, Tn	DO	Drying oil
	Shiny red coating, body.	---	---	TO. OF, Ac, Tn	DO	Tung oil, urushi (*Rhus verniciflua*)
5c	Matte, dark brown, back of arm	---	Gum, OF, CS, atacamite	DO, BA,Tn, caffeine	Probably DO, nicotine	Drying oil, gallotannin
	Shiny, on forearm	---	---	DO, BA,Tn, caffeine	Probably DO, nicotine	Drying oil, gallotannin
5d	Localized, clear	---	*Pinaceae* resin	---	---	*Pinaceae* resin
5e	Matte brown / black, PR leg/base	---	---	OF,BA, Tn	Probably DO	Drying oil, fat, gallotannin
5f	Brown, body (front)	---	Gum, OF, CS, atacamite	OF, Ct	OF, nicotine	Oil/fat, catechu
5g	Very thin, even black, body	---	---	OF, BA, Ct, Tn	Unknown components, DO?	Oil/fat, catechu, other gallotannin

Figure 6. Table 1 – Analytical results

Discussion

Several FTIR spectra of gum-containing residues showed absorption bands characteristic of catechin. Samples of these residues were further analyzed by GCMS techniques to confirm the presence of catechin, and other chemical components characteristic of catechu plant extract. For example, the occasional presence of caffeine may specifically suggest the use of Acacia catechu leaf extract in some coatings (Shen 2006).

Hofenk de Graaf (1969) described catechu, or "cutch," as the catechin-containing extract from any of several plant species: Acacia catechu, Areca catechu, Uncaria gambier, Ceriops candolleana. Catechu has traditionally been used as a brown dyestuff. Shen (et al. 2006) mentions the medicinal use of cutch specifically from Acacia catechu, and Huntington (2009) noted this in India, as well, though not necessarily in Tibet. Rockhill (1895) indicated its past usage by Tibetan women in a greasy coating mixture, probably as a facial skin protectant.

Pinaceae resin was further confirmed by the presence of dehydroabietic acid and its oxidation products. Drying oils were identified on the basis of characteristic fatty acid patterns and the ratio of azelaic to palmitic acids. Among the oils, tung oil was indicated by the additional presence of 9-(o-propylphenyl) nonanoic acid. Tung oil / urushi formulations were also identified in orange coatings over foil gilding, where specific alkyl and alkenyl catechols (pentadecyl- and pentadecenyl-catechols) typical of the sap of Rhus verniciflua, from which urushi is harvested, were detected.

Tung oil and urushi are well known artist materials in Asia, as is their combination in lacquer coatings (Grove Encyclopedia of Arts 2008).

Non-drying oils and a few animal-derived fats were also detected. Fat and oil residues may be related to greasy soot, as described by von Schroeder (2001), on statues in monasteries from burning butter lamps. Some of these oil and fat residues are comparable to accretions analyzed in a butter lamp (catalog number 70.0/4529) and a yak butter container (70.3/6585A), both from the collections of the AMNH Anthropology Division. Reedy (1991) also lists oil and butter in several patination recipes by Ju Mi-Pham.

Some coatings contain gallotannins from plant extracts other than catechu, and may comprise a distinct coating classification. Additional analytical techniques could provide more information on the nature of these and other coating components that were not detected by the techniques used in this study.

Each of the substances detected by analytical means is contextually appropriate. The clear layers of localized Pinaceae resin were probably applied to protect, consolidate or enhance the color of the underlying paint. Some of the translucent applications may be the 'warm reddish glow' suggested by Dagyab, to simulate lacquer coatings (Huntington 2009). Maybe they were applied with the intent of 'preventing oxidation (Lo Bue 1981)'.

The presence of catechu on numerous figures is puzzling. Perhaps its application was related to its use as a materia medica (Huntington 2009), possibly to ritually infuse divine power into human medication.

Conclusion

A variety of organic coatings are present over the gilding on Tibetan Buddhist figures from the AMNH collection. Residue samples from 24 figures were analyzed, and their components were found to include catechu, Pinaceae resin, and tung oil, the latter often in conjunction with urushi.

Further analytical and anthropological/art historical research on other similar figures is needed for a more complete interpretation of these coatings, residues, and accretions and to comprehend the reasons for their presence on the AMNH figures. Therefore, removal of these coatings through conservation treatment is unwarranted. The most prudent and only currently justifiable treatment course is minimal surface cleaning that leaves the surface materials intact.

It is hoped that the results of this study will aid the conservation community in making informed decisions on the treatment of these and similar objects.

Acknowledgements

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Endnotes

[1] FTIR analysis conditions: Magna 560 FTIR spectrometer (Thermo Nicolet) with a SplitPea (Harrick) Si crystal single bounce ATR accessory. Spectra average 32 scans at 4 cm-1 spectral resolution. An ATR correction routine compensated for variations in penetration depth with wavenumber.

[2] PY-GCMS set-up: Double-shot pyrolyzer 2020iD (Frontier laboratories Ltd, Japan), interfaced to an Agilent 6890 GC with 5973 MSD. Conditions: inlet temperature 320°C; transfer line 320°C. 20:1 or 30:1Split ratio; 30m×0.25mm×0.25μm film thickness J&W DB-5MS

column; flow rate 1.5mL/minute. Oven: 40°C 1 minute, then 10°C/minute to 320°C, hold 10 minutes. Samples were treated with (tetramethyl) ammonium hydroxide (25% in methanol) prior to pyrolysis at 550°C.

[3] GCMS set-up: HP 6890 GC with 5973 MSD. Conditions: inlet temperature 300°C; transfer line 300°C. 1µL injection (splitless); 30m×0.25mm×0.25µm film thickness DP-5MS column; flow rate 2.3mL/minute. Oven: 55°C 2 minutes, then 10°C/minute to 325°C, hold 10.5 minutes. Samples treated with BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) at 65°C deg for one hour.

Materials

BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide)
Grace, 2051 Waukegan Road
Deerfield, IL 60015
Part No. 18085
(800) 255-8324

(+)-Catechin hydrate,1g Sigma Aldrich
Product Number Aldrich 22110
CAS# 225937-10-0
(800) 325-3010

Catechu/Cutch references obtained from the following suppliers:
Aurora Silk
434 NE Buffalo Street
Portland, OR 97211 USA
(503) 286-4149

Alliance Import Company
1021 "R" Street
Sacramento, CA 95814
(916) 920-8658

Kremer Pigments Inc.
247 West 29th Street
New York, NY 10012
(212) 219-2394

Tanakanao Senryoten
Tokyo, Japan
(03)-3400-4894

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Q & A SESSION

Tom Chase: Karl I wanted to make one comment. The middle guy on the top row there, that particular surface I have seen on Buddha's in temples in Yunnan and also in the Lama Temple in Tibet. It is that deep orange – and also in some of the museums here, but I have seen them in both those contexts and I think it is a very distinctive surface – I think that tung oil plus urushi sounds like a good guess.

Karl Knauer: Yes, that's exactly what it is.

Mark Erdmann: Were any of these coatings sticky to the touch? And did they therefore create any problems with sticking to the storage materials?

Karl Knauer: That's a very good question. No, none of them were sticky. There was a study done a few years ago on tung oil and painted Balinese shadow puppets at the Museum and those tung oil pieces were sticky, but these are completely not at all sticky, although they had been in the past – there were some fingerprints in a few.

Molly Carlson: First, that was a lovely paper. I really enjoyed seeing all the statuary. You said you had someone come in and you consulted with them about the ethical nature of removing a sample. Was this a religious person?

Karl Knauer: He is a religious and Lozang Jamspal is a lecturer at Columbia University and he had gone through monk training. He is consulted quite often by several museums.

Molly Carlson: Do these statuettes have prayers up inside?

Karl Knauer: Many do actually yes. A lot do have consecration plates on the underside and offerings would be put inside - often rolled prayer scrolls. We didn't open any of them if that's what you're getting at.

Molly Carlson: No, I know, you would have said, I'm sure.

Karl Knauer: We tried to follow the outlines as suggested by Lozang Jamspal and ethical practices for approaching Tibetan Buddhist materials and he had suggested contacting Tibetan Buddhist practitioners to establish guidelines.

Molly Carlson: Thank you I was just curious.

DDN Singh: Thank you. Your presentation was very informative. But there were some facts which were misplaced. One is that Buddhism did not spread from Tibet – in fact it was born in India. From India it spread all over the world. So please correct your slide.

Karl Knauer: Yes. It definitely came from India – 6th Century B.C. I'm sorry if that map didn't make that clear.

DDN Singh: Number 2 [question] is that It is really surprising to note that some of the sculptures/figures, didn't have any palmitic or stearic acid and you are attributing that it is indicative of animal fat? The Buddhists have a very strong belief in non-violence and they cannot use animal fat, that is impossible [because of their religion]. As a matter of fact [the treatment with drying vegetable oils] it is still practiced in India in many places.

Tom Chase: Karl, let me make one more comment. In the Field Museum of Natural History, when I visited many years ago, they were in the middle of a cleaning project on the Buddhist statuary and they cleaned most of them with air abrasives. So on those there are no coatings remaining at all and I couldn't marshal any arguments why they should not clean them at that point but I was a lot younger than I am now! So that is one more cautionary tale about cleaning, I think!

Karl Knauer: Absolutely, yes it is definitely something to think about now. If these are there at all, you might lose them if you're not careful. I've heard about some of the pieces at the Field Museum – some of them were gifts from Walter Leo Hildberg, the same collector and some of those have been heavily cleaned and in addition the fact is the gilding is lost on some of those.

IMITATION-BRONZE PAINTS ON AMERICAN ZINC SCULPTURE

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Abstract

A study of imitation-bronze paints on American zinc sculpture reviews historical information on bronzing, presents analytical results for original paints sampled from zinc artifacts, and surveys outdoor statues repainted recently to imitate bronze. Guidance is provided for conservators who seek to apply historically appropriate replacement coatings.

Keywords: zinc, zinc sculpture, bronze paint, metal powders, American, nineteenth century

Introduction

Zinc is a dull gray metal that became available in large quantities in Europe during the early 19th century and quickly became one of the least expensive metals. By 1825, supply had exceeded demand to the point that a prize was offered by a Prussian industry association for new uses of zinc (Smith 1918). Zinc's first documented sculptural use in Europe followed in 1832 in Berlin (Hierath 2004). The metal's availability, relative low cost and low melting point (420°C) contributed to production of several thousand statues in the United States during the half-century following the American Civil War (1861-1865) (Grissom 2009). These statues filled an increasing demand for low-cost war memorials and for the decoration of civic fountains, county courthouses and grounds of private homes as the nation expanded.

Surfaces of zinc statues were invariably treated to resemble other materials. Bare zinc statues would have been unattractive on account of the dull luster of the metal and multi-piece assembly, which left most criss-crossed by disfiguring lead-tin solder seams. Treatments imitated stone and polychromed wood, but most often bronze. Methods for imitating bronze consisted primarily of paints, sometimes colored only with pigments, but more often incorporating brass or copper powders. For centuries, the latter have been referred to as bronze powders, although they never included copper-tin alloys (Rogers et al. 1973, Schiessl 1983); rather, the term referred to the metal that they imitated.

'Bronzed' statues cost about 10% above base prices for statues with 'one coat of paint' according to trade catalogues of the principal purveyors, the New York-based J.L. Mott Iron Works, J.W. Fiske, Wm. Demuth & Co., and M.J. Seelig & Co. In a rare statement, one catalogue spelled out subjects suitable for bronzing:

> Mythological subjects, such as the Sphinx, Griffin, Dragons, larger Dogs such as the Antique and St. Bernard, also Lions and Horses, should either be painted a stone color, or bronzed; large emblematic figures such as Industry, Justice, Commerce, and other figures used chiefly for buildings, look well bronzed... Figures representing the best works of art, ancient and modern, can either be bronzed or painted white...Such figures as Kiss' Amazon... should always be bronzed, in fact, nearly all the Statuary herein represented look well bronzed... Some of the most elaborate designs in Fountains and Vases look beautifully bronzed, which can be done at a very little extra cost, and will last and look well for a long time (Mott 1873).

Today, the original appearances of many statues have been forgotten, often leading to inappropriate surface treatments, such as painting statues a silver color in imitation of zinc. This paper attempts to aid conservators who seek guidance in applying replacement coatings. To accomplish this goal, historical information on bronze paints will be reviewed, samples of original paints detailed, and examples of recently applied imitation-bronze coatings surveyed.

Historic bronze paints

Nineteenth-century European coating literature described bronze powders and paints, and British and translated

French references were reprinted in the United States, e.g., Roseleur's *Galvanoplastic Manipulations* (Roseleur 1855, 1872). German-made bronze powders dominated commerce from at least the 17th century (Stalker and Parker 1688), however, and were generally referred to in English as Dutch metal, a corruption of *Deutsch* (German). Three companies from historical brassmaking centers of Fürth and Nuremberg were the exclusive exhibitors of bronze powders at the New York Crystal Palace Exhibition in 1853-54 (Association 1853). Eight other German firms exhibited at the Centennial Exhibition in Philadelphia in 1876, as well as one of the Fürth firms that had exhibited earlier, but was now listed in New York, presumably a branch of the German company (U.S. Centennial Commission 1880). The only other exhibitor was the American Bronze Powder Co., started by a pair of German '*meisters*' in Brooklyn in 1873 (Rogers et al. 1973).

Structurally, imitation-bronze powders consist of metal platelets that 'float' in media parallel to the surface, maximizing coverage and brilliance. The color of bronze powders becomes more golden as the percentage of zinc to copper increases, up to about 30%. Heat also alters coloration.

Production methods for making metal powders were in transition during the 19th century. Still in use were traditional manual methods that made powders costly on account of the work involved: reduction of metal to foil (requiring pickling and annealing), grinding the foil into flakes with a muller, and polishing. Around 1845, Henry Bessemer invented an all-mechanical process that produced flakes much less expensively, but since he kept it a secret for the next 35 years, traditional production no doubt continued (Bessemer 1989). Manuals also describe dissolution of copper in acid followed by precipitation (Debonliez and Fink 1870), but this would not have produced the requisite plate-like structures.

The historic process for applying bronze paints was often described as beginning with a base coat similar in color to the bronze powder. Green, blue, and yellow ochre pigments were also named (Mussey 1987), and green base layers have been found in England (Bristow 1996).

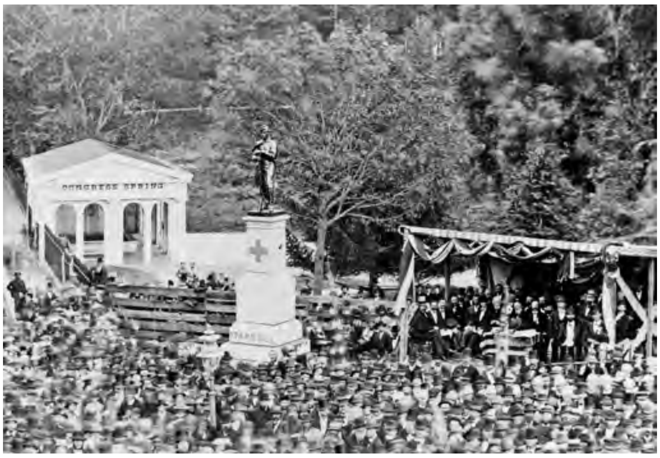

Figure 1. Dedication of the Civil War Monument, Saratoga Springs, NY, in 1875. Courtesy of the Saratoga Springs History Museum.

Two methods were described for application of bronze powders. By the first method, using velvet, soft leather, or a cotton ball, they were pounced onto a tacky oil varnish, gold size (probably an oil/resin mixture), or a mixture of asphaltum, boiled oil, and turpentine (*Painter's Manual* 1868). Alternatively, powders were mixed with a binder and applied as paint. Some manuals suggested limiting use of bronze powders to relief areas (Debonliez and Fink 1870, Mussey 1987). Finally, to prevent corrosion of the metal powders, manuals recommended use of varnish coatings, including shellac, spirit varnishes, and copal (Ure 1866, Hiorns 1892). However, these coatings would have been unsuitable for outdoor use. Documents identify 'spar' (marine) and 'carriage' varnishes as original coatings used on particular statues (Fiske 1893, Bazille & Partridge 1905). Since both coatings were meant for finishing exterior wood, they generally had elastic and weatherproof properties, but exact constituents cannot be known in the absence of analyses of paints from the statues.

Historical descriptions of bronze color on zinc statuary are absent from the literature, but representations provide evidence that most ranged from golden to dark brown, like contemporary bronze sculpture. For example, a photograph shows that a zinc Civil War statue in Saratoga Springs displayed a shiny, dark surface when it was unveiled (see Figure 1). Postcards of monuments were subjectively colored by print processes, but their copper and brown tones reflect perceptions of what was appropriate (see Figure 2). Also providing guidance are original coatings on indoor statues, which appear dark brown unless polychromed (see Figure 3). For gas fixtures made of zinc, 16 bronze colors are named in a catalogue of Cornelius & Sons (1876), including greens, lavenders, and silvers, but they almost certainly represent tints rather than strong colors. A mixture of 10 parts white, 5 parts raw umber, and 4 parts chrome yellow is suggested to imitate bronze without metal flakes in a 20th century manual (Pattou and Vaughn 1927).

Figure 2. Civil War Statue, New Jersey Home for Disabled Soldiers, Kearny, postcard, undated. Both the zinc statue and cast-iron fountain it rests on are toned brown on the postcard.

Figure 3. Departure statuette (ca. 1855-1870), Cornelius & Baker, 34 cm, private collection.

A survey of bronzing would not be complete without mentioning copper plating, used for imitating bronze in Germany and France soon after the discovery of electroplating around 1840 (Smith 1978). Copper plating was applied to statues made of zinc on the seminal *City of New York Civil War Monument* (1869) at Brooklyn's Green-Wood Cemetery. Probably because of the difficulty of electroplating entire sculptures, this instance of plating on outdoor statues was unique until the Daprato Statuary Company introduced its trademarked 'orbronze' in 1913 (Grissom 2009). Copper-plated statues have such poor durability outdoors, however, that they are frequently painted or replaced. Mosaic gold (SnS_2) is also mentioned for bronze coatings in historic literature alongside copper-alloy powders, but it has not been identified on any American zinc statues to date.

Cross-sections

Representative examples of paints sampled from 25 zinc items and examined in cross-section are listed in Table 1, including three samples examined by other conservators. In addition to reflected-light microscopy (bright field, dark field, and fluorescence), X-ray fluorescence spectroscopy (XRF) and scanning electron microscopy accompanied by energy dispersive spectroscopy (SEM EDS) were used for elemental analysis. SEM also proved useful for imaging metal flakes.

Original bronze paints were found below modern paints on most outdoor statues. In cross-section, the majority was applied in multi-layer systems: an undercoat (often reddish brown paint), followed by a layer containing copper or brass platelets in a transparent medium and a transparent coating (see Figure 4). Others consisted of a single layer containing copper-based flakes (see Figures 5, 6). In both cases, the copper-based flakes measured less than 1 μm in thickness and from 5 to 65 μm in diameter, oriented more or less parallel to the surface. We had hoped to differentiate pounced-on powders from those applied as paints according to flake locations, i.e., at the top or mixed throughout the film, respectively. However, we found that flakes were distributed throughout the layer or had settled to the bottom. Transparent media usually fluoresced, indicating the presence of natural resins or oils, although fluorescence was often difficult to see when non-fluorescing metal flakes were present. Zinc corrosion was observed below original paints, as well as penetrating into them and surrounding copper-based flakes (see Figure 6). In two cases, metal flakes were not found in the oldest paint layers, but it is possible that original layers were lost. Typically, paint samples showed numerous campaigns of repainting (20 or more), with many layers containing copper-based flakes. Flakes in subsequent paints tend to be larger and more regular than those in original paints.

We found some consistency in paints on outdoor statues, probably because Seelig's foundry produced statues sold by Fiske, Mott, and Demuth, as well its own. In some instances, customers must have exercised the option to purchase statues with one coat of paint and finish the statues themselves. On-site painting would have the advantage of precluding damage to foundry coatings during installation.

Original paints on Cornelius & Baker's zinc statuettes displayed indoors are thinner and contain more finely

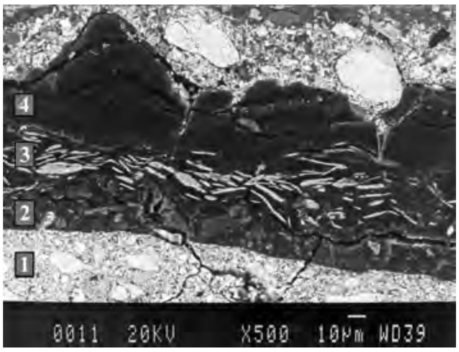

Figure 4. SEM of original bronze paint cross-section at 500x, showing (1) white-lead paint, (2) reddish brown paint, (3) copper-flake layer, and (4) varnish; *Neptune* (1892), Sailors Snug Harbor, NY.

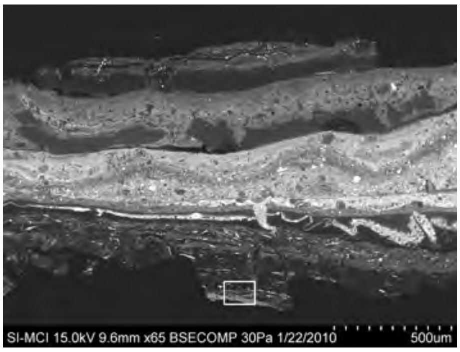

Figure 5. SEM of paint cross-section taken at 65x, showing many layers of paint; *Class of 1879 Lions* (1879), PP308.1-2, Princeton University, Princeton, NJ. Box indicates location of Figure 6.

Figure 6. Detail of previous at 1000x, showing original paint layer: copper flakes (white) suspended in medium, penetrated by zinc corrosion (gray) from below.

Statue	Seller	Original Layers[1] (1=bottommost layer)	Fluor.[2]	Avg. layer thickness	Predominant flake diameter	Flake morphology
OUTDOOR STATUES						
Pair of lion statues by A. Schiffelman:						
Class of 1879 Lions (1879) PP308.1-2, Princeton University Princeton, NJ		copper flakes in clear medium infiltrated by zinc corrosion[3]	NF	70 µm	6 µm	irregular
Theo and Leo (1920s) National Park Seminary Silver Spring, MD	Mott	copper flakes in clear medium infiltrated by zinc corrosion	NF	40 µm	5 µm	irregular
Fiske Civil War Infantryman statue:						
GAR Fountain (1893) Pottstown, PA	Fiske	1: a few copper flakes in clear medium [4]		50 µm	15 µm	regular
		2: copper flakes in clear medium		30 µm	30 µm	regular
		3: a few copper flakes in toned medium		25 µm	5 µm	regular
Soldiers' Memorial Fountain (1890) Oak Bluffs, MA	Fiske	brown & green oil paints (no metallic flakes)[5]				
Indian Chief statue:						
Squantum (1890) Tilton, NH	Mott	dark gray brown oil/resin mixture (no metallic flakes) [6]				
Hiawatha (1920s) National Park Seminary Silver Spring, MD		copper flakes in clear medium	NF	15 µm	10 µm	irregular
Neptune Fountain (1892), Sailors Snug Harbor, Staten Island, NY	Fiske	1: white lead paint		80 µm		
		2: reddish brown paint		25 µm		
		3: copper flakes in clear medium		20 µm	15 µm	irregular
		4: varnish		40 µm		
Psyche with Butterfly James Graham, NY		1: reddish brown paint (Pb, Fe. Si, O)	NF	35 µm		
		2: brassflakes (95/5) in clear medium	NF	2 µm	15 µm	regular
Justice (1889) Redding, CA		1: red lead paint	F	40 µm		
		2: brass flakes (90/10) in clear medium	NF	30 µm	30 µm	regular
		3: varnish	F	10 µm		
INDOOR ITEMS						
Departure statuette private collection	Cornelius & Baker	1: brass flakes	PF	2 µm	<2 µm	--
		2: varnish	NF	10 µm		
Armorial gaselier (1858), U.S. Capitol Washington, DC	Cornelius & Baker	1: tin flakes in clear medium	PF	15 µm	10 µm	regular

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[1] Analyses were performed at the Smithsonian Museum Conservation Institute unless indicated otherwise.

[2] F=fluorescence, PF=partial fluorescence, NF=no fluorescence

[3] Smithsonian results; specimen courtesy of conservator-analyst John Scott, NYC.

[4] Andrew Lins, 'Report on the Grand Army of the Republic Monument', 30 May 1996.

[5] Susan Buck, private conservator, Williamsburg, VA, personal communication, December 2009.

[6] Susan Buck, 'Cross-section microscopy analysis results,' 5 December 2001.

Table 1. Representative examples of historic metal paints on zinc artifacts examined in cross-section

MONUMENT	LOCATION	CONSERVATOR/ DATE OF PAINTING	PAINT SYSTEM	CONDITION	SIMULACRUM OF BRONZE
GAR Fountain (1893), Fiske	Pottstown, PA	Douglas Kwart 1997	phosphoric-acid wash primer PPG acrylic urethane primer NCP 250 PPG Deltron DAU (acrylic urethane) plus mica powders	fair: well-attached paint but possible color loss	fair (light)
Soldier's Memorial Fountain (1891), Fiske	Oak Bluffs, MA	Mark Rabinowitz 2000	acrylic urethane primer acrylic urethane paint	well attached paint, but dull	fair (unmodulated)
Squantum (1890), Mott	Tilton, NH	Ron Harvey 2002	phosphoric-acid wash primer Dupont zinc chromate paint Dupont clear acrylic urethane paint plus mica powders Dupont U-POL clear coat & wax	good	good (a bit dark)
Hebe Fountain (1909), Mott	Beacon, NY	Tallix Foundry 2000	unknown primer probably PPG acrylic urethane brown paint with flakes clear top coat	fair	fair (too dark & metallic)
Soldier's Monument (1893), Mott	Candia, NH	Rika Smith McNally 2007	Golden MSA (acrylic) Colors plus Sepp micro-bronze mica powder Incralac & wax	good	good
Spirit of the Fighting Yank (1958), E.M. Viquesney	Chicago, IL	Jane Foley 2009	Golden Gel (acrylic) plus pigments and mica powders Incralac & wax	good	good
Benjamin Franklin	Poughkeepsie, NY	Abigail Mack 2009	Golden GAC 200 (acrylic) paint plus pigments (phthalo green & blue) and sparing mica powder Golden Hard MSA varnish & wax	good	excellent
Fireman's Memorial (1892), Fiske	Trenton, NJ	Moorland Studios 2002	Randolph phosphoric-acid primer Randolph zinc chromate (yellow) primer Randolph acrylic paint plus mica powders	poor	good
Volunteer Fireman Memorial (1915), Fiske	Ottawa, OH	McKay Lodge 2004	Statuary Bronze Sheffield Gold Leaf Metallic Paint (alkyd), containing copper-alloy powders		fair (too glossy, unmodulated)
Chief Hopocan (1911), Fiske	Barberton, OH	Tom Podnar 2001	Statuary Bronze Sheffield Gold Leaf Metallic Paint (alkyd), containing copper-alloy powders		fair (too glossy, unmodulated)
Benjamin Franklin (1879)	San Francisco, CA	Genevieve Baird 2002?	red lead primer metallic grey paint	satisfactory	inaccurate

Table 2. Outdoor zinc statues recently painted with modern imitation-bronze paints (organized by paint type), evaluated in 2009

divided copper-based powders or consist simply of toned translucent coatings. A tin-flake powder was identified on zinc gaselier decorations made by the company, but has not been found on any statuettes to date. Coatings on the statuettes are visibly pockmarked by corrosion and cross-sections display thick layers of zinc corrosion, probably because of minimal protection afforded by the thin coatings.

When examined with the naked eye, plating could be mistaken for metallic paint. However, in cross-section its appearance is unmistakable as a continuous, solid layer rather than distinct flakes (see Figure 7).

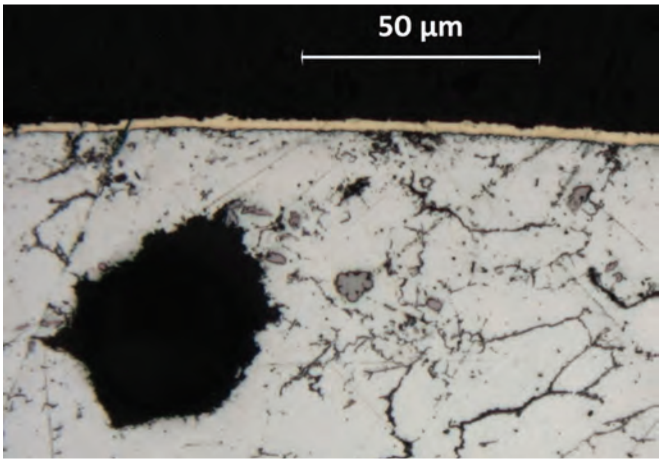

Figure 7. Cross-section of a twentieth-century zinc lamp part, showing copper-based plating.

Modern Replacement Paints

Foregoing surface treatment on outdoor zinc statues that were meant to be painted is an ahistorical and unsatisfactory option in several ways. The zinc was never intended to be seen, and sculptures without coatings are criss-crossed by the darker colored solder that joins the zinc sections. Finally, zinc should be protected from atmospheric corrosion, which occurs at roughly twice the rate of copper corrosion.

Complete understanding of the intended appearance of a particular sculpture may be hampered by the fact that, after more than a century outdoors, its original paint has been covered by later paint, or lost altogether. Thus, as an initial step in the treatment process, cross-sections of paint samples should be made, historic photographs and documents sought, and references consulted regarding typical treatments for particular statue types and manufacturers (Grissom 2009). Products of the Monumental Bronze Co. and its affiliates, for example, were sandblasted to imitate stone and should not be painted.

Producing a satisfactory imitation-bronze paint can be a challenge, and to assist conservators in this endeavor, recently painted statues were surveyed; representative examples are listed in Table 2. From an aesthetic viewpoint, our admittedly subjective evaluations found that the most believable coatings were achieved by applying slightly different colored layers of paint followed by sparing application of imitation-metal colorants. Given the premise that bronze paint was meant to imitate real bronze to which a brown chemical patina had been applied, variations of dark earth tones seemed to be most successful, especially with darker paints in recessed areas and lighter paints on highlights (Figures 8, 9). Also found to be useful in creating depth and variation was the application of cool-colored underlayers, such as phthalo green and blue, mimicking historic base layers. The least satisfactory coatings were commercial bronze paints applied without modulation, resulting in appearances reminiscent of radiator paint on account of high metallic flake content. Commercial dark brown paint without metal colorants would be a more satisfactory option than commercial bronze paints. In general, darker paints seemed to produce better results than lighter ones.

Greening of copper-alloy powder paints on iron objects was observed by Watin in 1755 and can be seen both on outdoor statues and in cross-sections. To avoid such changes, mica-based flakes rather than metal flakes were added to imitation-bronze coatings by most conservators. No changes were observed in the appearance of coatings containing mica-based powders. In fact, inclusion of mica may increase paint durability (Preston 1973). However, one conservator had difficulty getting sufficient color using mica-based flakes, and has reverted to using copper-alloy flakes (Kwart 2009). Application of both metallic and imitation-metallic flakes achieved a better appearance when sparing, but it is noteworthy that we did not find their inclusion essential. Many outdoor statues are viewed from a distance, where the subtleties provided by flakes may be lost.

While it is understood that outdoor paints have limited lifespans, good results for some paints were observed after a decade or more of exposure without maintenance (see Table 2 for specific paint systems). Given that zinc is difficult to coat, good surface preparation is crucial. This generally requires removal of all old paints, with the disadvantage that sampling of original paints will be precluded in the future. Most conservators used methylene chloride-based paint strippers to remove old paints, in one case assisted by walnut-shell-abrasive blasting. Application of a good quality primer is also important in an outdoor setting, but the best choice of primer requires additional research. Mixed results have been noted for phosphoric-acid-based primers (Mottner 1995). A phosphoric-acid-based wash primer may have contributed to excellent adhesion of coatings on the *GAR Fountain* statue in Pottstown after 13 years. On the other hand, the *Fireman's Memorial* in Trenton treated with this type of primer exhibits detachment of coatings at the primer/zinc interface after seven years.

In this limited study set, acrylic urethane paints have achieved excellent results to date. Illustrative is the *Soldier's Memorial Fountain* in Oak Bluffs, Massachusetts, standing in an aggressive saline atmosphere less than 50 meters from the Atlantic Ocean. Although somewhat dulled after 10 years, its coating remains intact, similar to the condition of the acrylic urethane coating observed in Pottstown after 13 years. Acrylic paints have the advantage of reversibility and easier reapplication compared to acrylic urethanes. However, since the longest any of the acrylic paint examples has been exposed is seven years, their durability compared to acrylic urethanes cannot be determined. A German laboratory study showed best adhesion on zinc for acrylic paints, followed by urethanes,

Figure 8. Benjamin Franklin (1858) in its original location on the Franklin Lyceum, Providence, RI; now in the collection of Citizens Bank. The invoice for the statue stated that it was purchased 'bronzed' for $300, and the statue appears dark in this historic photograph. From the Rhode Island Collection at the Providence Public Library.

Figure 9. Benjamin Franklin, Vassar College, Poughkeepsie, NY, after repainting in 2009. Nothing remained of the original coating on this statue, a different cast of the statue shown in Figure 8, but the Providence statue provides guidance regarding a suitable treatment.

and poor results for epoxy resins and oil-based coatings (Mottner 1995). In practice, however, oil-based paints have performed well in Germany (Riederer 1997).

Conclusion

Sampling of historic coatings informs the conservator as to materials used during manufacture and repainting. In concert with an understanding of original surfaces of particular statue types, reasonable inference of intended appearance may be determined. Attractive and historically accurate imitation-bronze paints on zinc statues were found to be produced by brown paints modulated according to relief and containing sparing amounts of imitation-bronze flakes. Owing to the limited study set, the most durable coatings could not be determined with certainty, but acrylic urethane paints show excellent durability after as long as 13 years.

Acknowledgments

We would like to thank all those conservators who generously provided us with information about treatments, especially Andrew Lins.

Materials

Dupont
1007 N. Market Street
Wilmington, DE 19801
http://pc.dupont.com/

Golden Artist Colors
188 Bell Road
New Berlin, NY 13411-9527
www.goldenpaints.com

PPG Industries
19699 Progress Drive
Strongsville, OH 44149
www.ppg.com

Randolph Products
33 Haynes Circle
Chicopee, MA 01020
www.randolphproducts.com

Sepp Leaf Products
381 Park Avenue South
New York, NY 10016-8819
www.seppleaf.com

Sheffield Bronze Paint Corporation
17814 South Waterloo Road
Cleveland, Ohio 44119
www.sheffieldbronze.com/

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Q & A SESSION

Paul Mardikian: I have no experience what-so-ever with this topic. So I have a question which is related to the reversibility of acrylic urethane paint on those statues. What would be your approach?

Carol Grissom: I think it would probably have to be blasted off in some way. That's the downside of it…

Paul Mardikian: I was thinking about using a chemical of some sort – so what kind of chemicals would you consider for zinc.

Carol Grissom: You can use methylene chloride paint stripper. I don't actually know if that would work on acrylic urethanes – I wouldn't think it would. I think you would probably have to blast it.

Paul Mardikian: Does anyone have any experience in this?

Carol Grissom: You don't want to use any acids or strong alkalis.

Arlen Heginbotham: Just a thought that certain unnamed brilliant people in the room know about stripping methods that might work well with using lasers.

Joe Sembrat: From what I understand we used an acrylic urethane on the rocket and Sherwin Williams had described it as a non-cross-linking urethane. So they are still soluble in most solvent-based strippers. In addition to laser stripping, there is soda blasting – there are quite a few things that you can do, but they are still supposed to be soluble. Technically they do not cross-link.

Carol Grissom: Soluble in what?

Joe Sembrat: In most solvents and it doesn't necessarily have to be the methylene chloride.

Carol Grissom: It's a big problem what you do with these. There's no question about it.

Joe Sembrat: It's the same argument – people had argued that Incralac had cross-linked and we've been able to remove Incralac after Phoebe's treatments back as early as the early '80s with solvent-based strippers. Waterjetting work that we had done on the zincs in North Carolina was effective and those were treated with 10 or 12 layers of paint – epoxies, everything else that was on there came off in the treatment.

Carol Grissom: Those I think were sheet metal. I didn't say anything about those. I don't think paint sticks so well to those either.

Joe Sembrat: It was sheet zinc yes. We've done some research on removing coatings and not disturbing underlying patinas, but that's another paper.

John Scott: There are some things that have been developed for the Department of Defense, whether or not the allegedly non-cross-linking urethanes cross-link or not, but there are some things that are based on benzyl alcohol that are very effective and you can buy them in large quantities. I'm trying to remember the name of the company I got them from last summer. We took an epoxy coating off a steel sculpture very readily. It just swelled up overnight and we came back and scraped and blasted it off. So there are products that you can use to take off things you just wouldn't think you'd be able to take off without abrasive blasting.

Michael Drews: SmartStrip is a benzyl alcohol based product and we've used it to remove epoxies.

John Scott: The particular product wasn't SmartStrip but it was probably very similar; I got one from a company in Canada. So things like that have been developed for the Defense Department taking care of their airplanes and so on. The thing to watch out on all of those is to make sure you are not getting any kind of formic acid, because that's often in the same products to help the stripping. I had another couple of questions or comments about this really good paper. We have to have a lot of great respect for Carol and her work on zinc. I know I got very interested in zinc back in the '80s; I was interested at that time in the bronzing lacquers that I found by doing microcopy of residual coatings on some sculptures including the Fiske Neptune that you showed at Sailors Snug Harbor. I did analysis of paint from that – from parts of the surface before it was restored and replaced with bronze. I think it would have been really good if we could have seen not just SEM but also other optical color images of those samples because you need both sets of data. When I analyze for these kinds of things, including the one at Sailors Snug Harbor, the flakes are yellow, they're not copper although I didn't analyze them elementally. I don't see whether you did but when you look at the flakes and they're yellow and you look closely you can see the crystalline structure of a bronze or a zinc alloy – I would like to see something showing that those are copper flakes or that copper flakes were used in bronzing lacquers at that time.

Carol Grissom: I'm not understanding your question. We did do EDS on it and in fact I can't remember right now off hand whether those were copper or brass but they definitely were one of the two.

John Scott: Yes, I would totally agree, although I doubt that they're copper because I've never seen copper flakes. The particular one that you showed – I've analyzed the exact same sculpture, probably in a different location than where you got your sample and the color – I didn't do any EDS on it – but the color of the flakes in the entire sample was yellow, so I agree with you, they're not copper but probably brass.

Carol Grissom: You're saying that the statue itself would have looked more yellow than bronze, than brown, is that what you're saying?

John Scott: I'm commenting right now about what those flakes were because you describe them as being copper and in my experience, especially in that particular sample, they didn't seem like they could have been copper. So it would have been nice to see a color photograph through an optical microscope of your sample. I know I've seen mine, but I presented my work on that many years ago.

Carol Grissom: Actually in the samples I've looked at I've seen a lot of – I'd say maybe half are copper and half are brass, but I'm actually not convinced it makes that much difference in terms of the ultimate appearance.

John Scott: Well, what can I say to a comment like that? In reading your paper which I enjoyed very much and appreciated a lot. I think we have to keep in mind that sometimes we bring a 20th Century point of view to another period's aesthetic and this has a big effect on the impact of our publications and our discussions about what should be done for connoisseurship by people who depend on conservators for the information upon which they base their connoisseurship decisions; for instance what a restored sculpture should look like. In my practice I try to do the stratigraphic analysis in such a way that I can give a good discussion and account of what the actual original appearance seems to have been. I stay away from broader comments like if a sculpture should all be brown or should be this or that. We have to go empirically case by case; that's something I think is important not to forget. Thanks very much for your presentation.

Carol Grissom: You're welcome. I would say one reason why I wrote this paper – I know at least one case where there is absolutely no paint left on the surface and no history of how the statue had been painted so that was one of the imperatives for looking more broadly at how these were painted.

Technical Studies

Chair: Tom Chase
Panelists: Ellen van Bork, Karl Knauer, Carol Grissom

Arlen Heginbotham: That was a great talk about the zinc sculpture, and it brought up a lot of things to me that might be useful to you about some things that I looked at on a late 17th century bronzed wooden sculpture. I had the chance to do a lot of researching of old bronzing recipes and when you said 'He sent his best bronzer', it meant somebody who was highly skilled with this and presumably then the work that he did reflected a lot of skill and nuance, which I also tried to put into my mind when I was researching our wooden sculpture looking at all the recipes, looking at all of the materials that were used. I think it's true that to recreate them [the recipes] is a great challenge because the people that have been doing it have been doing it for years and years and years and really refining techniques of probably glazing and toning and a lot of different things. Interestingly, in the 17th and early 18th century copper flakes show up quite a bit in the recipes but they say even in that period that you can control the color of the copper flakes by heating them before you apply them. You can go from bright copper to all kinds of reddish colors and if course it goes to blue and all of that. But also I think the brass powders were produced in a wide variety of colors, presumably a lot of them were just controlled by alloy but others maybe by heat treatment and other things, so probably they had access to a wide variety of different colors of materials and would have been able to pick and choose and maybe not even use the same thing in different places, which is something that I have seen before too.

Carol Grissom: Yes, absolutely, for some reason I didn't go into that at all but we know from the recipes that they had different colored grounds and they mixed different colors in and also modulated the finishes over a statue. There's one reference that I think is in the paper that says something about how you should only put the bronze flakes on the highlights and then there are recipes that say that you should paint the depth dark and that sort of thing. In fact the bronzing job that I preferred, and I admit that this is a personal opinion, was the one that my colleague did where she really modulated the colors and also went fairly skimpy on the imitation bronze flakes. I think that if you are going to use those you should do it sparingly to get the best result.

John Scott: I think it is really important to look at the particular type of material whose finishes we are talking about and also to look for primary sources and sources of information that are specific to what we are talking about. It's really true that on a lot of types of furniture and hardware and high-end sculpture and so forth, there is room in budgets to send out a craftsperson who is highly skilled. However, the zinc sculpture was a sort of mid to low cost replacement, an alternative to commissioning in bronze and commissioning in stone. In fact, the dollar amounts that we saw at that time were very substantial they were much less than the dollar amounts for getting other more traditional materials. When I was looking into this and I tried to spend as much time as I could, everything I found didn't indicate that there was a lot of special expertise in applying the bronzing lacquers and even some of the examples that we were shown of painted sculpture were simple of very sort of blocked color examples. We don't see really see much evidence if any that these sculptures were treated for instance, the way patination was treated at the time in a bronze foundry. At that time, late 19th century, we had the introduction of a lot of French patinists for the bronzes, we had a lot of subtlety in carving stone. The zinc sculpture even though by the time the Fiske Neptune was produced the casting technology was much higher, they could get a better finish and fit of the metal itself and the joining as Carol mentioned. There isn't much indication to suggest that they had a subtle approach to the way they applied their final finishes even though in the technology at the time they could have. But in the economics of that business and the taste for that business I don't think there was a demand for it and it wasn't supplied and that really is different from other kinds of bronzing that was done.

Carol Grissom: I would point out that that example from Sailors Snug Harbor [NY] was a four- layer system, it wasn't totally simple.

John Scott: These sculptures were maintained through time after their first finish and on the ones I have analyzed including the Fisk sculpture at Sailors Snug Harbor, you can see that the multiple layers are multiple renewals of the bronzed effect until the time when whoever is taking care of the sculpture starts to just put on maintenance paint, that very commonly the sequence. We are not seeing the sort of thin layers that you would see if you had a bronzed lacquer that then was modulated by glazes over that, it is not there.

Carol Grissom: What I am saying is that the original paint system was a four-layer system, I am convinced - you may not be. [Chair shows the slide of the relevant sculpture]. I have to say I went and sampled this statue - it had so little paint on it – I sampled it on two occasions before I was convinced that I had a real sample and I believe that this also had zinc corrosion at the bottom which convinced me that it was the lowest layer.

Tom Chase: When I was working at the Freer we had to repatinate the architectural bronzes at the Freer, especially the courtyard, and we got some bids, and they were very different and then at some point I said ‘let’s go back and see if we can tell what the courtyard looked like when it was new’, because we actually had some very good black and white photographs of the courtyard bronzes when they were new, and they had relived the roundels, they had done a lot of work to relive it and brighten up highlights and everything, so we could specify with the company how we wanted it done. AS john says, you want to go back to the historical documentation and then think about it and try to do the right thing.

Paul Mardikian: I’ve always been amazed to see funeral monuments made out of zinc, I remember going to the Magnolia cemetery with Patty Miller and she would point out to me the monuments made out of zinc and basically you cannot differentiate stone or other materials from it [zinc] unless you look at it very closely. I was wondering if when the intent was to imitate stone, obviously they have not used any painting, they used some kind of patination or would they let the material age naturally? My second question is what kind of fitting they have inside to assemble different pieces so they didn’t have galvanic corrosion. How did it work together?

Carol Grissom: You are talking about the so-called white bronze monuments?

Paul Mardikian: Yes.

Carol Grissom: We know that they sandblasted them at the foundry, there are illustrations that show that and they advertised it. There is also one account that says that they put some kind of solution on it, we don’t know what, I speculate something like oxalic acid to maybe pre-whiten it. They were made extremely carefully and typically these are made in sections that then are bolted together on the inside, typically one bolt on each side, the bolts are brass, and then they’ll often have a zinc head on this plaque that you see in sort of the middle, there are three bolts and those probably have a brass shaft. In this case the statue itself has been fiddled with, with a new base around the perimeter but usually on something like this they would bolt the statue to the base on the inside by climbing through the panel or by sticking one’s head through the panel and then put the panel on last. They would also make these interchangeable panels, not in this case as this was a monument to Fido, but often they would be a monument to a family so they would make it so that when somebody else died you could purchase another panel and stick it on.

Gerhard Eggert: I just want to say that you rightly mentioned German architect Karl Friedrich Schinkel who used a lot of zinc sculpture as decoration of his buildings, and I can only say how they did it in Germany, to imitate sandstone, it should look like sandstone. They simply took a drying oil which you would use for oil painting and then just sprinkled sand on it and this then looked like sandstone and that’s the way they imitated it and it looked quite good. It’s an imitation technique, it’s the beginning of the age of mass production the first plastics came out to imitate precious natural materials and it’s a way to make it more accessible, to make it cheaper. I really loved your talk just showing that it is used everywhere in the world not only in Germany.

If I may jump from zinc to fire-gilding. Peter [Northover] has supervised a thesis by Kilian Anheuser about fire gilding and he found at least 7% mercury left in fire gilding. The mercury is left in solid solution in the gold, it is not in droplets and cannot easily evaporate. So, it is still there even after 1000 years and I wonder if there is any speculation Peter on why an unburnished fire gilding loses the mercury and the others don’t, I would really love to know that.

Peter Northover: I am not sure I can help on that specific question. Go back to the beginning on how color forms on fire-gilding because the mercury gold amalgam used is rather a nasty gray color, and if you look at the gold mercy phase diagram, as you heat it and lose mercury you go through a whole series of gold mercury intermetallics until you get to one that’s yellow which is at 20 something percent. The Anglo Saxons were lazy; as soon as it turned yellow they stopped, they did burnish their gold very thoroughly, and if you look at cross-sections of some early Saxon gilt copper alloy saucer brooches, I don’t know about gold on silver because at that stage the Saxons didn’t do it, they didn’t really use silver, but it is well burnished and the burnish layers come off in one piece partly shifted by corrosion. So if you look at the cross section it looks just like a piece of leaf gilding that has come off, but that still had about 25% [mercury content]. A lot of Chinese gilding has a few percent left. You have to go to quite high temperatures and long times to get rid of it all and then there is a danger of oxidizing the substrate, the same would apply to silver if you’ve got any typical European silver of sterling or a bit less for some Continental silvers. So, with your heating experiments, were you using fine silver, I can’t remember from your talk?

Ellen van Bork: Sterling silver.

Peter Northover: So there was a danger that you were oxidizing the silver underneath which can affect the appearance, so you have particles of copper oxide underneath it, but there’s no relation between the oxidation and what’s happening on the surface in terms of the structure of the gilding coming off.

Ellen van Bork: I haven’t proved that so I am not sure that has an influence on it.

Peter Northover: But the sort of temperature you’re going to, I would have thought you would lose the mercury eventually from both, so you might have to do it the hard way and do microprobe analysis or something like that to really measure your mercury content and that has its own nuisance because the normal standard for the microprobe is mercury, cadmium, tellurite and it’s one of the most miserable things to polish there is.

A quick thought I had, going back to the paints, looking at your cross section again sort of solves the problem for me - on the whole the metal flakes don't get into contact with the zinc, so you don't have a corrosion problem?

Carol Grissom: Oh yes you do, the cross section I showed you where the copper flakes are embedded in the zinc…in fact I was rather pleased to find that as I was pretty sure it was the original layer then if you have all that zinc corrosion.

Peter Northover: Just a cautionary thought, the first job I ever had between school and university was working for western aircraft British hovercraft, and a hovercraft going across the sea is quite a tough environment and hover travel, which was the first real commercial hover craft passenger service between the mainland and the Isle of Wight, they thought they would have this splendid paint scheme with a bronze paint which was actually copper powder with a very reddish bronze paint which they put straight onto aluminium and then took it through salt spray. 6 months later they had a lace hovercraft. But none of your statues seem to be quite that bad, presumably they bronzed them because they wanted them to look bronze, but did they at the time realize that there might be problems and try and take precautions to stop them corroding?

Carol Grissom: We don't really have any information about that from that time period anyway.

CARING FOR OUTDOOR CULTURAL HERITAGE

Session Chair: Shelley Sturman

REGILDING THE GOLDEN GODDESS: THE CHALLENGE OF CONSERVING A MONUMENTAL BRONZE STATUE 20 STORIES OFF THE GROUND IN MADISON, WISCONSIN

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Abstract

Conservation of outdoor monumental statuary placed in difficult locations presents unique challenges to examination and treatment. Thorough examination should precede treatment, but this is not always possible; sometimes both must operate concurrently. This was the case with the conservation and regilding of a monumental bronze statue by Daniel Chester French (1850-1931) named 'Wisconsin.' Installed in 1914, the 5.4 meter figure is perched 20 stories (over 100 meters) above the ground atop the dome of the Wisconsin State Capitol. This paper describes the many challenges faced when conserving this state icon in 1990 and 2005, including studying its condition remotely by telescope, scaffolding the site, conducting chemical analyses, stripping and repairing the surface, and gilding with 18,000 sheets of gold leaf. Also included are costs, conservation history of prior gildings in 1932 and 1957, material research, coating systems, gold leafing techniques and the impact of peregrine falcons that nested near the statue and damaged the gold.

Keywords: challenging outdoor statuary conservation, bronze, metal, gold leaf

Introduction

The American artist, Daniel Chester French (1850-1931) created the statue 'Wisconsin' to surmount the new state capitol in Madison, Wisconsin. The statue commission was the result of French's personal ties with capital architect George B. Post (1837-1913), who had requested a monumental gilded bronze statue to cap the granite dome of his Beaux Arts style building. The dome statue was intended to compliment the ambitious sculptural program that Post envisaged for the new capitol. French was well known for his statuary work that now include some of the most prominent public sculptures in America, including the Lincoln memorial in Washington, D.C. and the life-size figure of John Harvard at Harvard University. He received the Wisconsin commission in 1911 and produced a maquette (scale model) that the Capitol Building Commission approved in December 1912. The statue was cast in bronze in at least 12 sections at the Roman Bronze Foundry in Brooklyn, New York, in 1913. After assembly of the multiple components, the 5.4-meter-tall statue was painted red and gilded by the C. Speahr Co. in New York with 22-carat gold. She was then crated and shipped by rail to Madison. The gilding sustained damage in transit and necessitated repair. The estimated 3-ton statue arrived in March 1914 and was hoisted to the dome on July 20, 1914, and bolted into place, facing southeast toward the federal capitol in Washington, D.C. French was paid $20,325 for the Wisconsin commission (French 1914).

The statue remained untouched until 1932 when the steeplejack firm A.E. Olsen from Janesville, Wisconsin, regilded her for $444. Nothing is known about the actual work or materials used[1]. In July 1957, Wallace Jaka of Madison was paid $1,100 for the next gilding effort using 9,500 sheets of gold. He used ropes tied around the statue's neck as a means of accessing the surface and, before gilding, applied a base coat of aluminum paint[2]. He applied the sheets of gold leaf with one hand while holding on to the rope with the other.

Condition Analysis and Research

In 1990, the Wisconsin Building Commission undertook a project to replace the windows on the dome lantern. As an extension of this effort it was decided to conduct a condition survey of the statue, prompted by its deteriorated appearance. Getting close to the statue was our greatest challenge, so the window replacement project offered some hope with scaffolding.

In spring 1990, at the request of the Building Commission, a detailed visual examination was made using a high-powered telescope with camera, borrowed from the University of Wisconsin's Department of

Astronomy. The telescope was placed on various buildings around Capitol Square to observe the statue’s surface, which afforded close-ups in remarkably fine detail (see Figure 1).

Figure 1. The Wisconsin statue before conservation in 1990. Note the worn appearance of the gold surface.

In addition, access to the statue’s interior was made through the top of the dome lantern and into the statue base. Samples of metal were taken and analyzed. Joints and casting chaplets resembling spikes — which held the many sections together — were found to be mostly intact throughout the statue. In addition, Roman joints indicated a high level of skillful construction with bronze nuts and bolts. White casting plaster residue covered most of the interior surfaces, which made it hard to examine the metal surface. No structural damage was noted except a small 4 cm hole, which was probably from a casting chaplet that had worked its way out over many decades of daily heating and cooling of the statue. The other areas within the statue were examined to the extent possible within the tight confines of the interior space (see Figure 2). Ironically, dozens of business cards, some dating back decades, were found inside the statue attesting to the many curious visitors who had climbed to an area not normally opened to the public. Analysis of the metal samples revealed a mixture of elements including a range of proportions of tin (10-12%) to copper (84-89%), and traces of zinc, aluminum, lead, and manganese[3] (Stork 1990).

Comparative Research

During the analysis phase, a debate arose among government officials about whether the statue should be removed and lowered or worked on in situ. In the 1980s, the State of Texas had removed its capitol dome sculpture by helicopter and had substantial problems putting it back. Because the Wisconsin statue was structurally sound and well bolted to the steel superstructure of the building, it was decided to perform the conservation work in situ. This seemed the most logical approach, though it presented a danger for the workers at such great heights.

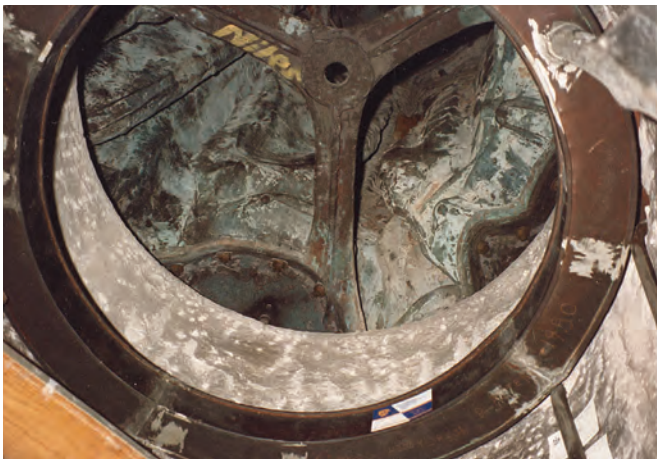

Figure 2. The interior of the statue before cleaning. Note the white plaster residue from the original casting and green corrosion products.

To gather information concerning the techniques used for other projects of this scale, the author conducted a comparative research on exterior gilding projects in North America and Europe. In the United States interviews were conducted with conservators and gilders who had performed work on the Sherman Monument and Prometheus statues in New York, as well as the Potomac Bridge Sculptures in Washington, D.C. Realizing that Augustus Saint Gaudens’ Sherman Monument (1903) was one of the earliest gilded statues in America and had recently been regilded in 1989, a visit was made to the site and small areas of corrosion and the bright glare of the new gold was noted.
The work was performed by LMC Corp. using brass brushes, pressurized water and walnut shells, to remove corrosion, without cleaning to bright metal. Epoxy primer was used followed by a gelatin layer, followed by German 23.5 carat gold (Wiart 1989).

Several years after the 1990 *Wisconsin* gilding, the author had the opportunity to examine French’s *Quadriga* at the Minnesota State Capitol and compare notes about the artist’s intent to tone the gold leaf to reduce glare (Marck-Gould 1990). The 1995 conservation and gilding effort by Linda Merk-Gould on the *Quadriga* took into account research in the D.C. French archives at Chesterwood that noted French’s desire to reduce glare by ‘this effect can be easily produced by giving the gold a coat of wax and turpentine with a little oil color (French 1906).

In Europe, the author met with conservators at the Instituto Centrale del Restauro (ICR) in Rome regarding the second century Roman statue of Marcus Aurelius from the Campidoglio. The intent of their on-going project, which began in 1981 after a terrorist attack nearly damaged the statue in 1979, was to stabilize the statue and remove corrosion products from the interior and exterior surfaces with trisodium EDTA (Ethylene Diamine Tetra Acetate), as well as mechanical methods including small power tools. The horse and rider are separate components that can be taken apart allowing access to the statue’s interior. An elaborate steel structure was constructed in the ICR labs to allow turning of the statue for accessibility. From historical records dating back to the Middle Ages, it is known that parts of the statue’s bronze and gilding were repaired between 1466 and 1468 by Cristoforo di Germania, 1474-75 by Leonardo Corbolini, and by Michelangelo Buonarati in 1538, and again between 1834-1836 by Carlo Fea. In

1912, the statue was again repaired with various bronze dowels, screws and bronze plaques to cover holes, but no regilding was done. Remnants of the previous gilding campaigns, some dating back centuries, were left in place and cleaned. After cleaning, the entire statue received three thin coats of Acryloid B-72 followed by inpainting with watercolors, followed by a thin application of Acryloid B-72 to cover the inpainting. The inpainting style chosen was the *Rigatino Method* of fine vertical lines so that the recent intervention could be detected upon close examination. This was the first time that Rigatino had been used on a sculpture. Cleaning revealed many fine details of the modeling and of earlier repairs, as well as gilding (Sommella 1990). Art Historians and scientists played a critical role in this work and gave insight to the history, construction and preservation of this unique monument from antiquity: the only monumental gilded bronze statue to survive from ancient Rome. Treatment decisions were based upon the opinions of conservators, art historians and scientists. With the treatment completed by 1990, the decision was made to bring the statue indoors into a climate controlled environment at the Capitoline Museums, where recently installed HVAC could control relative humidity and temperature. A life-size bronze copy, without gilding, is now exhibited in the Campidoglio Piazza (Sommella 1990).

During the 1992 regilding of D.C. French's 25-foot high *Republic (*1918*)* in Chicago's Jackson Park, problems were encountered with active corrosion that necessitated multiple cleaning with walnut shell, wallnut shells with limestone blasting, glass bead peening, and other mechanical methods, to achieve bright clean metal. This was followed by the application of Incralac as a primer and 23.5 carat gold without toning. Pitting through the gold was noted only a few years after the gilding effort and has continued to this day (Adair 1992).

Gilders of Les Invalides dome project in Paris were helpful in explaining the challenges of gilding lead sheets on the dome with high karat gold and Mixtion 12 hour sizing by LeFranc and Bourgeois. The consensus from these project discussions was, 'Don't move the statue unless you absolutely must' and 'use the highest grade of gold possible and thoroughly prepare the surface before gilding and don't coat the gold with any lacquers' (Thornton 1991).

Gradually, a strategy evolved for conservation of the bronze Wisconsin statue, but with the realization that the original gold leaf surface could not be uncovered because it was buried under many layers of paint and subsequent gilding efforts. It could not be determined if the original gilding had been toned, as French had requested in other gilded bronze works by him. It was decided that a complete stripping and regilding would be necessary to make the statue visually presentable to the public and able to withstand decades of weathering atop the dome. One of our chief concerns was the issue of durability. The example of the Sherman Monument in New York and its poor aging almost immediately after gilding called for caution concerning the use of nontraditional priming systems, such as epoxy or Incralac. In order to ensure longevity, many complex processes come into play, such as surface cleaning and preparation, primers, size, gold-leaf quality, protective coatings and weather conditions.

Bid Evaluation Process

Following the technical examination phase, a detailed report with recommendations and a request for proposals (RFP) was prepared, with the proviso that additional information would probably surface when scaffolding reached the statue and full access became available. Several pre-qualified firms with expertise in gilding and statuary work were asked to submit proposals. Five firms submitted three proposals, as joint ventures, realizing that no single firm had gilding and statuary conservation expertise at the level required.

The bids were evaluated by two independent state-appointed teams that reviewed technical approach and price separately. After calculating the various technical factors, such as proposed cleaning, general conservation philosophy, backgrounds and other factors, recommendations were put forward and another group of state employees made the actual decision, followed by the governor. In addition, it was decided to use high quality gold as close to 24 carat as possible because of it durability when exposed to the elements. Seep Leaf products in New York supplied the 20,000 leaves of German gold all in the same color. This was important to ensure the statue would have a uniform appearance without color variation. The cost of the gold alone was $16,000. Two of the conservation bids were within $500 of each other, around $40,000. The third bid was for a lesser amount (Rajer 1990).

In a separate effort, beginning in September 1990, Safeway Scaffolding of Milwaukee, Wisconsin, erected the 9-meter-high tower of scaffolding to surround the statue and give full access to the site. The scaffolding, which rested on the dome, had two concentric series of tarps to control wind and reduce surface disturbance (see Figure 3). Rental of the scaffolding over a five-month period cost about $60,000. Other additional miscellaneous project costs totaled about $15,000.

Figure 3.The nine-meter high scaffold tower surmounting the dome of the Capitol in September, 1990.

Conservation and Gilding Effort

It was only when the statue was finally reached in September that examination of the surface could commence. Pumping the water to the top of the dome allowed cleaning to begin on September 24, 1990, with the use of high-pressure water jets to remove old surface layers. Water pressure ranged between 3,000-5,000 PSI, in tandem with mechanical scrubbing. This allowed conservators to reach the bronze surface. Without authorization, the contractors used paint stripper, Methylene Chloride, (DCM) CH_2Cl_2 (Dichloromethane) to remove old paint and gilding. There was concern that the DCM might weep into the porous surface of the bronze, outgas and weaken the new substrate (Rajer 1990).

To preserve the chromatic history of the statue, a small 5-centimeter-square control area was left untreated, showing all stratigraphic layers. Cross-sections were taken in various areas and examined with SEM and visual microscopy. They revealed at least six, perhaps seven, layers, including the original red oxide primer, gold leaf, white primer, gold leaf, Aluminum paint, and gold leaf. This accounts for the first three gilding efforts in 1914, 1932, and 1957. SEM also revealed that the 1932 and 1957 gold products were below 20 carat in quality, though it could not be determined if the first gilding effort was toned[4].

The casting chaplet hole was repaired with a brass screw, which was threaded into place. Numerous small flaws and pinholes in the surface were noted. These were filled with a high-grade industrial epoxy and sanded. A weep hole was drilled at the base of the left arm elbow allowing more than a pint of dirty water to flow out, attesting to the condensation environment within the statue.

While conservation of the exterior was underway, an effort was made to clean the interior of the statue, which consisted to removing plaster residue left over from the casting process. This was done using hand tools and a small vacuum.

By October 6, 1990, the surface cleaning was complete and the entire bronze statue was degreased. A coating of Benzotriazole, (heterocyclic compound), $C_6H_4N_3H$. was applied to the clean metal as a corrosion inhibitor and rinsed with water. After much discussion, an oil-based industrial red primer, similar to the original, followed by yellow primer (zinc chromate) was applied to the entire statue surface to act as a base for the gold leaf. Red primer had been used on the original gilding in 1914, but yellow was chosen to better blend with the new gold. The primer was applied by hand because of the frequent high winds at the site. The scaffolding site was double-tarped — that is, there was an outer protective tarp and inner tarp to further reduce winds. On October 8 the gilding process started, working from top to bottom using 12-hour, Mixtion-gold sizing (LeFranc and Bourgeois) from Sepp Leaf Products. In all, 18,000 sheets of gold were used in the effort. No surface coating was applied over the gold, as it is a nonreactive, stable element. The gilding process took approximately three weeks (see Figure 4). Adverse weather and high winds slowed the process. By November 30, the restoration process was complete and the scaffolding was removed (see Figure 5).

Figure 4. Applying gold leaf to the head of Wisconsin in October, 1990. 18,000 sheets of gold were used in the process.

Figure 5. Gold leafing completed and disassembly of the scaffolding in November, 1990.

Other factors including weather conditions

Madison, Wisconsin, has harsh, long, cold, snowy winters and hot humid summers. Surface temperatures in the winter can be as low as -20F (-28°C) and in the summer above 120F (48°C). Uneven heating and cooling of metal can cause uneven thermal expansion and affect the laminates of metal, primer and gilding and hasten deterioration. The RH and weather conditions were monitored from the nearby National Weather Service at the Madison airport. There were only a few days of rain, but many days of high winds were experienced, which on two occasions tore the protective wind tarps from the scaffolding. The average September high temperature was 65F (18.3°C) and the average low 45F (7.2°C) and average 28%RH. By November, the average high temperature was 54F (12.2°C) and low 34F (1.1°C) with average 23%RH. As Maria Tabasso and M. Marabelli have demonstrated in their thermal research on the Marcus Aurelius statue with acoustic-emission measurements, the sun's rays produce uneven warming of the statue and wide variations in thermal expansion of the metal with resulting loss of adhesion to the substrate. In addition, environmental factors such as wind, severe cold, and rainfall contribute to surface weathering (Marabelli and Laurenzi-Tabasso 1992).

Because of the high profile location of the site and statue, there were many hundreds of inquiries from the public about the project. In order to satisfy public curiosity, two public display boards, one in the State Capitol rotunda and the other in a nearby government office building, were used for project photographs and updates. The public felt that they had a right to know what was going on under the scaffolding tarp. Periodic press reports helped to satisfy this need.

Three years after the project, the Wisconsin Department of Natural Resources placed a pair of peregrine falcons and a nesting box near the statue as part of an endangered species recovery effort. The falcons loved perching on the statue, but unfortunately scratched the gold in many areas, causing considerable damage to the arm, head and globe. Their acidic droppings also caused streaking of the surface. To correct this problem, the state undertook another gilding effort in 2005, regilding the extended arm, head, globe and shoulders. The nest box by that time had also been removed. The site was scaffold as before and 2,000 gold sheets, held in reserve from the last effort, were used so that there was a near perfect color match (see Figure 6).

Conclusion

In less than 100 years, the Wisconsin statue has been gilded five times, despite its lofty location 20 stories off the ground on the capitol dome. All of the gilding projects, including the 1990 and 2005 efforts, were completed in situ without removing the statue from the dome. In the 1990 effort, high-pressure water at maximum 5,000 PSI (345 bar) cleaned the surface, which was later prepped with a red, and then yellow industrial primer, and over 18,000 sheets of 23.5 carat gold were applied. That effort took four months. Unfortunately nesting Peregrine falcons on the dome scratched the gold, which necessitated regilding some areas in 2005. Our main challenges in this project were location atop the dome, limited access to the statue before the conservation project, no technical history of previous efforts and birds that damaged the 1990 gilding.

In summary, the challenges of the site were overcome, but the continuing problem remains of how to monitor the 1990 and 2005 treatments. Because of recent economic conditions, only occasional photo documentation continues, without the telescope. There is no viable way to closely monitor the statue's condition and gold leaf surface.

Figure 6.The Wisconsin statue in 2005 after the repair of the damaged surface from the birds scratching the gold.

Endnotes:

[1] August 6, 1932, Wisconsin State Journal article about the regilding of "Wisconsin" on the state capitol dome, page 1. Madison, Wisconsin

[2] July 25, 1957, Wisconsin State Journal article about Wallace Jaka and the regilding of the "Wisconsin" statue, page 2. Madison, Wisconsin.

[3] Technical analysis of the metals was performed by the Stork Co. and Forest Products laboratory, Madison, Wisconsin. SEM samples were run that showed a variation in tin to copper ratio that are typical of bronze and the foundary technology of the early 20th century.

[4] Correspondence from W. Adair, Gold Leaf Studios, regarding the conservation and gilding efforts on the Republic Statue in Chicago. Washington, D.C. 1992.

[5] Further SEM analysis was done at Forest Products Laboratory to ascertain content of gold, paint and other metals in the chromatic history of the statue's surface.

Materials

Sepp Leaf Products
301 Park ave south
New York, N.Y. 10016

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Author

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Q & A SESSION

Molly Carlson: I don't know anything about gilding but how does a gilded surface hold up under hail and bad weather? Is there a lifetime that you have to go back and then re-gild this?

Anton Rajer: Yes, and it was estimated, Molly, that the gilding would have a durability of about 50 years. In talking with the men who had done the gilding at *Les Invalides* in Paris, there are many generations of gilding on that dome and they were very forthcoming in information to explain about durability and their insistence on getting the highest quality gold possible. Because the gold does not have any type of surface protection over it, as you know the gold is itself stable.

Tim Foecke: First I wanted to congratulate Wisconsin for being so proactive and fixing the thing. I was involved in repair of the capitol dome – the U.S. Capitol Dome, and it took them 140 years to repair the damage that a gutter clogged with pigeon [feces] had caused. Water with pigeon [feces] went into the inside. I wanted to just relate what we did with that. We were looking at the cached steel beams between the outer copula and the inner dome. We were going up on an inspection tour – we had a similar thing, in that the elevator stops at the 6th floor and only Senators are allowed to use it. We crawled up on the spiral staircase inside of the dome and we were inspecting the various beams, and I reached out just to touch one of them and my finger went clean through a 1-inch thick beam. Up until 3 years ago, the Capitol Dome was being held together by 23 coats of lead-based paint and force of habit. We helped them work out a recipe for welding so they could connect the old material to the new material. But pigeon [feces] problems permeate dome systems apparently, although Wisconsin seems to be a little more proactive.

Anton Rajer: Thank you. I shall refer that to my superiors.

Tom Chase: Tony, you didn't put any toning lacquer or anything over the gilding? Some of the projects you referred to, the Quadriga [Minnesota State Capital], for instance use some toning on that, but you didn't put anything over the gold, you didn't use any in this case?

Anton Rajer: We didn't use any toning. And I talked with Linda about that matter and I read Linda's article about it and, you know the Quadriga is so large and so intense and I totally agreed with her. I know she did the research and in the Chesterwood archives, which you're probably familiar with, there were specific instructions left by French about the Quadriga, but for our statue we found nothing. So I didn't put any toning on it. But that was an excellent question.

Emma Schmuecker: I think you've been really good with not talking about the stresses that probably your outdoor activity of gilding created for you. We just finished a large project outside – probably about as high a project as you did, in England. But in the middle of the countryside so I had similar problems with access to water and scaffolding and our scaffolds wouldn't allow us any wind protection. So that was a major problem with transfer leaf. But I was just wondering, after we finished our project our client was quite concerned suddenly about the durability of the gold as well. I was just wondering if you'd considered double thickness gold or two layers of gilding – what sort of discussions did you have with your client?

Anton Rajer: We did have discussions about double gilding. But we weren't sure what the cost would be. And now with that outstretched arm, it essentially is double-gilded. So we'll see how that holds up. But I would concur that that would be an excellent option. Because you know it is only once in a generation or once in a lifetime you'll go up there to actually do it, so if the layer of gold is a little thicker all the better.

Emma Schmuecker: Yes it is quite interesting how late on you completed your project – in November as well, because we've just finished ours and I'm quite concerned about the hardening of the oil size underneath the gold over the several weeks, and the potential frost damage maybe.

Anton Rajer: Exactly. During the break-time I'd like to discuss the matter with you.

Emma Schmuecker: Yes, lovely. Thank you.

Mark Erdmann: You mentioned a similar project in Texas, was it where they actually used a helicopter? Do you know what the problems were that they ran into and could you elaborate on the process by which you decided not to use a helicopter?

Anton Rajer: The person who would be much more expert in this matter would be Brian Howard. Brian, stand up a moment – he's right there. Brian is much more familiar with that project in Texas than I. But I do know that they had difficulty with the helicopter and the replica statue, trying to get it back on to the dome of the Capitol. There was an acute possibility of crashing!

Joe Sembrat: When I worked with Linda Merk-Gould on the Pennsylvania State Capitol they removed that with the Sikorsky Sky Crane and I mean it's incredible the precision of that thing. In that case there wasn't a problem with reinstalling it, but it required extensive work and things that really couldn't be done up on the dome at that time. The same situation: no elevator to the top. I guess it was a prerequisite.

Alisa Vignalo: That's a great project. I was wondering if you could elaborate on your rationale with the primers, to first use a red primer and then a zinc chromate primer on top of that?

Anton Rajer: I did it in that manner because I felt we had a moral obligation to Daniel Chester French to put the red on as he had originally specified. We then utilized the yellow as a base, so it would be more reflective and give a slight more intensity to the gold.

Brian Howard: A comment on the Texas sculpture: There was an issue with helicopter availability in Texas. They wanted to use the Texas National Guard and they didn't have a helicopter of adequate size. So they tried a helicopter that couldn't lift the weight. So they had to go I think to Mississippi to get a helicopter, so there was some political wrangling. That was one of the issues. They had to drop it down over a mass that had been built into the top of the dome. That gilding – there were 2 issues: one there was a texture put in the paint on the replica in Texas but that texture allowed algae and lichen to grow. So that was what they saw as the problem and also after 25 years the gilding was failing; it was 23.5 carat gold, oil-size.

Anton Rajer: And Brian, you had pointed out that it was the star that was gilded and not the entire statue.

Brian Howard: Yes, just the star and as of 3 weeks ago they decided they couldn't afford gold after putting up 1 million dollars worth of scaffolding!

SURFACE PREPARATION AND COATING APPLICATION PRACTICES FOR THE CONSERVATION OF LARGE-SCALE METAL ARTIFACTS

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Abstract

The protective coating of large-scale metal artifacts (LSMA) presents challenges, not least of which is scaling treatment to the sheer size of these objects. The conservator must develop and implement a solution that is thorough enough to achieve the goals of the project, yet practical enough to be applied by non-conservation professionals. Development of this regimen requires a delicate balance between the micro issues of surface preparation and coatings technology — which focus on surface profile, preparation, durability and reversibility — and macro issues relating to sustainability, safety and health, environmental controls, and economic necessities. The coatings industry produces a vast amount of research and technical articles annually on the subject of premature coatings failure. The National Association of Corrosion Engineers (NACE) and the Society for Protective Coatings (SSPC) have developed stringent preparation and application guidelines to combat this problem. Innovations in test equipment and techniques used in coatings inspection and monitoring provide more accurate information about whether a coating is correctly applied and performing as expected. Conservators have successfully applied these guidelines to their otherwise unconventional approach to treatments. This paper illustrates how to identify coating failures and test for their root causes. It also discusses how to choose an appropriate coating system, proper surface preparation prior to coating, and using industry tools and techniques to correctly monitor coating application and performance.

Keywords: artifact, large-scale, protective coating, surface preparation, monitoring, quality control

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Introduction

This paper will discuss the coating systems (primers and paints) of large scale metal artifacts (LSMA) that are life-size or larger, and can include sculptures, monuments, and industrial objects that typically are on static display and frequently situated outdoors year-round (see Figure 1).

As well as being large-scaled, LSMA are likely to be complex assemblies of metallic and non-metallic elements, including unusual or rare materials or composites. They often have difficult-to-reach or wholly inaccessible sections, limiting options for inspection and treatment, and are usually immovable.

This paper focuses on treating technology artifacts, however, the information is appropriate for works of art as well.

The conservation treatment of large technology artifacts occupies an expanding area of heritage preservation. Unless identified as an artifact worthy of conservation, care of these objects often falls to untrained personnel, who frequently employ techniques that are not unlike those used when the object was in service.

Figure 1: The Saturn V rocket is an extraordinary example of a large scale metal artifact.

However, as the goals and ethics of care shift away from daily operation towards preservation, there is a need to apply different technologies commensurate with different standards.

A conservator should perform the condition assessment and undertake testing to define the materials and deterioration mechanisms at the start of the project to avoid scope of work omissions or inappropriate treatment goals. Ideally, the conservator should continue to be involved though the entire treatment.

Because of both the technical and logistical size and complexity of these projects, conservators must be flexible and delegate more work to other specialists. Partnering with engineers, coatings professionals and other experts during the assessment phase is extremely beneficial.

Skilled painters are essential; however, they will usually need education to understand the conservator's requirements or standards. In addition to painters, the skills of other specialty contractors, including water jetting firms, auto-body restorers, and aircraft refinishers, can be incorporated in the treatment (Sembrat et al. 2004).

The conservator may act as general contractor, project manager, and/or quality control monitor in directing a team of specialists. Throughout this process, the conservator should maintain and promote the holistic concept of the artifact, understanding its materials, significance, and history, and should be the point of communication with its owners.

Furthermore, it is the conservator's responsibility to monitor and manage these specialty sub-contractors to ensure the intended treatment occurs.

Coating Failures: Identifying Problems Visually

When initially designing a treatment program for a LSMA, it is crucial that the conservator's treatment plan is rooted in an understanding of potential coating problems to identify and avoid issues before they occur.

Type of defect	Visual appearance	Failure type	Specific cause(s)	Consequence
Sagging	Appearance of "curtains" on the paint surfaces; pools on horizontal surfaces or in corners (while wet); cracking (when dry)	Application-related failure	Paint applied in excess of the recommend film thicknesses; too much thinner added to paint; spray gun held too close to the surface	Excess material may crack exposing unprotected metal; unsatisfactory aesthetic appearance
Pinholes and pores	When visible, appear as tiny pin-point voids.	Application-related failure	Using the wrong spraying technique: excess air pressure, excess film thickness, strong winds, too great an application distance, incorrect nozzle size	Pinpoint corrosion of underlying metal, followed by undercutting of the coating around the pinhole
Orange peel	Finely pebbled or dimpled surface	Application-related failure	Improper atomization due to low air pressure; spraying too close to the surface; rapid solvent evaporation	Primarily a cosmetic defect
Delamination/peeling	Peeling paint, separation of paint layers	Application or design related failure, or contamination	Unsatisfactory surface preparation; incompatible primer/topcoat; substrate or inter-coat contamination; excessive cure time between coats	Complete failure of the coating which could leave the metal vulnerable to corrosion.
Lifting	Wrinkled surface	Design-related failure	Strong solvent in the top coat dissolves the underlying paint coating	Failure of both coatings, exposing unprotected metal substrate
Cracking/chipping	Fissures in the paint, flakes of paint coming loose	Design-related failure, weathering	Impact; inability to withstand expansion/movement	Micro-fractures may develop into larger losses, exposing unprotected metal substrate; poor aesthetic appearance
Blistering	Hemispherical blisters, may be dry or filled with liquid; size varies	Contamination	Pressure exerted by soluble salts trapped between paint layers; contamination of paint surface by dust, oil, wax, etc affecting subsequent paint layer; inadequate solvent release/entrapment	Voids in the coating may result, inviting further failure of the coating and exposing unprotected metal substrate
Chalking/Fading	Loss of color vibrancy/change in color, staining of adjacent materials, chalky appearance	Design-related and weathering	Sunlight (UV), heat, chemical degrade binder and/or pigment	Significant reduction in the protective quality of a coating system; poor aesthetic appearance

Table 1. Visual Identification of Coating Failures- Proper identification of typical coating defects based on their visual characteristics may help the conservator assess possible causes as well as ramifications for the artifact.

Although many of these problems are attributed to improper surface preparation, coatings fail prematurely for other reasons as well. Research published on the failure analysis of coatings should be consulted (Bayer and Zamanzadeh 2004, Mallick 2008) (see Table 1).

The coatings industry studies the mechanisms that lead to premature failure and promotes standards to mitigate them. Advocacy groups such as the National Association of Corrosion Engineers (NACE), the Society for Protective Coatings (SSPC), Water Jetting Technology Association (WJTA), and the Advisory Council[1], among others, research and develop standards to address these problems.

Larger organizations, such as the American Society for Testing Materials (ASTM) and the International Standards Organization (ISO) in the United States, and the Comite Europeen de Normalisation (CEN) and Deutsches Institut fuer Normung (DIN) in Europe, continue to develop many useful tests for applying and monitoring protective coatings, many of which can be performed in the field to help determine the cause of failure and evaluate coating performance (see Table 2).

Standard Test Method	Title
ASTM D6132	Test Method for Nondestructive Measurement of Dry Film Thickness of Applied Organic Coatings Using an Ultrasonic Gage
ASTM D523	Test Method for Specular Gloss
ASTM D5162	Practice for Discontinuity (Holiday) Testing of Nonconductive Protective Coating on Metallic Substrates
ASTM D4541	Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers
ASTM D1005	Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers
ASTM D1212	Test Methods for Measurement of Wet Film Thickness of Organic Coatings
AST D3359	Test Methods for Measuring Adhesion by Tape Test
ISO 8502-6	Preparation of steel substrates before application of paints and related products -- Tests for the assessment of surface cleanliness -- Part 6: Extraction of soluble contaminants for analysis -- The Bresle method
ISO 8502-9	Preparation of steel substrates before application of paints and related products -- Tests for the assessment of surface cleanliness; Part 9: Field method for the conductometric determination of water-soluble salts
NACE SP0508	Methods of Validating Equivalence to ISO 8502-9 on Measurement of the Levels of Soluble Salts
SSPC-TU 4	Field Methods for Retrieval and Analysis of Soluble Salts on Substrates

Table 2. Coating Analysis Test Methods-The following standards are commonly referenced to prescribe coating analysis test methods.

Coating Selection

'Coating' refers to a multi-layer paint system, typically a primer layer, intermediate layer, and finish layer or top coat. It is crucial to consider the entire system, not solely the finished appearance.

Primer layers may be preceded by a metal pretreatment, or conversion coating, a chemical solution that improves corrosion resistance and bonding of the primer to the metal.

Primers provide the last line of defense for the metal substrate. Intermediate or tie-coats build essential protection through film thickness and may or may not be the same material as the top coat. Fills and repairs may be integrated into this layer.

The top coat is essentially the aesthetic coating that imparts the desired color, texture, and gloss qualities. In high performance coatings, the top coat may have added properties, such as special chemical resistance, UV protection, non-stick surfaces, and anti-fouling properties.

Modern coatings are continually being challenged to offer greater corrosion protection, while also balancing increasingly stringent regulations regarding public health, safety and the environment.

The conservator need not be an expert in modern coating technology but should reach out to experienced professionals to choose the best available system. As the advocate for the artifact, the conservator is best qualified to assess any risks that may be associated with a particular coating, its surface preparation requirements, performance expectations, and reversibility.

Other considerations, such as existing conventional coatings, waste containment, health and safety, and cost, must also be factored in.

The primary coating types encountered when selecting a coating system from a major paint manufacturer for a LSMA project are presented in Table 3. The general properties of each coating are listed for consideration (see Table 3).

Surface Preparation

Before selecting a coating, it is necessary to understand what surface preparation is required and determine whether it is appropriate for the artifact.

Proper surface preparation is critical, as the service life of the coating is directly related to the quality of the surface preparation. The Advisory Council defines surface preparation as, 'Creating the situation so that coatings will perform as expected'.

Coating Property	Epoxy	Epoxy-Urethane Hybrid	Urethane Polyesters	TGIC Polyesters (Powder Coating)	Acrylics	Alkyd
Hardness	Excellent	Excellent	Very good	Excellent	Very good	Good
Flexibility	Excellent	Excellent	Very good	Excellent	Fair	Fair
Exterior Durability	Poor	Poor	Very good	Excellent	Very good	Very Good
Corrosion Protection	Excellent	Excellent	Very good	Excellent	Very good	Very Good
Chemical Resistance	Excellent	Excellent	Very good	Very good	Very good	Fair
Colors Available	Many	Many	Many	Many	Many	Many
Clears Available	Yes	No	Yes	Yes	Yes	Yes
UV Resistance	Good	Good	Good	Very good	Very good	Poor

Table 3. Common Criteria in Coating Selection- This table presents typical performance criteria which should be considered in coating selection. This table was developed based on a model created by the Environmental Protection Agency, www.epa.gov

This definition includes not only the technical aspects of surface profile, visible cleanliness, and non-visible cleanliness, but also the integration of safety and health, waste minimization and pollution prevention, economic, and performance concerns (Advisory Council 2010).

Conservation concerns of reversibility and retention of historic fabric are generally not part of the coating industry vocabulary. The conservator must balance surface preparation standards that often require stripping to a bare metal substrate against the need to preserve historic material. While preserving historic paint is valuable, its retention can compromise the longevity of a new coating system applied over it.

One of the greatest causes of deterioration of metal artifacts is soluble salt contamination. Chloride, sulfate, and nitrate salts can result from pollution, fertilizers, wind borne aerosols, and animal waste.

If the salts are not removed, and the surface is painted, these invisible hygroscopic salts can form corrosion cells and cause problems ranging from extensive coating failure to complete destruction of the metal substrate.

It is crucial they be removed, but care must be taken as manufacturer's original surface treatments may still be protecting the underlying metal. For example, despite being extremely thin, original anodizing and/or Alclad sheathing layers may still be intact on aluminum artifacts, particularly aircraft[2].

These treatments are vulnerable to loss if aggressive surface preparation techniques, such as abrasive blasting, are used. In addition to damaging this original protective layer, abrasive blasting may introduce or spread salts and other contaminants.

When the Saturn V rocket at the Johnson Space Center (JSC) was repainted in the 1970s, the authors found that sand-blasting undertaken to prepare the metal surface had removed the original anodizing and subjected the metal to rapid deterioration (see Figures 2 and 3).

Similar failures were seen on the cast iron Victoria Bandstand in Hamilton, Bermuda, in which sandblasting not only removed the intact original mil scale and galvanizing, but introduced chloride contamination when it was blasted with beach sand.

Since then, the authors and other conservators have extensively researched and demonstrated that water-jetting is a viable method for the removal of both existing coatings and soluble salts without the need for additional chemicals, or without causing damage to the underlying metal. This information has helped to solidify this technique as a crucial step in the surface preparation of LSMA (see Figures 4 and 5).

SSPC and NACE produce technical standards for surface preparation and cleaning that have been adopted by coatings manufacturers to ensure specific tolerances are met for optimal coating performance.

Conservators should reference these standards to prescribe the appropriate means of coating removal. These procedures must first be tested and refined on coupons of metal similar to the artifact to determine safe practices before wholesale application.

If justified by the nature of the artifact, it may be possible to work with the manufacturer to develop an alternate approach to their standard specifications for surface preparation.

This is particularly relevant when the conservator wishes to retain original/historic paint layers or avoid overly aggressive preparation, yet still have the manufacturer warranty their product(s). Testing of the adhesion of a new coating over an existing one can help establish the feasibility of this choice.

The authors faced this particular challenge in the treatment of the Saturn V rocket at the U.S. Space and Rocket Center in Huntsville, Ala. Through adhesion testing, conservators were able to demonstrate that the existing coating was failing at the interface of the primer and the top coat.

Figure 2. An historic photo of well-intentioned but aggressive sand-blasting, which actually removed original protective treatments from the Saturn V rocket at the Johnson Space Center.

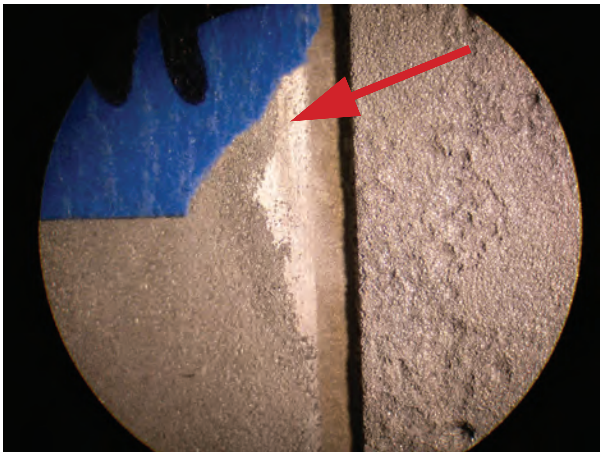

Figure 3. Fragments of the original protective surface treatment on the Saturn V survived only in protected areas which were not exposed to sand-blasting.

Figure 4. (top) and Figure 5. (bottom) A test on a SI tunnel cover from the Saturn V demonstrates the ability of ultra high pressure waterjetting to remove coatings without damaging delicate underlying surfaces, such as this original epoxy makers stamp.

Surface Preparation Standards	Specified Removal	Methods	Degree of Removal
SP-1 Solvent Cleaning	oil, grease, dirt, soil, salts, drawing and cutting compounds, and other contaminants	Solvents, emulsions, cleaning compounds, steam or other similar materials	100%
SP-2 Hand Tool Cleaning	rust scale, mill scale, loose rust and loose paint	Wire brushing, hand sanding, hand scraping, hand chipping or other hand impact tools or by a combination of these methods	Up to 100%; remaining mill scale, rust, and paint should be tight and the surface should be sufficiently abraded to provide good adhesion and bonding of paint
SP-3 Power Tool Cleaning	rust scale, mill scale, loose rust and loose paint	Power wire brushes, power impact tools, power grinders, power sanders or by a combination of these methods	Degree specified (up to 100%); remaining mill scale, rust, and paint should be tight and the surface should be sufficiently abraded to provide good adhesion and bonding of paint
SP-5 White Metal Blast Cleaning (NACE 1)	rust scale, mill scale, loose rust and loose paint	Abrasives propelled through nozzles or by centrifugal wheels	Uniform metallic color, slightly roughened to form a suitable anchor pattern for coatings
SP-6 Commercial Blast Cleaning (NACE 3)	rust scale, mill scale, loose rust and loose paint	Abrasives propelled through nozzles or by centrifugal wheels	Less than 100%; remaining mill scale, rust, and paint should be tight and the surface should be sufficiently abraded to provide good adhesion and bonding of paint
SP-7 Brush-Off Blast Cleaning	rust scale, mill scale, loose rust and loose paint	Abrasives propelled through nozzles or by centrifugal wheels	Less than 100%; remaining mill scale, rust, and paint should be tight and the surface should be sufficiently abraded to provide good adhesion and bonding of paint
SP-10 Near-White Blast Cleaning (NACE 2)	rust scale, mill scale, loose rust and loose paint	Abrasives propelled through nozzles or by centrifugal wheels	At least 95% of each square inch of surface area shall be free of all visible residues. The remainder shall be limited to very light shadows; very slight streaks; or slight discolorations caused by rust stain, mill scale oxides, or light, tight residues of paint or coating that may remain.
SSPC-SP 11, Power Tool Cleaning to Bare Metal	rust scale, mill scale, loose rust and loose paint	Power wire brushes, power impact tools, power grinders, power sanders or by a combination of these methods	100% (where abrasives or other methods are not suitable)
SP-12 Surface Preparation and Cleaning of Metals by Waterjetting Prior to Recoating (NACE 5)	oil, grease, dirt, soil, salts, drawing and cutting compounds, and other contaminants; rust scale, mill scale, loose rust and loose paint	Water only through specialized rotating nozzles at specified pressures and rates	Surface Cleaning: 100%; Corrosion: up to 100%; Coatings: Less than 100%
SSPC-TU 6, Chemical Stripping of Organic Coatings from Steel Structures			Coating Removal: 100%; Surface Cleaning: 100%

Table 4. Common SSPC Standards-The following SSPC standards are commonly referenced for proper surface preparation prior to coating LSMA. Note: most standards are written for steel substrates.

Coatings experts concurred and determined that the failure was due to the fact that the primer had been allowed to fully cure before application of the topcoat, resulting in no chemical bond between the two layers.

Adhesion testing also confirmed how well adhered the primer was to the metal substrate (see Figure 6). A creative solution was collaboratively developed, whereby the failing topcoat was removed through waterjetting, allowing much of the sound existing primer to remain, but creating a surface profile that enabled proper bonding of the new primer.

Correct adherence of the new primer was also confirmed through adhesion pull tests (see Table 4).

Coating Application Methods

Spray application is the most common method of coating

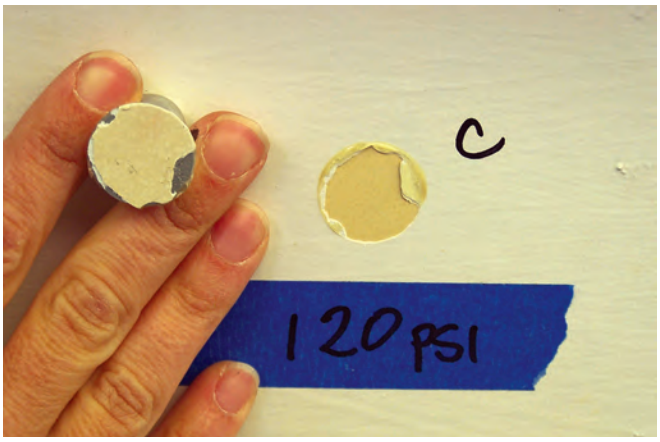

Figure 6. Adhesion pull testing demonstrated paint failure consistently occurred at the interface between the primer and topcoat.

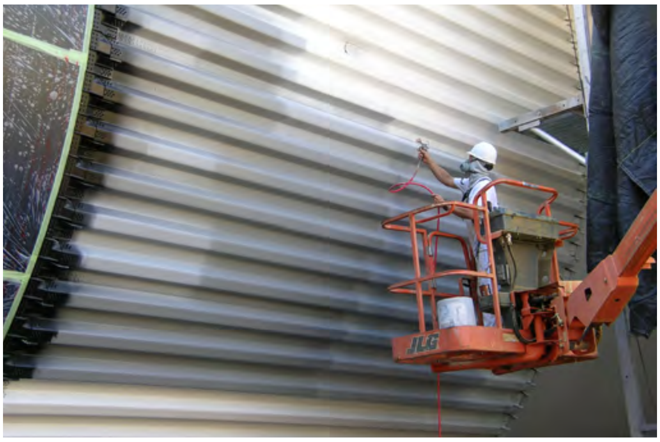

Figure 7. A new high-performance coating is spray-applied to the Saturn V at the US Space and Rocket Center.

application for LSMA[3]. In general, spray methods use specially designed guns to atomize liquid coatings into a fine spray, transferring them to a metal surface (see Figure 7).

Most spray systems are easy to operate and have low equipment costs. However, paint can be spray-applied to surfaces in a variety of ways. Accordingly, the paint application process should be chosen depending on the type of substrate, the type of coating, the size and shape of the object and the profile of the surface to be coated (see Table 5).

Coating Monitoring: During and After

Maximizing the life of a protective coating requires monitoring and proactive care, both during application and over the subsequent life of the coating. Monitoring techniques should ideally be reproducible and objective. Although visual observation is an essential method of monitoring, semi-quantitative techniques will provide results that are comparable.

Monitoring during application is best achieved qualitatively through 'quality control' of the painting process. The conservator should possess a basic understanding of coating application principles, and should monitor the following conditions and techniques:

- Track ambient conditions (temperature, humidity, dew point) to ensure they are within the proper ranges
- Track application sequences (primer, intermediate, topcoat) to ensure sufficient cure times between coats and that the application window has not expired for time sensitive coatings
- Observe the spray distance and angle for equipment used, as this effects porosity and adhesion of the coating
- Ensure overlap percentage is appropriate for the spray equipment being used to produce uniform coating thickness
- Observe essential application techniques such as 'stripe coat' for welds, bolts, bolt holes and sharp edges to ensure edge retention

Quantitative monitoring should also accompany coating application. The recommended film thickness can be observed during application using a wet film thickness (WFT) gauge, whereby a metered comb is pressed into the paint film, allowing direct measurement of the coating.

Because testing occurs during the painting process, the operator can make immediate adjustments to application procedures. The technique is 'destructive' to the paint layer where tested unless the coating is able to 'level' itself out.

Alternatively, a dry film thickness (DFT) gauge can be used after a coating has dried. First, a set of baseline readings are taken on a clean metal substrate; subsequent readings are taken in the same locations after each coat has cured to confirm that the recommended DFT was achieved.

In tandem, a coating continuity tester — or 'holiday detector' — is used to identify pinholes and voids in a coating. This should occur immediately following initial cure because even miniscule voids may invite moisture and salt ingress, which cause premature coating failure. Early detection allows the conservator to correct these defects before treatment is concluded (Sembrat 1998).

Adhesion testing quantifies the bond strength of a coating once it is completely cured. This test can confirm that the applied coating meets the criteria specified by the manufacturer.

The test is destructive to the coating, therefore, the coating will require immediate repair in the test area. Alternatively, during the coating application process, conservators can recommend that test coupons of an equivalent metal be prepared alongside the artifact,

Name	Technology	Power source	Transfer Efficiency	Advantages	Disadvantages
LVHP (low-volume/high-pressure; Conventional)	Low volume of air at high pressure used to atomize liquid paint	Air compressor	30-60%	Finest atomization and finest finishes; can handle widest range of coating types	Significant overspray, low transfer efficiency, high VOC emission, significant consumption of compressed air
HVLP (high-volume/low-pressure)	High volume of air at low pressure used to atomize liquid paint	Turbine air blower or air compressor	65-75%	Portable and easy to clean; lower risk of blowback to applicator; improved transfer efficiency over LVHP	Coarser atomization results in less fine finish
Airless sprayer	Paint is pumped at increased fluid pressures	Air-driven reciprocating fluid pump	65-70%	Less turbulent application results in less bounce-back; heavier coating achieved per pass; portable; greater transfer efficiency; ability to handle high-viscosity coatings without solvent thinning; good penetration into recessed areas	Paints limited to those which are finely ground which can pass through small nozzle orifices, resulting in excess coating, runs and sags if gun movement is too slow; limited to large areas; difficult and possibly dangerous to clean because of high pressures involved
Air-Assisted Airless Sprayer	Variation on airless spraying	Supplemental air jets guide paint spray and boost level of atomization	70-80%	Finer paint particles are produced resulting in a finer finish than a typical airless sprayer; improved transfer efficiency	Paints limited to those which are finely ground which can pass through small nozzle orifices, resulting in excess coating, runs and sags if gun movement is too slow; limited to large areas; difficult and possibly dangerous to clean because of high pressures involved
Electrostatic Sprayer	Negatively charged objects are attracted to positively charged ones: atomized paint droplets are charged at the tip of the spray gun (conventional, airless, rotary) by a charged electrode	Turbine air blower, air compressor, air-driven reciprocating fluid pump; electrode	LVHP-based, 60-70% Airless-based, 70-95%	Best transfer efficiency including "wraparound" effect (particles coat front and back of object in one pass), good attraction to inaccessible areas	Large capital investment; significant safety precautions necessary to ensure proper grounding and reduce fire hazards; paint is indiscriminately attracted to grounded objects other than artifact as well

Table 5. Comparison of Spray Application Techniques- Spray application techniques offer a variety of advantages and disadvantages which should be carefully weighed according to the parameters of a specific LSMA project.

specifically for destructive testing purposes.

Once monitoring has confirmed proper application of a new coating, the conservator should provide a comprehensive maintenance plan, which includes cyclical monitoring, maintenance, and repair guidelines to detect, prevent, and mitigate alterations in the coating before they become catastrophic failures.

By the time failures become visible as peeling, blistering or staining, the underlying metal may already be deteriorating.

Monitoring guidelines can be performed by other professionals, such as site collections care or maintenance staff, as long as the conservator provides adequate training and analyzes data collected.

Monitoring should begin with a complete visual survey of the artifact. Typical areas of wear caused by water runoff and physical (visitor) contact, areas of pooling or trapped water, and other problems, such as animal and insect activity, should be recorded.

Baseline DFT measurement taken at the time of treatment can be compared with later examination. DFT and continuity measurements can be repeated annually to track coating wear rates, project remaining service life, or determine the need for localized touch-up of the coating.

These measurements may be supplemented by objective evaluation of gloss and color. Increasingly sophisticated gloss meters and colorimeter/spectrophotometers can quantify extremely subtle and gradual changes in color or gloss.

In addition to the obvious aesthetic implications, a reduction in gloss may also indicate a deterioration of that coating; the reduction in gloss also translates to reduced resistance of the coating to ultraviolet light.

Changes in color can indicate the degradation of the pigment and binder, visible most notably as chalking (Escarsega et al. 2003)[4] (see Figure 8).

Figure 8. Long-term exposure to extreme environmental conditions caused chalking and degradation of the coating (at left) on one the

training modules for Skylab, also located at the US Space and Rocket Center in Huntsville, AL, USA.

Conclusion

Coating industry standards and the tests developed to help achieve them were established with the goal of extending the service life of coatings and the underlying substrates they protect.

Preservation treatments of cultural and historic artifacts often require adapting or modifying these standards to remain consistent with conservation ethics. This is particularly true in the case of large-scale metal artifacts, which present a unique confluence of challenges including size, complexity, access, display and interpretation.

Coating industry guidelines are essential tools to assist conservators to understand the implications of these compromises, and in collaboration with other experts, determine and implement treatments that can best serve the needs of the client and the artifact in terms of coating longevity and cost effectiveness.

Endnotes

[1] The Advisory Council is a non-profit consortium dedicated to promoting effective surface preparation through water-blasting technology.

[2] Alclad is both a trademark (of Alcoa) and generic term used to describe a composite product in which an aluminum alloy core is clad on either side with a high-purity aluminum surface layer, thus combining strength of the core with resistance to corrosion, abrasion, and fatigue of the surface. This product is frequently used in the aircraft industry (Hunsicker 1976).

[3] Recent research by the Army Research Lab has concluded that humidity and moisture combined with UV radiation synergistically increase the degradation of a specific coating (Escarsega et al 2003). Changes in color could also be caused by soiling or staining by atmospheric contaminants. Although the net result of a change in color may be the same, the cause of the change should be properly understood so that an appropriate response can be implemented.

[4] The Eiffel Tower is cyclically painted every seven years using brushes and rollers rather than spray equipment, most recently in 2009-2010 ('Painting the Eiffel Tower' 2009).

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Q & A SESSION

Joe Sembrat: Sorry for the fast talking. Our paper is much different than this, but the Donhead publication, I think 2 years ago that we published in, that talks about the treatment with water jetting if anybody is interested in it and it also touches on the *Titanic*, the big piece from the *Titanic* that was also water jetted.

Peter Northover: Just a simple question just for general knowledge: the only thing I've ever pressure-washed is getting ivy roots off the stone wall of our house so that is going to get rained on anyway. So as soon as it got dry it didn't matter. You sort of partly answered my question by showing it'd attract water. How would you monitor that the thing was absolutely dry before you start painting?

Joe Sembrat: Visual inspections, and we're doing surface measurements also but this thing is not [a simple structure].

Peter Northover: I was going to say it is so complex – you almost can't guarantee it…

Joe Sembrat: But these are just basically large tanks that held fuel. They're extremely tight. We entered one of the Stage 4 tanks – it was like the day it was built inside. So they're extremely airtight and watertight. So basically we were looking at the ends where water was collecting. We had a dehumidification system that was set up (a huge diesel-run drying system) and the structure was bagged and dehumidified for a period of time before the coating systems went on. So then there were also surface moisture measurements taken prior to the coating application and I'm sorry we're so brief but 20 minutes is not a long time.

Peter Northover: Thank you.

Patricia Miller: Just one other thing also, right before they would do any kind of painting, they would go over with an air system and go right over the surface and then come back and immediately paint. So if they saw any kind of trailing water or anything like that the painting wasn't continued. They made sure they went back and cleaned everything.

Vasilike Argyropoulos: I wanted to ask you a bit about the Cortec products – the corrosion inhibitors, or the corrosion inhibitor additives that you use. When we started the PROMET project we contacted Cortec to send us a bunch of corrosion inhibitor additives that we could use with testing with the coatings. They were extremely helpful. They sent us a whole bunch of products that they felt would work with the waxes, although we couldn't get a lot of product information as to what was contained in them. But they were very helpful and we got a lot of products to test but the corrosion inhibitors didn't seem to help. Our short-term testing found that they weren't very helpful in providing improved performance of these coatings. So I just wanted to know a bit more about these products and which ones do you find useful. What do they contain - if you know what they contain?

Joe Sembrat: Most of the products are based on the Vapor-Phase Corrosion Inhibitors. And they are altered depending on whether you need an oil-based or a water-based solution and so forth. I don't know how you did it, whether you mixed it in with waxes or….

Vasilike Argyropoulos: We mixed it in.

Joe Sembrat: The systems works and I could give you an example why. However if the coating itself is flawed the corrosion inhibitor will only work so much to protect the surface. As Patty showed in that one image of the plated surfaces that were oxidizing. They were coated but they were flawed and that's why the surface was oxidizing. One of the products that we use a lot is the 415 by Cortec, it's a detergent wash that we used on the big piece [from the *Titanic*] after water jetting it. In that case, we water jetted the surface – we wanted it to oxidize because we were doing a tannic acid treatment. But we had washed it with the 415 and we couldn't get it to oxidize. It was incredible. It was in Houston, it was in a very humid environment and we could not get the surface to flash-rust.

Vasilike Argyropoulos: But you didn't do coupon-testing and so you rely on visual measurements to see how good they are. Practically you're applying them and you are seeing that they're working? That's the question I have.

Joe Sembrat: We have not run a systemized test using the various Cortec products. We typically integrate their raw materials into our out-door waxes and so forth.

Patricia Miller: When we were doing all the research for the Saturn 5 project, which was kind of concurrent with the re-treatment of the big piece and so we were very interested in all of the Cortec products. What we actually got were several coupon tests and studies and salt spray studies and things like that that actually came from KSC [Kennedy Space Center]. There's a ton of naval research and another specification I don't mention here but I have gone to in the past is Mil Specs – Military Specifications. Military Specifications go right to the point of coupon testing because of the amount of equipment that they have to maintain and protect. Especially for short-term storage in various atmospheres and that is what they are looking at – tanks, airplanes, things like that – that are in these variable storage spaces.

David Hallam: I think adding someone else's inhibitor system to our own waxes is not a particularly good way of going. When that company actually makes - and you can buy material that has been tested - wax-based systems. I have done some very rudimentary tests on some of the Cortec stuff and it certainly does work.

Joe Sembrat: Have you ever seen their waxes? I have, for a sculpture – they look awful. They sent me that, and I said 'this is unacceptable' – they were sticky and tacky. Ultimately what we did is send them our wax and said: 'provide me with a corrosion inhibitor that will work in it'.

David Hallam: Yes I think that's an appropriate way of doing it.

Joe Sembrat: I have never added it to a paint or a coating system. That would just negate the warranty of the coating system but in waxes, the way we use them in conservation, we add the raw material to it or we will do pretreatments with the corrosion inhibitors.

David Hallam: But I think the important thing is: you have worked with the company. You haven't just taken something off the shelf and dumped it in.

Joe Sembrat: Yes, extensively. Correct.

Stéphanie Cretté: Thank you for the talk it was very interesting. I had one comment and now I have two. I guess I'm going to start with the Cortec: I haven't looked at all the corrosion inhibitors from Cortec but from my previous life I know that some of their corrosion inhibitors are based on fatty acids. Actually those fatty acids are usually oleic acid and they are coming from the paper industry and the company I used to work for would sell the raw material to produce the corrosion inhibitors.

Joe Sembrat: Do you know which products those were?

Stéphanie Cretté: They were not VPI [Vapor-Phase Inhibitors].

Joe Sembrat: Because I do know that they purchase other companies' products, and then over a period of time they alter them. I know a lot of the rubber anti-oxidants were too aggressive for our liking and we did not utilize them.

Stéphanie Cretté: There is one in particular - and if people are interested they can contact me – I'm on the list of attendees there – that I looked at, and I'm sure it's oleic acid. The other comment is that for people interested in coatings in general, there is also the American Coating Society – I think a resourceful association. You have the universities involved in coating research and the manufacturers working together. So you can find a lot of the recent research. Maybe not everything will be removable as a coating but at least you can find new ideas for your way of using your coatings.

Joe Sembrat: Thank you. And it's a point I'd like to bring up, maybe in our discussion panel: this idea of reversibility when you're dealing with artifacts like this and things that are displayed outside. Reversibility in relation to longevity and so forth. If you're retreating something ten times because you're stuck on reversibility in many ways is worse than applying a coating that is considered non-reversible – an epoxy coating or a urethane coating. We have yet to find a coating that we cannot reverse chemically. Unless if it is a molecular bond, like galvanizing or something to that effect. So it's just something I'd like to pick up on – I'm not necessarily saying that you should use a non-reversible coating but it is something, I think, for outdoor use should be discussed further.

Stéphanie Cretté: Well actually we have a project right now at the lab, where we agreed with the National Park Service to test alkyds, which is what the National Park Service have been using for years. We also try the new type of coating – the industrial coatings, like epoxy and urethane on their different artifacts and monitor it over time to see if it is worth doing it with a new and better coating that will last longer.

Joe Sembrat: I'd be interested to hear more about that.

Stéphanie Cretté: You've been involved with the project.

Joe Sembrat: This is at the Fort? [Forts Moultrie and Sumter, Charleston, SC]

Stéphanie Cretté: Yes.

Stefan Brueggerhoff: Thanks a lot, it was a really great, interesting talk. My question is: you showed that you have an awful lot of different materials in your objects. If you apply water jetting, how can you prevent the other material from getting influenced in a way that would not be so good for them? Foams, rubbers and so on?

Joe Sembrat: That is a part of the 'heartburn issue' that I was talking to Tony about. When you have cork right next to a painted aluminum surface that you are trying to strip. We would be out there, or I should say Patty – she was out there constantly with them. But we basically try to shield them. They have a tape system that the water jet bounces off. But it's the sort of thing where you can't just let people go loose and start water jetting. They wanted to water jet the command module which is a phenolic resin surface. And somebody had done that before and torn it apart. So it is oversight once again and understanding of what's going on. We would have meetings every day before we started water jetting and after lunch about where you're working, how far you're going, where the areas are and the limits of what they're doing.

Stefan Brueggerhoff: And so develop also other conservation techniques for the other materials – would be very interesting for me.

Patricia Miller: Yes, when we would abut other materials, like the foam – it just happened that the foam was completely deteriorated so it had to be mostly removed. But with the cork materials and the phenolic materials we stopped at a certain distance and then we actually went and would do that region with a paint strip product. It was basically a gel paint stripper which would then be slowly hand-removed so you were doing more careful techniques right next to those materials, and not putting the water jet right at the interface. We did have accidents where people went a little bit beyond their area and tore up some materials and they all got screamed at and sent home. However the whole project on that command module and the S2 is a completely different developed system of treatment than the water jetting.

John Scott: Like everyone else, I think this is a wonderful presentation. I appreciate having it and I look forward to the final version of the paper. Something that Joe innovated long ago is the use of the industrial, the electronic holiday detectors in your application process. It just occurs to me that industry uses these technologies mainly in the maintenance phase later on to find failures of applied coatings and there is a great tendency in the surface coating industry to know that coatings always have some holidays and so use things like second applications, applications of dissimilar coatings that are compatible to address the problem that you will have some micro-holidays that you might not be able to detect. So in the cost/benefit aspect, which is so important in your type of projects especially, and also to lower budget projects with art and monuments, could you say something about the cost effectiveness or how much time does it take. Do you actually use the holiday detection on the entire surface? I know on something like this maybe there is a reason for it or maybe it is just in the budget but a lot of times I just wonder about that extra step. Just address that please.

Joe Sembrat: I have found that you need to – when you bid the work – you need to let the coating applicator know that you want it to the level of the ASTM standards using the holiday detector. As soon as you bring that up the guys give you a sick look that there's going to be problems. The problem with this coating specifically is - one of the downsides of it is – it has very poor edge-retention. As you could see all these stringers on the rocket have very sharp edges on them and this is where the contractor and I got into an issue that their coating thickness was less than I think 0.2 mil, or 5 microns and it was ringing the holiday detector at that point. His thing was: ' I did not bid this for using a holiday detector'. We went back and forth about this. But ultimately the argument was that you have a specified mil thickness that you agree to apply it to and that's what we were expecting to see on these edges of the rocket. So the holiday detector was there but it ultimately was the coating thickness. Yes I agree with you in that it is more of a maintenance tool and that sponge is fairly wide and it's basically you just wet it with a wetting agent like Photoflow and water and you run it over the surface. And it's quick and it's like Pavlov's thing, it rings a buzzer and a light goes off and you just mark it with blue tape, move along and 'here's another holiday'. If I'm finding just random holes and so forth, it's not generally a major issue at that point also that sponge type is non-destructive. They also make a spark one that actually arcs with the substrate and destroys the coating. That's more used in the pipeline industry.

TRADITIONAL ARCHITECTURAL IRONWORK: SCIENTIFIC APPROACHES TO DETERMINING BEST CONSERVATION PRACTICE AND THE BUTE CANOPY CASE STUDY

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Abstract

This paper outlines recent scientific research conducted by Historic Scotland in partnership with Edinburgh Napier University, investigating methods for cleaning and repairing traditional ironwork. In particular, we have examined cleaning of grey cast iron and repair of grey cast iron and wrought iron. The aim of this work is to translate these findings into recommendations and guidance for conservation and repair. Details are given in this paper of a 19th century cast iron entrance canopy on the Isle of Bute, Scotland, which was intended to provide a case study of best practice.

Keywords: traditional architectural ironwork, conservation, conservation science, best practice, Bute Canopy

Introduction

Scotland has a long tradition of manufacturing high quality wrought and cast ironwork. At the peak of production during the 19th century, Scottish architectural iron (primarily cast) was exported across the world, in addition to its abundant use in townscapes in the United Kingdom. A great amount of this traditional ironwork remains today in varying states of preservation. Much of the current guidance on conservation, repair and maintenance of ferrous metals is largely derived from an ‘accepted practice’ viewpoint rather than a scientific basis. However, the use of potentially inappropriate techniques can often be to the detriment of the iron — for example, by accelerating corrosion processes. The scientific research programme of Historic Scotland is at an early stage, but aims to systematically assess the optimum techniques for cleaning and repairing traditional ironwork. Scientific findings will be translated into technical guidance and advice on best conservation practice.

Post-WWII technological change has led to a significant loss of the skills required to understand traditional ironwork construction and repair it in a sensitive manner. Consequently, inappropriate repair techniques are often applied, original fabric is unnecessarily replaced, and small but crucial steps in the planning and programming of work are often overlooked. The ultimate aim of the conservation work carried out to the cast iron entrance canopy on the Isle of Bute was to conserve the canopy using best practice techniques that would be used as a case study to inform similar projects in the future. Stages in the project will be discussed here from inception to completion.

Materials and Methods

Assessment of best practice for cleaning and repair of traditional ironwork was facilitated by a systematic program that assessed a wide range of cleaning and repair techniques, followed by a scientific assessment of the effects and considerations of the practicalities of each technique.

Cleaning trials were carried out using (as near as possible) uniform specimens of sacrificial grey cast iron to assess the removal of accumulated paint, corrosion layers, water-soluble corrosion salts and oil/grease, while retaining, where possible, any surviving protective oxide layers formed on the iron surface immediately after casting. Samples used in the cleaning trial were heavily painted and corroded 19th century balusters, with the addition of two uncleaned control samples. A total of 25 cleaning techniques were investigated (see Table 1). These included the use of manual and power cleaning tools, flame cleaning, laser cleaning and chemical cleaning. Blast cleaning was investigated utilising a wide range of blast media. This is an ongoing research programme and we intend to investigate wrought iron and perhaps other forms of cast iron at a later date. We also intend to look at additional cleaning methods that were not looked at in this initial study due to time and availability constraints.

Cleaning Method	Details
Control samples	Not cleaned
Manual and power tool cleaning	Wire brush (manual) Wire brush (power) Rotary abrasive disc Needle gun (low pressure) Needle gun (high pressure)
Flame cleaning	Propane torch Oxyacetylene torch
Laser cleaning	Nd-YAG laser
Chemical cleaning	Methylene chloride Caustic soda Hydrochloric acid Sulphuric and phosphoric acid mix
Blast cleaning	Aluminium oxide Copper slag Chilled iron Garnet Olivine Glass beads Glass grit Walnut shells Plastic media Dry ice 'Sponge-Jet' 30 'Sponge-Jet' 120 Wet blast with glass grit

Table 1. Methods trialled for cleaning traditional grey cast iron. Operating parameters were standardised throughout the tests wherever possible. Abrasive blasting techniques were carried out at 7 Bar pressure and at a distance of 0.5-1.0 m from the sample.

Repair trials were carried out using sacrificial samples of newly cast grey cast iron and salvaged 19th century wrought iron, which were uniformly cut to allow direct comparison, then repaired and assessed. A total of 20 repair techniques were investigated, including a control sample (see Table 2). Repairs included mechanical fixings, such as riveting, bolting, pinning and stitching. Thermal repairs were investigated, including welds, brazes and solders. Finally, chemical repair techniques were trialled. Infrared thermography was used as an investigation technique during thermal repairs (welds and brazes) to look at the distribution of heat and to identify possible stresses on the parent metal. A FLIR SC660 camera recorded thermal sequences during the repairs. Figure 1 shows two thermogram snapshots from the sequences for cast iron: manual metal arc (MMA) welding and silicon brazing.

Repair Method	Details
Control samples	Unbroken
Mechanical	Riveting Plating/bolting Pinning Cold metal stitching
Thermal	Welding – fire (wrought iron only) Welding – Arc (MMA/Stick) Welding – Arc (MIG) Welding – Arc (TIG) Welding – Oxyacetylene Welding – Gas Fusion Brazing – Mn Bronze Brazing – Si Bronze Brazing – Ni Bronze Soldering – tin/lead solder Soldering – silver solder
Chemical	Epoxy glue Carbon fibre (bi-directional) Carbon fibre (uni-directional) with cold metal stitching

Table 2. Methods trialled for repairing traditional grey cast iron and wrought iron.

Temperature profiles can also be extracted directly from the thermograms. The examples in Figure 1 illustrate in the weld repair, how heat is concentrated at the repair site, placing stress on the cast iron. The lower temperature braze has a more even distribution of temperature across the parent metal, so there is less likelihood of fracture during repair.

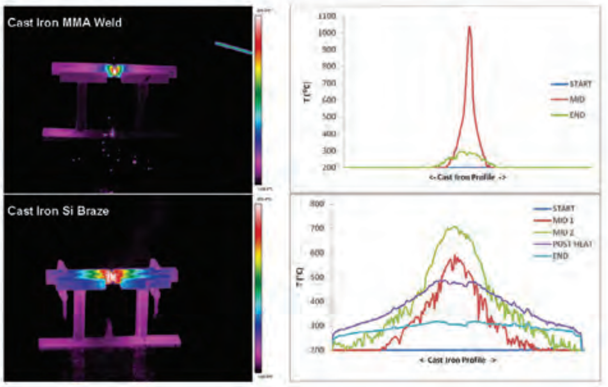

Figure 1. Infrared thermography to visualise thermal repairs to grey cast iron. The thermogram displays surface heat (*left)* and the associated temperature profile extracted from the thermogram (*right*). Examples shown for manual metal arc (MMA) weld and silicon braze.

The efficacy or cleaning and repairs were assessed scientifically and in terms of the practicality of each method, using the following techniques:

- Aesthetics and visual assessments
- Ethics
- Ease, time, cost and skill level needed to carry out cleaning techniques
- Health and safety considerations of each method
- Metallography

- Optical microscopy
- Scanning electron microscopy with elemental mapping (SEM-EDAX)
- Load bearing strength (Bend Test)
- Microhardness testing

For metallographic examination, a cross-section was cut from each sample and mounted in cold-curing epoxy resin, ground and polished to a 1 micron diamond finish and etched using 2% Nital. Samples were first viewed under a Leitz Aristomet optical microscope. Secondly, detailed imaging was carried out using a Field Emission Scanning Electron Microscope (SEM) with associated Energy Dispersive X-ray Analysis (EDX). Elemental analysis and mapping was also carried out with the SEM-EDX using INCA software.

Results

Initial results from a selection of the cleaning and repair trials are briefly discussed here.

Cleaning

Visual cleanliness was assessed using pictorial surface standards (ISO 2007; The Society for Protective Coatings 2000, 2001, 2002, 2004). According to these classifications, blast cleaning removed paint and debris to a level of 'near white metal/very thorough cleaning' in many cases and, where glass beads were used, to 'visually clean steel/white-metal'. However, these assessments do not take into account that traditional ironwork should be treated differently to commercial iron and steel, where the objective is to clean to bare metal. A thermodynamically stable oxide layer forms immediately after casting and offers a good degree of protection to the underlying metal. Cleaning of traditional cast ironwork should seek to retain this oxide layer where intact, while removing subsequent paint and grease layers. Since there are no viable alternatives, the ISO and SPC pictorial standards were used in this study, following the guidelines for commercial iron/steel. Different cleaning methods produced significantly variable results in terms of visual cleanliness and in terms of retention of this oxide layer, as the examples in Figure 2 show.

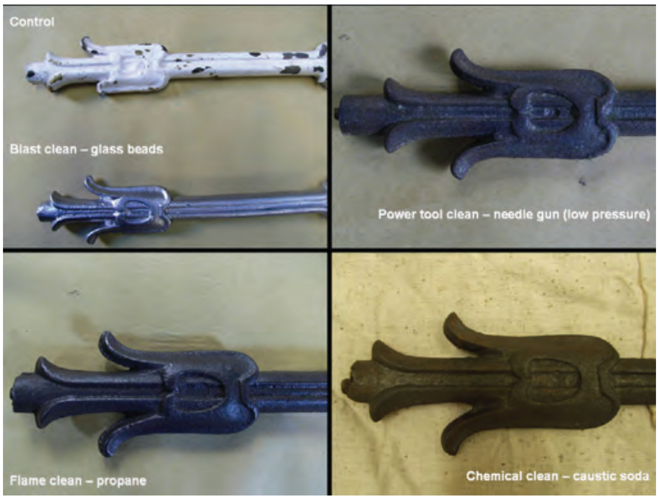

Figure 2. Visual results of various cleaning techniques trialled on 19th century grey cast iron test samples.

Optical microscope examination of edge profiles on the prepared polished sections allowed estimation of percentage retention of the oxide layer post-cleaning (see Table 3). Oxide layer retention is considered by the authors as important criteria in evaluating treatments, since this layer provides passive protection to the metal beneath from the time of casting. Flame cleaning appeared to preserve the oxide layer well, as did the softer blast media, walnut shells and plastic media. Harder blast media generally did not appear to successfully retain the oxide layer. Chemical cleaning using a sulphuric and phosphoric acid mix also appeared to retain the oxide layer very well but requires further investigation to determine the potential effects of phosphoric acid on a ferrous substrate. Preservation of the oxide layer is only one of many assessment parameters: where such a layer no longer exists, other criteria (e.g. examination of cleaning effect on surface profiles, impact on load bearing strength and microhardness, etc.) are used to determine the optimum methods for cleaning.

Cleaning Method	**Oxide layer Retention (%)**
Control 1	75
Control 2	100
Chemical clean - hydrochloric acid	0
Chemical clean - caustic soda	0
Blast clean - garnet	5
Blast clean - aluminium oxide	5
Blast clean - chilled iron	5
Blast clean - Sponge-jet 30	5
Blast clean - Sponge-jet 120	5
Blast clean - glass beads	10
Blast clean - copper slag	20
Chemical clean - methylene chloride	50
Blast clean - wet blast with glass grit	50
Blast clean - glass grit	50
Wire brush (power)	60
Rotary abrasive disc	60
Needle gun (high pressure)	60
Blast clean - dry ice	60
Needle gun (low pressure)	70
Laser clean	75
Blast clean - plastic media	75
Blast clean - walnut shells	75
Wire brush (manual)	80
Flame clean - oxyacetylene	90
Flame clean - propane	90
Blast clean - olivine	90
Chemical clean - sulphuric and phosphoric acid mix	95

Table 3. Oxide layer retention on grey cast iron test samples after cleaning, estimated by examination of edge profiles under optical microscope.

Examination with SEM showed several examples of embedded foreign particles in the cleaned cast iron surface. Elemental mapping confirmed in each case that the particles were derived from the cleaning process. One example was a blast cleaned sample using glass grit;

elemental maps show the embedded particle contained no iron, but sodium, calcium and silicon, indicative of a soda-lime-silica glass (see Figure 3. From a conservation perspective, this suggests some blasting techniques may not be the best choice for preservation of traditional cast iron microstructures — further analysis is required to clarify this.

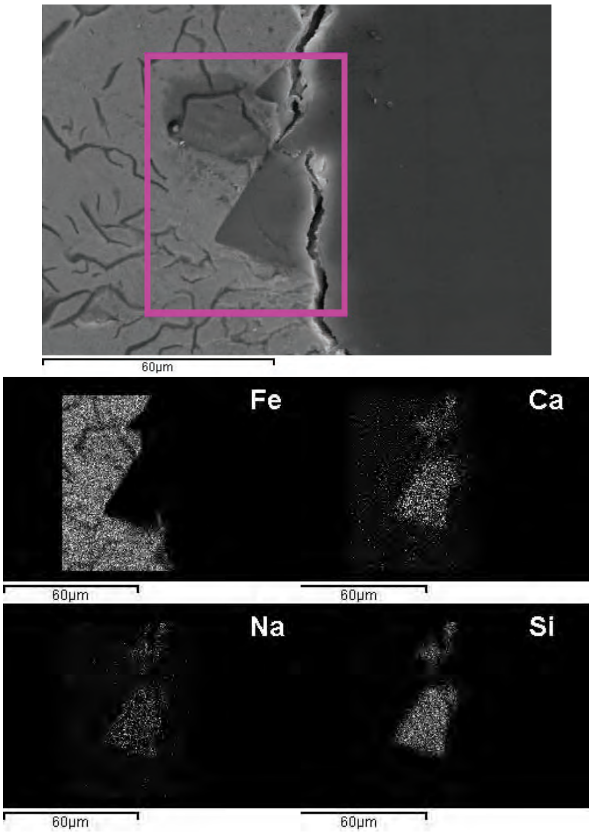

Figure 3. Scanning electron microscope image of cast iron surface cleaned using glass grit blasting. Impacted particles can be seen in the highlighted area. Elemental mapping using SEM-EDAX confirms this is from the blast process: there is no iron present, but sodium, calcium and silicon are present, indicating it is a particle of soda-lime-silica glass.

Repairs

Although subjective, assessment of the ethics and aesthetics of the repair are particularly important where traditional metalwork is involved. Are repairs reversible? Has the historic fabric been retained? How does the repair look? Is the repair self-documenting? As Figure 4 illustrates, there is considerable variation in appearance between the repaired samples.

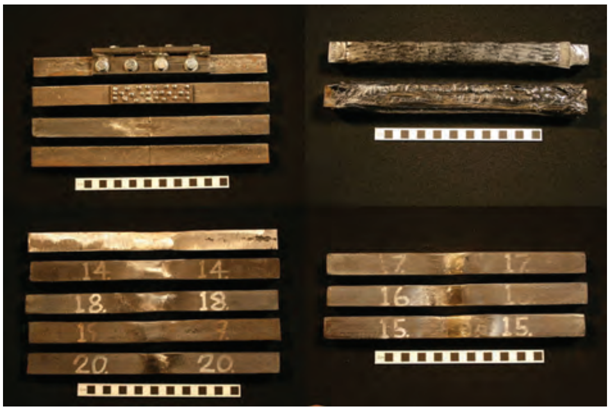

Figure 4. Visual results of various repair techniques trialled on sacrificial cast iron test samples. *Clockwise from top-left*: mechanical repairs, carbon fibre repairs, braze repairs, weld repairs.

Optical microscopy of polished metallographic sections has been useful to examine the interface between parent metal and filler material in thermal repairs. In Figure 5, the distinction between parent and filler metal is very clear in the manual metal arc (MMA) weld, with evidence of some ferrite grain enlargement in the heat-affected zone. In the gas fusion weld, there is little distinction.

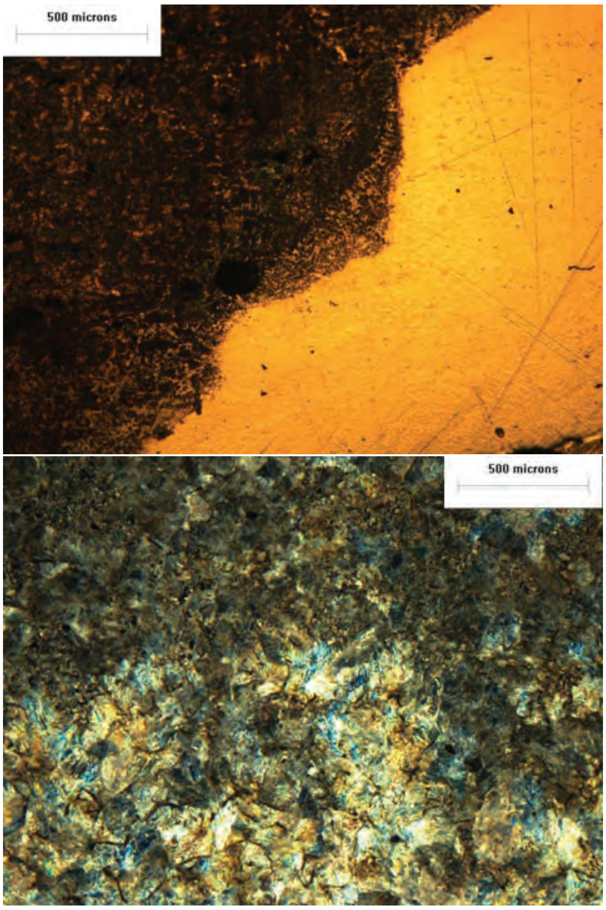

Figure 5. Optical microscopy images of polished metallographic samples showing heat-affected interface between parent metal and filler material in thermal repair to cast iron samples: MMA weld repair (*top*) and gas fusion weld repair (*bottom*).

Initial observations indicate particular thermal and mechanical repairs performed better under scientific testing than others. It is important that the repair is fit for purpose — some repairs will be stronger and more suitable for structural ironwork, while other techniques will be more aesthetically pleasing and more suited to decorative ironwork. Data from this study will be assessed, comparing against the control samples.

Following further analysis on a wider sample pool, the results of all scientific tests and assessments from our research into cleaning and repair will be peer reviewed by a panel of conservation experts and translated in terms of recommendations for best practice, specifically tailored for particular audiences, and published as a Historic Scotland Research Report.

Case Study: The Bute Canopy

This rare and exceptional Scottish example of a 19th century pre-fabricated cast iron canopy survives in a coastal location at the entrance of a former hotel in

Rothesay, Isle of Bute, on the west coast of Scotland (see Figure 6). Manufactured by the Sun Foundry towards the end of the 19th century, the structure had fallen into a state of disrepair by the late 20th century. Historic Scotland funded and managed the conservation, repair and reinstatement of this special canopy in 2008. The canopy was composed of four sets of double candy twist columns set into two low sandstone walls. A ring beam was set atop these columns, supporting a glazed roof. Decorative brackets and spandrels ornamented the level directly below the ring beam. Decorative cast iron finials were placed at each corner of the roof, while cresting and a terminal ornamented the ridge of the roof.


Figure 6. The *Bute canopy*, June 2009, after conservation

Research was conducted to gain a better understanding of the history and origins of the structure. Although no written records relating to the structure could be found, many of the components were identified in the Sun Foundry's 'Illustrated Catalogue', dating to around 1890, and a number of archive images were sourced that provided crucial evidence for the repair methodology.

Paint scrapes were taken from a number of places on the canopy for analysis. Regrettably, no early or original coating layers survived beneath the topcoat.

A condition and photographic survey was conducted to inform the project approach. Up to 85% of the fixings holding the structure together had failed due to the extensive degree of corrosion at these points, resulting in a number of decorative elements detaching from the main structure, either due to fracturing caused by corrosion developing at fixing points, or through the loss of fixings. The loss of fixings holding the glazing bars in place also caused the roof to slump. Galvanic corrosion caused by fixing the cast iron gutters directly to the steel ring beam had caused such severe corrosion that these had to be entirely replaced. Despite extensive areas of localised corrosion, the structural cast ironwork itself was in sound condition (see Figure 7). No original glass survived.


Figure 7. View of the *Bute canopy* during tagging and dismantling, November 2007.

A range of traditional and innovative survey techniques were utilised to record the structure before it was dismantled, from measuring by hand and drawing in AutoCAD to the use of laser surveying technology (a technique that had never been applied to a structure of this intricacy before). Further detail on laser scanning of the Bute Canopy can be found in Wilson et al. (2010).

The specification and bill of quantities (an itemised list of costs) was then written for the works that was one of the most important stages in the project. The document was specific about:

- Dismantling methodology: ensuring in particular that all components were tagged and numbered according to the numbering system on the survey drawings.
- Cleaning and repair techniques: ensuring that an inert mineral grit was used as the blasting medium and that no welding was carried out.
- New castings: ensuring that the green sand moulding technique was used in combination with timber patterns.
- Paint system: ensuring that a red-lead primer and compatible top coats, as well as a red lead paste filler, was used.
- Transportation: ensuring that adequate protection was given to the components during transit.
- Re-assembly and tools: ensuring that all fixings were tightened by hand only and that all paintwork was touched up where necessary on site.

An important aspect of selecting a contractor was devising a scoring system for tenders that weighted points more heavily towards the competency and experience of the contractor rather than the lowest price.

A number of interesting previous repairs, some of which seriously compromised the structural stability of the roof structure, were discovered during the dismantling phase. These had not been noted during the condition survey due to the fact that they were largely obscured from view when the structure was intact. The fixings holding the glazing bars in place that support the roof ridge had failed, causing the roof to slump. Once the roof was removed, it was discovered that the supporting ring beam was composed of three individual sections of steel. These sections were not connected to each other in any way. Nor were they connected to the supporting columns. Nor, in fact, were they properly fixed into the masonry building façade, which meant that the roof essentially was supported by three loose beams merely resting on the columns below.

The components were then blast-cleaned using an inert mineral grit (fine calcium silicate). Once the iron had been cleaned, each component was assessed for any previously hidden defects, damage or areas of weakness as these might affect the repair methodology that had been agreed with the contractor.

Where small sections had been lost, only the missing section, wherever possible, was re-cast and then pinned into place using Grade A2 stainless steel pins to minimise sacrificial corrosion. Where the section thickness was not sufficient to permit pinning, brazing was used as an alternative.

Missing components were recast in grey iron by a foundry that had expertise in green sand moulding techniques to ensure that the castings had the appropriate level of surface detail and finish. Great care was also taken to ensure that the patterns were accurate and of a high standard (see Figure 8). The year of manufacture (2008) was cast into all new castings so that they would be distinguishable in the future from the original material, and thereby self-documenting.

Figure 8. Inspection of timber patterns for new castings.

During treatment of the canopy, a member of the public sent Historic Scotland a photograph dating to the 1920's, following an article in a local newspaper, which clearly showed there had once been a pair of decorative brackets at the front of the canopy. Consequently, new patterns were made and replicas cast in grey cast iron.

Given the coastal location of the canopy and consequent risk of salt deposits on the surface of the iron (which could accelerate the rate of corrosion and compromise new coatings), the cleaned surface was tested for the presence of soluble salts using *Quantofix* (chloride) and *Merck* (sulphate) test sticks. Surprisingly, no detectable level of soluble salt was found. Traditional red lead putty was used to fill all joints and to bed column capital details in place. Similarly, two coats of a red lead primer were applied to the cast iron (which had been cleaned to SA 2.5 standard), as well as one coat of micaceous iron oxide and two coats of a silicone alkyd paint. The contractor was requested to ensure that the coating system was applied to a maximum dry film thickness of 250 microns. The paint manufacturer was consulted on the best method of application for the selected coating system.

Final checks for defects were made to the canopy once it had been re-erected on site, resulting in a request to the contractor for stainless steel washers to be replaced with nylon ones and localised areas of damaged paint to be re-touched.

Conclusions and Future Research

The conservation and repair of traditional cast ironwork requires specialist knowledge and appointing the right contractor. Providing a detailed specification and demanding high standards of workmanship were the most important aspects of ensuring this conservation project was successful. Despite careful planning, a number of challenges arose during the project that required ethical decisions to be made concerning interventions to the historic fabric of the structure.

A new strand of this research is about to begin at Historic Scotland investigating appropriate cleaning for wrought iron. This research will look at the same cleaning techniques in the grey cast iron trials, plus several additional methods, such as waterjetting and ultrasonic cleaning (using acidic, neutral and alkaline cleaning solutions). While some methods may have negative connotations associated with their use (for example, it is often perceived that certain chemical treatments or waterjetting may be unsuitable for cleaning historic ironwork), it is important to test these scientifically to demonstrate why they are unsuitable for conservation work. The initial observations reported in this study are based on a very small sample pool and the authors intend to build on this before formulating the results into recommendations for practice. Once completed, full details of this research will be published in a forthcoming Historic Scotland Research Report.

The challenge of determining best practices for cleaning, repair and maintenance of traditional ironwork is no small feat. However, it is hoped that through the objective and scientific approach presented in this paper, practitioners can begin to make in-roads to ensure the longevity of the rich ironworking heritage in Scotland and beyond.

Acknowledgements

Edinburgh Napier University team: Bill Brownlee, Peter Bruce, Dr Neil Shearer.

Materials

Nital
Fisher Scientific UK Ltd., Bishop Meadow road,
Loughborough, Leicestershire, LE11 5RG, UK
www.fisher.co.uk

Sponge Jet
Aerotech Inspection and NDT Ltd.
Charlton Drive, Corngreaves Trading Estate,
Cradley Heath, West Midlands, B64 7BJ, UK
www.spongejet.com

Quantofix Chloride Test Strips
Macherey-Nagel, Fisher Scientific UK Ltd.
Bishop Meadow road, Loughborough
Leicestershire, LE11 5RG, UK
www.fisher.co.uk

Merck Sulfat-test
Merckoquant 10019, Fisher Scientific UK Ltd.
Bishop Meadow road, Loughborough
Leicestershire, LE11 5RG, UK
www.fisher.co.uk

StoneGrit Calcium Silicate blast material
Wolverhampton Abrasives Ltd.
Orgreave Drive, Sheffield, S13 9NR, UK
www.hodgeclemo.co.uk

Quick Drying Red Lead Primer*
Craig and Rose, Halbeath Industrial Estate
Crossgates Road, Dunfermline KY11 7EG, UK
www.craigandrose.com/trade

Where restrictions apply to the use of red lead, a zinc-based primer is generally considered to be the most effective alternative to a lead based one.

Micaceous Iron Oxide
Craig and Rose, Halbeath Industrial Estate
Crossgates Road, Dunfermline KY11 7EG, UK
www.craigandrose.com/trade

Silicon Alkyd Topcoat
Craig and Rose, Halbeath Industrial Estate
Crossgates Road, Dunfermline KY11 7EG, UK
www.craigandrose.com/trade

Red Lead Paste*
Traditional Boat Supplies, 31 Ravensmere
Beccles, Suffolk, NR34 9DX, UK
www.tradboats.com

While red lead putty is still freely available in the UK, restrictions on its use may apply in other countries – polysulphide mastics can provide a substitute although the appropriateness of this material should be determined on a case by case basis.

Grade A2 Stainless Steel Fixings
Swiftec Building Products, Penine House
Tilson Road, Roundthorn Industiral Estate
Manchester, Lancashire, M23 9GF, UK

Inert Nylon Insulating Material
AC Plastics Developments Ltd.
Old Bakehouse Works, Dale Side
Buxton, Derbyshire, SK17 6NN, UK
www.acplastics.co.uk

Dry Seal Glazing Adhesive
Dulux Decorator Centre, 3 Liversage Street
Derby, DE1 2LA, UK
www.duluxdecoratorcentre.co.uk/stores/derby

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Authors

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Q & A SESSION

Rozemarijn van der Molen: I was wondering if you could tell us a bit more about who carried out the different cleaning techniques? Because you said the only variable was the cleaning technique but we all know that person, location, time etc makes a huge difference and I was surprised to see that Olivine had a higher score on the oxide layer retention than dry ice and walnut blasting. So if you could maybe tell us something about that?

Lyn Wilson: We carried out all the blasting with the same contractor so we knew it was going to be the same instrument, the same blast chamber that was used and everything. So we were able to try to regulate the cleaning in that sense. The Olivine, yes it was a bit of a mystery to us as well and we still need to do a bit more research into why that gave us a better result because it didn't give us an improved result with for instance bend testing or anything. There was a sort of a hardening effect seen there, which you would expect from hard blast media, but we're not really sure why the Olivine gave us a better result there. But I can get back to you on that one once we've done a bit more interpretation.

Rozemarijn van der Molen: So let's say with the dry blasting media you were using the same machine but the dry ice would not be used in the same…

Lyn Wilson: No, sorry the dry ice would not be used in the same machine, but we tried to ensure that they used the same pressure, the same angle and the same distance from the sample.

Rozemarijn van der Molen: So you've got all those parameters?

Lyn Wilson: Yes, I can give you all those parameters and we can compare.

Mark Erdmann: Both presentations were fascinating, thank you very much. My question is, well I have several, but regarding the flame cleaning. Was there any mechanical cleaning necessary afterwards in order to prepare it for painting?

Lyn Wilson: We weren't painting the samples afterwards in this case. It was just really to assess the cleaning on its own. But we did use manual wire brush cleaning in association with the flame cleaning just to remove the loose paint and corrosion after carrying out the cleaning process.

Mark Erdmann: Because presumably the recommendation that you would essentially come up with would be for homeowners to clean and repaint?

Lyn Wilson: Yes of course, yes. We're going to be coming on to look at coatings as part of the research program. So we still have to cover that.

Mark Erdmann: Quickly, what is Olivine?

Lyn Wilson: It's used quite widely in Scotland certainly as a blast medium. So it was one we felt important to look at.

Olivine is magnesium iron silicate with the formula $(Mg,Fe)_2SiO_4$.

Vasilike Argyropoulos: I had a question about your laser cleaning. We've done research on laser cleaning of iron and we found it was one of the best methods to clean iron. We compared it to mechanical and chemical cleaning that was done by conservators with 20 years of experience. It was found that they could not do the kind of work that the laser had done. It really depends on the type of laser you are using, the wavelength and the contact time so that would be my first question, especially when you have surface detail – engravings or decorated surfaces – the laser is phenomenal. So I guess my question is: what was the laser? Maybe you should go back and revisit it, although it may be a slower technique than chemical or flame cleaning, but if you want fine detail – laser is very good.

Lyn Wilson: That's really interesting to know and I'd like to get more details from you.

Vasilike Argyropoulos: We published in LACONA.

Lyn Wilson: The last LACONA?

Vasilike Argyropoulos: The one before; we also had a poster in Metal 2007 and it is also published in the scientific literature as well.

Lyn Wilson: We can speak further about that. As I mentioned it was a stone cleaning laser that we used. It was a Nd:YAG 532 nm laser – the parameters were set up for stone cleaning. So it may be that if we had altered the parameters then we may have gotten a better result. Obviously it is not something we can use on a wide scale, we can't say to homeowners 'go out and get yourself a laser'. But for high quality detailed work – and if you've got good results then I'd be interested to find out more about that.

Jason Church: You talked a little bit about the welding repairs. Did you also test TIG welding [tungsten Inert gas] with cast iron filler rod? Is that also in the paper?

Lyn Wilson: Yes we did. It's mentioned in the paper as well, but as I said it is all very early stages of the results. But yes we did try it with the TIG welding too and actually got a good result.

Karen Stedmann Peterson: When testing cleaning techniques, you of course [are dealing] in such corroded parts, you both have to take care of getting something that is delicate enough and also something that is thorough enough i.e. still has enough residual mechanical strength because the chlorides are always in close contact with the metal. Have you tested how fast corrosion reappeared on your surfaces or how well you cleaned it, how stable it was?

Lyn Wilson: Not in the test samples that we looked at. We just analyzed the immediate effects of the cleaning. With the *Bute Canopy* we certainly have the facility to go back and to monitor any corrosion there. So certainly with in situ samples, that is something we can look at.

Randall Heath: Just wanted to make a comment on the flame cleaning method. At least here in the U.S. doing that process commercially is prohibited, primarily because of the health issues with the lead and things of that nature. I was curious at what pressure did you do all of your blasting?

Lyn Wilson: It was quite high a pressure – it was 7 bar. I don't know what that is in psi [101.5 psi] but that is the standard that we find is used in Scotland. This is architectural ironwork. So that's what the contractors used. So in this early sample pool we didn't want to say, go down to 3 bar, because that's not representative of what actually happens in real life. So we kept it at the 7 bar but are very conscious that that is a high pressure.

Randall Heath: Yes, I will have to go back to my computer and convert bar to psi. Because in our business we blast between 20 and 30 psi all the way up to 300 psi. So if you need more or less aggression there are ways. The process you did is nominal. It is probably most widely used here.

Lyn Wilson: Yes it was just difficult because we had so many cleaning techniques to look at and we just wanted to keep the pressure the same for this initial sample set.

Rozemarijn van der Molen: Just a general thing I wanted to mention is that blasting pressure is not the same as particle velocity. Actually we should be measuring particle velocity - something that I didn't do in my research. I was just wondering if anyone here had any experience in measuring particle velocity and if there is an easy way to carry that out?

Lyn Wilson: It's not something that we look at either, although maybe someone else has an idea.

Rozemarijn van der Molen: Because you can imagine if you've got a big heavy particle in a stream it might go slower than a light one etc.

Jannicke Nienhuis: What's a reversible weld?

Lyn Wilson: We found that with some of the cast iron samples the welds did actually come apart afterwards so we could hammer them out, I guess, if we wanted to.

Jannicke Nienhuis: Well, that's a BAD weld then!

Lyn Wilson: Yes!

A STUDY OF COATING MATERIALS FOR OUTDOOR IRON OBJECTS

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Abstract

This paper presents results from tests to determine the effectiveness of a coating system for outdoor cast iron objects. The anti-corrosion primer VpCI-383 and fluorocarbon topcoat V-Flon#200 were tested in different combinations that included cured V-Flon#200 (CF), uncured V-Flon#200 (F), topcoat V-Flon#200 combined with primer VpCI-383 (VF), uncured, and V-Flon#200 mixed with nano silica white (NF), also uncured. The tests also included samples coated with microcrystalline wax as a reference (MW), and all coatings were applied to samples of grey cast iron. The anti-corrosion properties and the weatherability of the coatings were studied through salt spray and field exposure tests. Results suggest that the coating system consisting of VpCI-383 primer and V-Flon#200 topcoat performed the best. A second phase of this study, which also gave promising results, involved the application of this coating system in the conservation treatment of an iron cannon from the Qing Dynasty.

Keywords: outdoor iron objects, coating materials, fluorocarbon, anti-corrosion primer, grey cast iron

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Introduction

In ancient China, iron artifacts were produced with traditional iron-smelting technology. Whereas, outside China and Korea, iron was usually produced through the process of forging. In China, charcoal has been used to smelt iron long after fossil fuel was introduced (Craddock et al. 2003). Differences in ferrous metallurgy and foundry techniques used to manufacture these objects are visible in their appearance, as well as the different corrosive mechanisms that affect these materials (Su et al. 1995). In addition to archaeological finds of small objects, such as swords and tools, many special outdoor iron objects, such as the iron men in Jinci Temple, Taiyuan, Shanxi Province and the iron lion in Cangzhou, Hebei Province, have been preserved in China. More attention is now paid to the iron relics and more and more funds have been put into research and improving conditions for display and storage of iron objects. In recent years, several projects were undertaken by the Chinese Academy of Cultural Heritage in Beijing to study appropriate conservation materials and techniques for the conservation of iron objects. The aims of this research were to select suitable conservation-grade materials and establish a systematic research methodology to assess potential coating materials for potential use in the conservation of iron artifacts. This paper presents the findings of this recent research.

Aside from more traditional materials, such as microcrystalline wax, modern synthetic materials like epoxy resin (Busse 1997) and inorganic-organic hybrid materials (Seipelt et al. 1998), have been tested in the conservation of outdoor iron artifacts. Fluorocarbon coatings are materials in which a polymer or copolymer of fluoroalkene are used as a binder. Fluorocarbon coatings have many excellent properties such as weatherability, corrosion resistance and chemical resistance (Vecellio 2005), which are important for the conservation of iron objects. In recent years, there have been some tentative applications of fluorocarbon coatings in the conservation of cultural relics in China (Li 2002). In this study, the conservation capability of the anti-corrosion coating VpCI-383 and the fluorocarbon coating V-Flon#200 were evaluated through the salt spray test and the field exposure test. Polymer/silica nanocomposites (or hybrid) materials have good mechanical strength and weathering resistance due to the silica nano phase, and have the potential to decrease the gloss of the coating. Therefore, nano-silica white was added to the V-Flon#200 to improve the properties of the coating. Finally, V-Flon#200 combined with the primer VpCI-383 was selected to test for the surface protection of an iron cannon from the Qing Dynasty (1644 A.D.-1912 A.D.).

Experimental

Many Chinese outdoor iron objects, such as cannons, are made from grey cast iron. Accordingly, grey cast iron plates were selected as the substrate for testing of the coatings. Grey cast iron is characterized by its graphitic microstructure, which causes fractures of the material to have a grey appearance. The average content of C in the grey cast iron samples was 3.3%, and the content of Si was between 2.8% and 3.2%. The sample size was 250mmx100mmx3mm.

As described, V-Flon#200 and VpCI-383 were the primary materials selected as test coatings in this study.

These two materials were tested together, (VF), and the V-Flon#200 was tested in three additional ways; cured (CF), uncured (F) and with the addition of nano silica white (NF). The V-Flon#200 is a copolymer of trifluoroethylene and Ethyl 1-propenyl ether, and the anti-corrosion primer VpCI-383 is an acrylate latex. Samples coated with microcrystalline wax (MW) were used as a reference.

After the samples were degreased with acetone and air-dried, the five coatings were applied. Six samples were made for each kind of coating material. The products and the number of the samples are presented in Table 1. The cured coating, CF, was mixed with the hardener isocyanate, and after 30 minutes the coating was applied by spraying with an airbrush. The uncured coating, F, was applied directly by spraying with an airbrush. The coating mixed with nano silica white, NF, was first mixed together with high speed stirring (3500r) then sprayed onto the substrate with an airbrush. The combination primer and topcoat, VF, was applied as follows: The VpCI-383 primer was first applied by spraying with an airbrush. After one hour, the topcoat V-Flon#200 was sprayed with an airbrush on top of the primer. For all coatings, spray application with an airbrush was used in order to control the thickness of the film. For the application of the microcrystalline wax, MW, to the reference sample, the wax was heated to melting point and applied to the substrate by brush. The samples were not edge sealed.

The glossiness at 60° and thickness of the applied films were tested in accordance with the Chinese National Standards of painting industry GB/T 9754-2007 and GB/T 13452.2-1992 respectively.

The salt spray test was performed according to Chinese National Standards of the painting industry, GB/T 1771-2007. No scribe was applied onto the plates prior to undertaking the corrosion tests. For the test, a solution of NaCl of 5 wt.% in purified water (the pH of the solution was between 6.5 and 7.2) was dispersed onto the samples at a constant temperature of 35°C. The test surface of the samples was placed face up, and the angle between the surface and vertical was 45°.

The weathering exposure test was undertaken according to the Chinese National Standards of the painting industry, GB/T 1865-1997. For this outdoor test, the samples faced south at an angle of 45° and were exposed for a period of one year. During the year, at regular intervals (approximately every six months), one coupon of each sample type was removed and visually assessed for corrosion. The morphology of the surface of the cast iron sample prior to coating was observed with SEM. The SEM image was collected by Hitachi S-3600N, with an accelerating Voltage of 20kV.

Result and discussion

Glossiness and Thickness

Results from the film thickness and gloss test are presented in Table 2. The most widely used gloss meters are simplified goniophotometers, in which one measures a response only at the specular angle. Those most commonly used in the coating industry can take a measurement when the angles of incidence and viewing are 20°, 60° and 85°. The glossiness measurement at 60° is usually used when the coating is medium gloss. In our study, the gloss at 60° was measured, and it was found that all of the coatings have a low gloss. The glossiness of CF is in the range of medium gloss (70%~30%). For all of the other coatings, the glossiness is in the eggshell sheen range (<30%). In addition, adding nano silica white led to a decrease in gloss.

With the exception of the V-Flon#200 mixed with nano silica white (NF), coating thickness ranged from 20µm to 30µm, which is in accordance with the effective thickness recommended by the manufacturer (DNT website). After the addition of nano silica white, the viscosity of the coating material increased, and the leveling ability decreased, resulting in an overall increase in thickness of the coating. The average thickness of the NF coating was 52µm.

Name	Thickness (µm)	Glossiness (60°)
CF	30	34
F	20	<30
VF	22	<30
NF	52	<25
MW	32	<20

Table 2. Average thickness and gloss of the samples.

Salt spray test

The salt spray test was used to evaluate the anti-corrosion properties of the coatings. The five samples, CF, F, VF, NF and MW were subjected to a continuous salt spray test for 200 hours (approximately 5 wt.% NaCl at 35°C). Table 3 presents the results of the test. Large areas (>50%) of surface rust were visible on coating F after just 20 hours neutral salt spray testing (the solution is in a pH range from 6.5 to 7.2 pH), which suggested that the anti-corrosion capability of the fluorocarbon coating for

Abbreviation	Product	Number of Samples
CF	V-Flon #200 cured with hardener	6
F	V-Flon #200 uncured	6
VF	VpCI-383 combined with V-Flon #200, uncured	6
NF	V-Flon#200 uncured, mixed with nano silica white	6
MW	Microcrystalline Wax	6

Table 1. Products tested and number of samples.

cast iron is not sufficient. The corrosion resistance of VF is similar to that of NF; after 200 hours, there was little corrosion on the margin of the substrates.

The anti corrosion property of CF, VF and NF is better than that of the microcrystalline wax (MW). Generally, in spraying flat sheets, the coating is thickest at the edges and thinner just in from the edge, because the solvent evaporates more rapidly from the coating near the edge where the air flow is greatest (Wicks 2007). Because the edges of the samples were not sealed, the salt solution is liable to reach the surface of the iron through the thinnest part of the coating, resulting in corrosion on the margin of the coupons. After curing, the fluorocarbon coating exhibited excellent anti-corrosion properties. For the CF samples, there was very little rust (area <1%) visible on the margin of the coupon after prolonged spraying of up to 600 hours.

Name	Results
CF	Only pitting corrosion on the margin of the coupons after 600h, area of corrosion <1%
F	Area of corrosion >50% after 20h
VF	Only pitting corrosion on the margin of the coupons after 200h, area of corrosion<1%
NF	Only pitting corrosion on the margin of the coupons after 200h, area of corrosion<1%
MW	Area of corrosion >10% after 20h

Table 3. Results of the salt spray test.

Field exposure test

The four samples were subjected to field exposure test to evaluate the weatherability of the coating materials. During one year, the change of appearance was recorded. The results obtained from the field exposure test are presented in Table 4.

With the exception of the samples coated with VF, all the coatings underwent visible changes during 12 months of field exposure. After six months exposure, for the samples coated with CF and F, a small amount of yellow discoloration appeared on the margin of the samples, and a small amount of corrosion appeared on the margin of the samples coated with NF and MW. After 12 months field exposure, the area of discoloration and corrosion increased.

Visual examination of the coupons revealed that the VF coating (combined primer and topcoat) provided good protection even after one year of exposure. The surface of the grey cast iron sample is not smooth, with many cracks visible in the surface (see Figure 1), which could induce defects in the film such as pinholes and cratering. These defects can cause the weatherability and durability of the coating to decrease. During the film formation, the low viscosity primer VpCI-383 is liable to fill in any surface flaws and thereby reduce film defects in the topcoat. As a result, pitting corrosion could be effectively prevented. In addition, the weatherability of the fluorocarbon topcoat is excellent, and the topcoat performed well during the exposure test. Consequently, the penetration of oxygen and moisture was more difficult. The results demonstrated that the anti-corrosion primer applied in combination with the anti-weathering topcoat can provide effective weather resistance for grey cast iron.

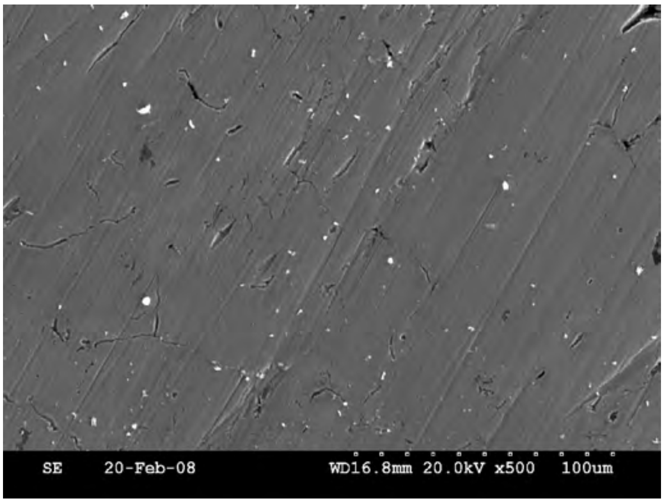

Figure 1. SEM image of the surface of the grey cast iron sample.

Coating application in real conditions

The combined application of the primer VpCI-383 and topcoat V-Flon#200 was used to coat a grey cast iron cannon from the Qing Dynasty, housed at Dagu Fort in Tianjin, which is located in the Tanggu District by the Bohai Sea, in northern China. During conservation treatment of the cannon, blast cleaning with glass beading (30-40mesh) as the abrasive, and an angle grinder, was used to first remove the rust on the cannon surface. The cannon was then soaked in a corrosion inhibitor solution of ethanolamine/0.75mM zinc gluconate (v/v=2/25) for 48 hours. After the cannon was dried with blast blower, VpCI-383 was applied in two spray applications at intervals of one hour. After the primer was applied, the V-Flon#200 was mixed with the hardener isocyanate, and cured for 30 minutes. Once the primer was dry, the pre-cured topcoat was sprayed onto

Name	After 6 months	After 12 months
CF	Little yellow discoloration on the margin	Little yellow discoloration on the margin
F	Little yellow discoloration on the margin	Yellow discoloration on the margin
VF	Unchanged	Unchanged
NF	Little corrosion on the margin (<1%)	Corrosion on the margin, little surface pitting (<5%)
MW	Little corrosion on the margin (<1%)	Pitting corrosion (>20%)

Table 4. Results of the field exposure test.

the surface of the cannon. Figure 2 shows the cannon before conservation, and Figure 3 after conservation is complete.

After treatment, the cannon was returned to Dagu Fort. This area experiences a high annual average relative humidity (RH) for the north of China. The monthly average RH in the Tanggu District in 2006 is shown in Figure 4 (the data was supplied by Tianjin Meteorological Bureau). The lowest monthly average RH in 2006 was 47%, and the average RH is higher than 70% for four months of the year.

After a period of one year, there is a little pitting corrosion visible around the tiny cracks on the surface. This result suggests that the application of the protective coating system comprising both the primer VpCI-383 and the topcoat V-Flon#200 can provide effective protection for outdoor iron objects, even those subjected to an aggressive salt-laden environment. Monitoring of the surface of the treated cannon will continue into the near future to determine the longevity of the coating system.

Figure 2. The grey cast iron cannon before conservation.

Figure 3. The cannon after conservation.

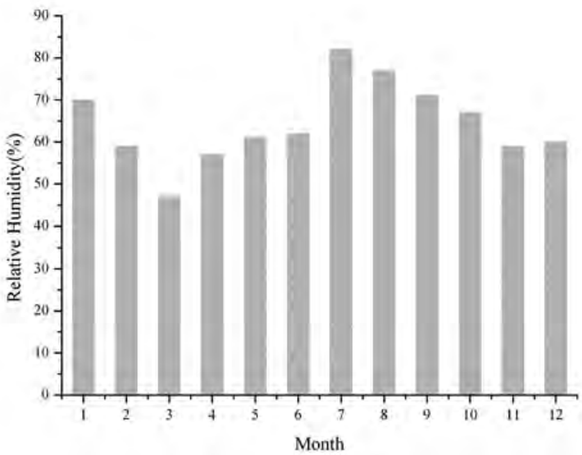

Figure 4. Graph of the monthly average RH in Tanggu District in 2006

Conclusion

The results of this study indicate that the cured fluorocarbon coating V-Flon#200 proved to have excellent anti-corrosion properties during a salt spray test. It was also found that the addition of nano silica white to the V-Flon#200 could improve the anti-corrosion performance of the coating as well as decrease the leveling ability.

The penetration of oxygen and moisture and the subsequent development of pitting appear to be effectively prevented with use of this coating. A combination of the cured fluorocarbon coating V-Flon#200 and the anti-corrosion primer VpCI-383 also demonstrate excellent weatherability and good corrosion resistance. The penetration of oxygen and moisture and the subsequent development of pitting appear to be effectively prevented with use of the fluorocarbon coating in combination with the primer VpCI-383. Results suggest that this coating system could provide effective long-term protection for outdoor grey cast iron objects. Acknowledgements

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Materials

V-Flon#200 top-coat and hardener isocyanate
DNT (DAI NIPPON TORYO) China
Room505, 17#, Shuicheng Nanlu, Shanghai, China, 201103
Tel: (86)-21-62198455, Fax: (86)-21-62190691
E-mail:dtcchen@hotmail.com

VpCI-383 (acrylic latex primer)
Cortec Corporation
Supplied by YanTai Rolmex Corrosion Inhibitor Co., Ltd.
Yantai, Shangdong Province, China, 264006,
Tel: (86) 535 6372823

Grey cast iron samples
Qinyou Instrument and Chemical Industry Co., Ltd.,
South Economic Development Zone, Gaoyou, Jiangsu Province, China, 225108,
Tel: (86) 514 84613838
E-mail: webmaster@qinyou.com

Nano silica white and microcrystalline wax
Beijing Midwest Group Technology Co., Ltd.,
Zengguang Road, Haidian District, Beijing, China, 100048
Tel: 86-10-51798242

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Q & A SESSION

Paper Not Presented

SAVING YOUR SPANGLES: THE CONSERVATION AND CARE OF GALVANISED STEEL SCULPTURES

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Abstract

Continuous or mill hot dip galvanised steel sheeting is the most commonly used type of galvanised steel for sculptures and has been extensively used by artists such as Donald Judd. This paper examines the main causes of degradation of this material. Current methods for replicating lost surfaces are evaluated and the results discussed. Common coatings, namely Frigilene (Cellulose Nitrate), Paraloid B48N and B72, Regelrez™ and Rennaissance Wax (Microcrystalline Wax Blend), were evaluated for use as an indoor coating on galvanised steel sheeting to slow down zinc corrosion based on appearance and ease of application. Three of the coatings were selected for corrosion testing using Electrochemical Impedance Spectroscopy. The results suggest that Regelrez 1094 is a more promising coating than either Paraloid® B48N or Renaissance Wax. Regelrez 1094 may form a pore blocking structure providing increased protection from corrosion.

Keywords: galvanised steel, sculpture conservation, electrochemical impedance, coatings

Introduction

Continuous or mill hot dip sheet galvanised steel (HDGS) sheeting is commonly used for constructing sculptures. Unlacquered continuous HDGS forms part of at least 49 sculptures by the artist Donald Judd. It was chosen for his sculptures due to its affordability, lack of historic baggage and portrayal as tough and durable (Williams 1998). The spangle pattern was an important ingredient of Judd's work: 'The artist's exactitude applied even to the spangles on a galvanised metal' (Temkin 2004). Other artists use the spangles and shimmer of HDGS, for example, Richard Wentworth's "Dip", in which the spangles recreate water in a bath tub.

Continuous galvanising was first used in France in 1936 (Evans 1992). In this type of galvanising, the steel is fed in a continuous sheet through several preparation baths into a bath of molten zinc. Rolls of steel are joined together to ensure the process is continuous. Traditionally, the sheets exhibit a spangled pattern of zinc crystals, as seen in Figure 1, called regular or spangled sheet. HDGS is made up of a number of different layers, from the steel substrate through the zinc iron alloys to the zinc top surface layer, which contains the spangle. The zinc layer is commonly around 25 µm thick (Zoccola 1978).

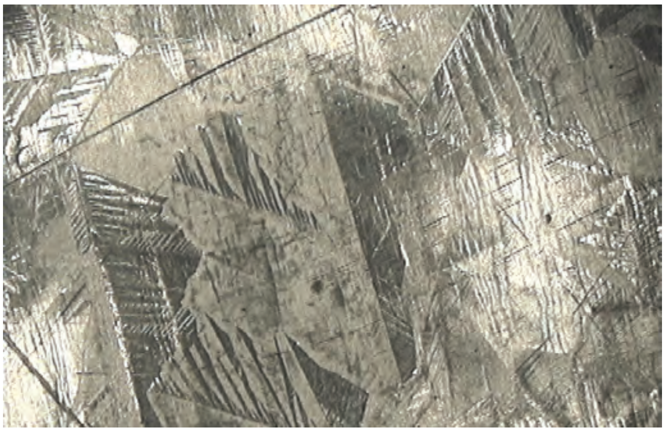
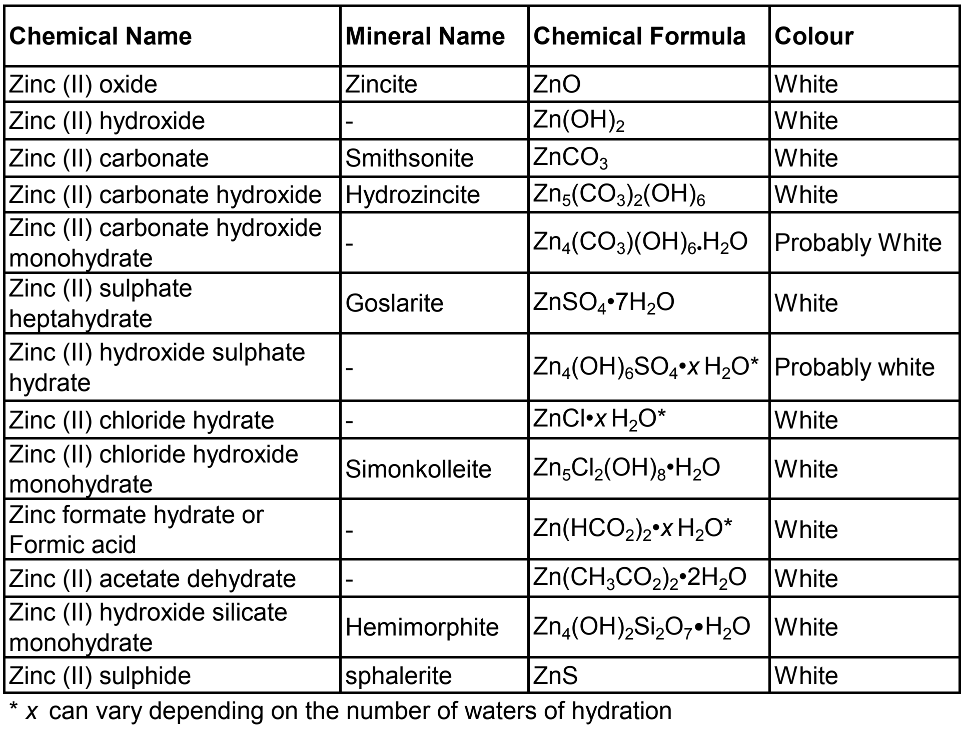


Figure 1. Spangle Pattern under magnification on Galvanised Steel.

Degradation

HDGS is designed to 'degrade' as the zinc layer corrodes to a white-grey matt zinc carbonate layer, which provides a layer of corrosion protection and a good surface for painting (Dunham 2002). However, this layer obscures the spangle pattern and completely alters the appearance of the object. Judd desired a uniform surface free of distractions from marks. Discussions with other artists, including Richard Deacon and Anthony Caro,



Chemical Name	Mineral Name	Chemical Formula	Colour
Zinc (II) oxide	Zincite	ZnO	White
Zinc (II) hydroxide	-	$Zn(OH)_2$	White
Zinc (II) carbonate	Smithsonite	$ZnCO_3$	White
Zinc (II) carbonate hydroxide	Hydrozincite	$Zn_5(CO_3)_2(OH)_6$	White
Zinc (II) carbonate hydroxide monohydrate	-	$Zn_4(CO_3)(OH)_6.H_2O$	Probably White
Zinc (II) sulphate heptahydrate	Goslarite	$ZnSO_4•7H_2O$	White
Zinc (II) hydroxide sulphate hydrate	-	$Zn_4(OH)_6SO_4•x\,H_2O$*	Probably white
Zinc (II) chloride hydrate	-	$ZnCl•x\,H_2O$*	White
Zinc (II) chloride hydroxide monohydrate	Simonkolleite	$Zn_5Cl_2(OH)_8•H_2O$	White
Zinc formate hydrate or Formic acid	-	$Zn(HCO_2)_2•x\,H_2O$*	White
Zinc (II) acetate dehydrate	-	$Zn(CH_3CO_2)_2•2H_2O$	White
Zinc (II) hydroxide silicate monohydrate	Hemimorphite	$Zn_4(OH)_2Si_2O_7•H_2O$	White
Zinc (II) sulphide	sphalerite	ZnS	White

* *x* can vary depending on the number of waters of hydration

Table 1. Zinc Corrosion products (adapted from Selwyn 2004).

found the white corrosion to be disfiguring, and it was often incorrectly assumed that the spangles would be preserved if the sculptures were displayed indoors (Nagy 2005, Fryer 2005).

Table 1 shows the most common types of zinc corrosion products. The first three products are commonly found in outdoor zinc corrosion. The last eight are more water soluble and are more likely to be found in indoor corrosion. These complexes form hazy, then matted grey-white powdery surfaces that obscure the spangle pattern. Zinc hydroxide and zinc carbonate are formed in the presence of wet and dry cycles and are unlikely to be found on indoor sculpture stored in an environment with relative humidity (RH) below 65% (Selwyn 2004). The protective zinc carbonate layer found on outdoor galvanised steel is not formed in interior corrosion mechanisms (Rahring 2002). If the galvanised steel is in an indoor environment with RH above 70%, and there are salts on the zinc surface such as chlorides transferred from contact with skin, then water is absorbed onto the zinc surface. Under these conditions, zinc hydroxides and carbonates may also form. However, other corrosion products, such as zinc chlorides, formates and sulphates, will affect the stability and formation of the protective carbonate coating.

Zinc degradation is accelerated by the presence of airborne pollutants, such as acetic acid, chlorides, formates, sulphates and ammonia (Grzywacz 2002). Acetic acid from plywood has been linked to corrosion on Judd's 'Untitled 1967', on which zinc formate hydrate corrosion product was found (Beerkens 1992). Handprints etched into the surface are commonly associated with these works, and are caused by the salts, in particular chlorides, found in perspiration (Nagy 2005). Dirt and dust, as well as residues from the manufacturing and fabrication processes, and previous use (re-use of the metal), create sites for corrosion to form. The degradation rate may be slowed or accelerated by oils and preservatives from manufacture remaining on the surface and not being washed away (Nagy 2004, 2005).

The corrosion of the zinc layer is hastened by contact with other materials. In particular, less reactive metals, such as brass, graphite and stainless steel, form a galvanic cell with the zinc, resulting in corrosion. Other materials known to degrade zinc include, beeswax, carnuba wax, lanolin, linseed oil, sulphur, alcohol/water mixes, insecticides in solution and nitrogen oxides from degrading cellulose nitrate. Zinc also corrodes rapidly in the presence of strong acidic or basic solutions. Its tolerance range is pH 6 to 10 (Mottner et al. 1995, Schweitzer 1998, Beerkens 2002, Gryzwacz 2002, Selwyn 2004).

HDGS sheets are also prone to physical damage. At the Tate, Judd's sculptures are frequently moved for display at numerous locations making them vulnerable to this type of damage. The steel sheets are only rolled to a maximum thickness of 3 mm so that the zinc can provide galvanic protection to the cut edges of the steel sheet (Everett 1994). Sheets can easily be dented or scratched, exposing the steel substrate beneath causing the zinc to corrode rapidly to protect the steel and cover the area with corrosion products.

Sample	Resin	Solvent	Matting Agent	Application Method	ΔE*94 value	Average Ranking
1	Uncoated (identified)	–	-	–	0	1
2	Frigilene	–	None	Spray	3.61	8.95
3	Frigilene	–	None	Brush	2.48	4.84
4	Paraloid B72 5g	70ml acetone, 30ml toluene	None	Brush	2.83	4.63
5	Paraloid B72 5g	100ml Acetone	None	Brush	2.54	7.05
6	Regelrez 30g	100ml white spirit	None	Brush	2.24	4.05
7	Uncoated (unidentified)	–		–	0.58	2.95
8	Renaissance Wax	White spirit	None	Brush	4.25	7.68
9	Paraloid B48N 5g	100ml Butyl acetate	None	Brush	2.57	3.84
10	Paraloid B72 5g	70ml acetone, 30ml toluene	None	Spray	3.16	-
11	Paraloid B48N 5g	100ml butyl acetate	0.1g fumed silica	Brush	2.75	-
12	Paraloid B48N 5g	100 ml Butyl acetate	none	Spray	2.09	-
13	Paraloid B72 5g	Shellsol A	None	Brush	2.07	-
14	Regalrez 30g	100ml white spirit	0.05g fumed silica	Brush	2.51	-
15	Regalrez 30g	100ml white spirit	None	Spray	3.42	-
16	50ml Frigilene	50ml reducer	None	Spray	2.02	-

Table 2. Results of the colourimeter and aesthetic tests.

Coatings

One method of assisting preventive conservation efforts is to apply a coating to an artwork. A large number of potential coatings for indoor display, which could be applied to HDGS in the confines of a museum lab, were selected for evaluation. The coatings were chosen purely to act as a barrier to pollutants and salts to slow zinc corrosion, in particular to provide a barrier to salts from accidental touching of the surface.

Following a literature review, common coatings used in the conservation of metals and commercially for use on galvanised steel were evaluated to reduce those tested to a manageable number. Only those that were clear, had good ageing properties, were reversible in the long term and had good adhesion to metals were chosen. Preference was given to coatings with the least health and safety implications.

Polyurethane, Epoxy and Heteropolysiloxane coatings were discounted due to their irreversibility on this particular substrate (Pilz et al. 1997, Mottner et al. 1995). Nitrocellulose lacquers, commercially available as Frigilene (UK) and Ercolene (USA) were chosen despite concerns over the toxicity of xylene (a component) for use on large objects, and that their degradation products may degrade the zinc layer further (Lins 2005). Acrylic co-polymer resins Paraloid B72 and B48N were also chosen. Neither are used commercially to coat galvanised steel, however, acrylic resins are becoming more common as commercial coatings (Horie 1994, Forsgren and Steihed 1999, Van der Abeele et al. 2002). Regelrez is a non-polar 100% hydrogenated hydrocarbon resin that is soluble in petroleum hydrocarbons and turpentine. It was chosen for its ability to saturate the surface and compares favourably to Paraloids in terms of stability and reversibility. It can also be mixed with microcrystalline waxes (Whitten 1995, de la Rie 1990). Natural waxes were discounted as they can cause zinc to degrade. In discussion with conservators experienced with the application of coatings to galvanised steel, Renaissance wax was the most commonly applied coating, so it was also selected for testing despite reversibility concerns (Beerkens 2004).

The appearance of the coated samples was subjectively evaluated by conservators. Samples were limited to 10 to aid comparison, and a quantitative analysis of the appearance of the coatings was performed first to further reduce the sample size for further technical analysis (Lins 2005).

Quantitative Analysis of Appearance

Colourimeter tests were carried out on 16 samples of coated galvanised steel and two uncoated galvanised steel control samples (A and G) shown in Table 2. The samples were 625cm^2 each. Only one coat of each coating was applied, although, in practice it is common for two to three coats to be applied for some of these coatings. For spray coatings, the amount of resin applied was 8 ml applied as one coat evenly across the 625 cm^2 sample.

For the colourimeter tests, a Konica Minolta CM-2600d colourimeter with 11/8 aperture was used. The results were analyzed with SpectroMagic software, which showed that all the coatings had a blue-green tinge compared with the uncoated samples. The values of ΔE*94 were analyzed, which indicates the overall difference in colour between a coated sample and the control sample. A ΔE*94 of 1 or less indicates a difference that the human eye interprets as natural variation, which was only achieved by the non-control uncoated galvanised steel sample. The majority of samples had a ΔE*94 of between 2 and 3. However, two had a value between 3 and 4 and one had a value over 4.

Qualitative Analysis of Appearance

Twenty-one curators, conservators and conservation scientists were asked to rank nine coated samples of galvanised steel, as shown in Table 2. Five were the best-performing coated samples from the colourimeter tests and two were uncoated samples. To act as controls, one of the uncoated samples was identified to the participants, but the other uncoated sample was not identified as such, allowing the participants to incorrectly believe that it was coated. An additional two coated samples that performed poorly in the colourimeter tests were added, so that the participants could compare the appearance of poor-performing coatings.

The participants found it very hard to distinguish between their top three or four ranked samples, indicating that some of the coatings were almost invisible to the naked eye. The identified uncoated sample was ranked 1, but 14 of the 21 people assessing the coatings did not place G (the unidentified uncoated sample) second. The two samples that performed poorly in the colourimeter tests were ranked as the two worst coatings.

Following the visual test described above, three coatings were selected for further evaluation:

- Brush-applied Regelrez 1094, 30% w/v in 100ml white spirit (de la Rie 1990, Whitten 1995) performed well in the aesthetic tests and gave a saturated appearance to slightly degraded GS.
- Brush-applied Paraloid® B48N, 5% w/v in 100ml butyl acetate (Van den Abeele 2002) as it performed well in the aesthetic tests.
- Renaissance Wax, a synthetic wax (25g polyethylene and 100g microcrystalline wax) because it has been used previously on works by Donald Judd (used without thinning out).

Frigilene was not selected despite scoring well in the aesthetic tests due to concerns over possible future degradation products causing the zinc to corrode.

Electrochemical Impedance Spectroscopy (EIS)

To assess the relative corrosion resistance the three coatings impart to the galvanised steel, samples were sent to Sheffield Hallam University Materials and Engineering Institute for EIS testing. This method has proven to be effective in evaluating protective coatings (Otieno Alego 1998) and has been used in conservation to assess coatings for outdoor bronzes (Price 1995, Letardi 1998). EIS measures the impedance of a sample over time. As the impedance rises and falls it indicates whether the sample is corroding, and therefore, how well the coating is protecting the underlying metal.

One application of each coating was applied to three samples of cleaned 100mm^2 HDGS sheet. In addition, three cleaned uncoated samples were tested. A 44mm diameter Perspex cylinder was adhered to the center of the sample with silicone sealant that does not release acetic acid on curing. An electrolyte of 0.35% sodium chloride in deionised water was placed in the cylinder. The samples were tested for 29 days to establish a ranking. Experimental parameters were a frequency range of 100 kHz – 100 MHz, AC perturbation, 10mV rms. Temperature was kept at 20 degrees Celsius.

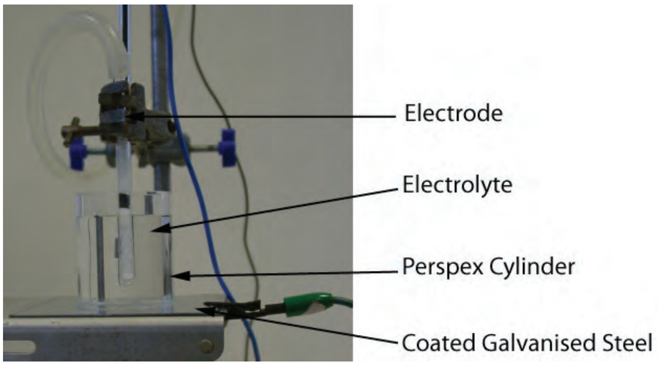


Figure 2. EIS apparatus set-up.

For the uncoated samples, the impedance values are initially high, falling after five days to a lower value, indicating the initiation of corrosion activity on the surface. The underlying steel becomes exposed forming a galvanic cell between the substrate and the coating. The corrosion products formed eventually create a barrier isolating the steel, and the impedance increases.

The data for Renaissance Wax are similar to the uncoated substrate, indicating little change in behaviour. For two of the Regelrez samples, the coating achieved impedance values in the 10^8 Ωcm^2 range. This was reached after an initial fall to 10^4 or 10^5 Ωcm^2. The initial fall in impedance suggests a breakdown mechanism occurring in the coating, allowing the solution access to the substrate. The subsequent rise of the resistance to a sustained level, several orders of magnitude greater than upon initial exposure, suggests some interaction between the corrosion products and the coating.

Paraloid® B48N initially behaved in a similar way to the Regelrez 1094, recovering to 10^8 Ωcm^2. However, the recovery is not sustained, indicating a breakdown in the coating.

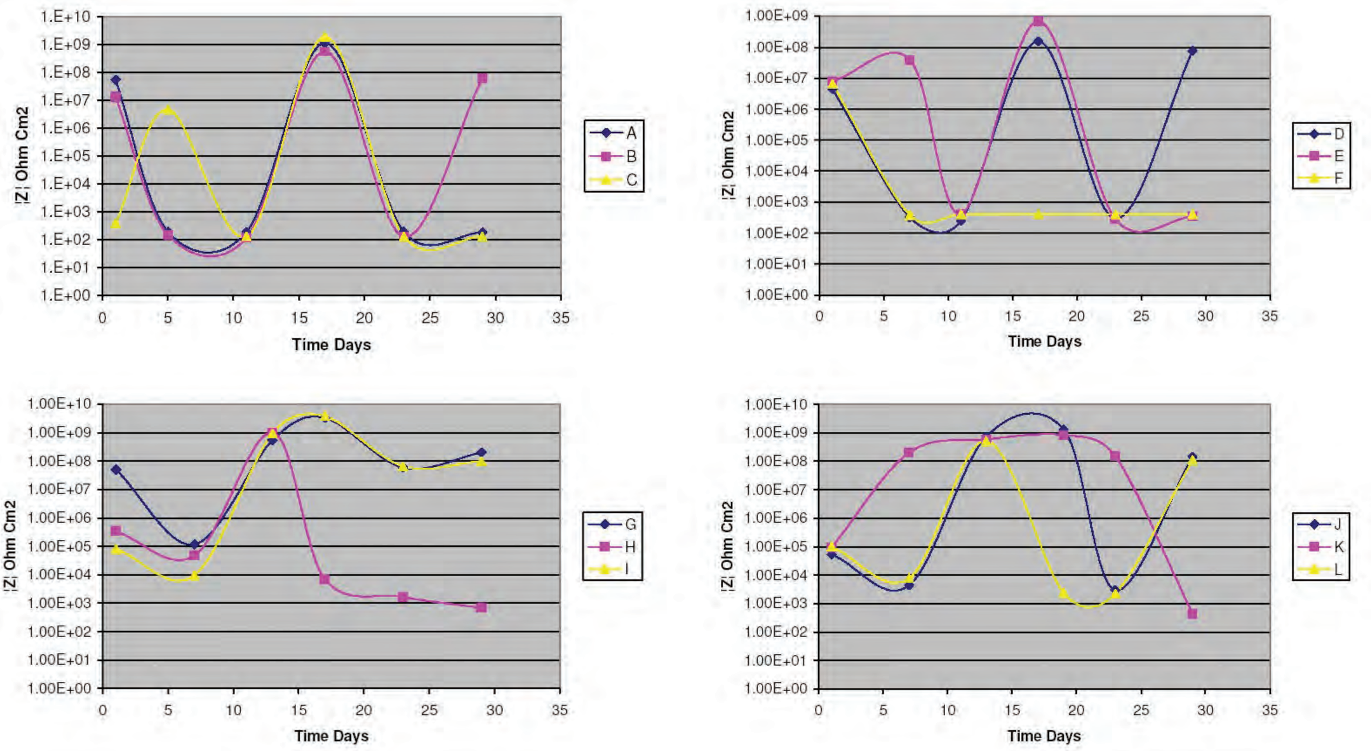


Figure 3. Graphs showing the overall impedance for the samples. Uncoated (*top left*, samples A, B and C), Renaissance Wax (*top right*, samples D, E and F), Regelrez 1094 (*bottom left*, Samples G, H and I) and Paraloid® B48N (*bottom right*, samples J, K and L).

Figure 4. Samples after 29 days of testing. Uncoated (*top left*), Renaissance Wax (*top right*), Regelrez 1094 (*bottom left*) and Paraloid® B48N (*bottom right*).

Interpretation of EIS Results

All the coated samples show initial protection afforded to the HDGS by the coating. After initial protection, the breakdown of the coating and subsequent zinc corrosion is seen. At this stage, white corrosion products will obscure the spangles and irreversibly change the object's appearance. Subsequently, some of the samples showed the galvanic properties of the zinc protecting the iron substrate, and finally, the iron corrosion occurring unhindered.

Regelrez: this coating performed best under EIS. The EIS results indicate that the early occuring corrosion products from the zinc effectively block the pore network of the coating increasing its barrier effects and slowing the rate of zinc corrosion. Further testing, of solutions modified with stabilisers and mattifiers commonly used with Regelrez 1094, is needed on a larger scale to assess its effectiveness in real life situations. Fadeometer-style testing for possible coating deterioration by light energy would be of interest. Expanding the tests to get data that model outdoor corrosion, such as standard alternating spray or condensation atmosphere testing, would be useful, especially when comparing against waxes and acrylic resins.

Paraloid® B48N: this coating ranks second as it does appear to provide some degree of protection to the underlying metal. However, the breakdown of the coating is quite rapid and there is no interaction with the substrate in terms of pore blocking.

Renaissance Wax: EIS data indicate this is a poorly protective coating that very quickly lost any initial protective properties. Due to concerns over removability, and its poor performance in these tests relative to the uncoated samples, it is suggested that Renaissance wax should be avoided.

The test represents an accelerated state of constant attack from salts on the coating and a 100% relative humidity level. Under indoor museum conditions, both Regelrez and Paraloid® B48N may be suitable to protect HDGS sculptures from handling. Both of those coatings showed an improvement over the uncoated and wax coated samples.

Replicating Spangle Patterns

If corrosion has already affected an object fabricated from galvanised steel sheets, replicating the spangle pattern is an option that might be considered by a conservator. The spangle patterns are unique and are difficult to replicate. Polishing off corrosion creates a flat surface different from the varied surface topography found on the original. Repeated polishing will expose the dark grey zinc-iron alloy layer beneath. The variation of thickness and topography of the layers means it is difficult to predict how much polishing will expose this layer. Lins (2005) has experimented with glycolic acid and electro-polishing, to remove corrosion from the surface although this also can reveal the grey metal substrate.


Figure 5. Minor fingerprint etching and degradation due to handling.

Re-creating the spangles through re-dipping the piece by batch hot dip galvanising is possible, but would create a very different appearance from the original. The joins and edges of the sheets would be covered and the spangle pattern altered. Re-fabrication of the piece is another option, but may not always be possible or desirable.

Options to optically recreate the effect of the spangles were explored. Zinc or aluminium-based paints are used commercially as they offer some corrosion protection, but are very thick and form obvious patches. Graphite-based resin has been used for an optical repair (Beerkens 1992), although graphite should not be applied directly to galvanised steel as it can create a galvanic cell. Mica pigments have been used in a wide range of media. They can be applied to reflect light in different directions mimicking spangles (Landgrebe 2005). Aluminium powder in a Golden Artist Colours™ Acrylic Gloss Medium or 24-hour oil size can be toned to give the impression of spangles as shown in Figure 6. Metal leaf can be toned to give a spangled appearance, but only aluminium is suitable for direct application onto zinc.


Figure 6. Aluminium powder in Golden Artist Colours™ Acrylic Gloss Medium.

Holographic sheet also gives the appearance of spangles. Created by sputter coating aluminium onto a polyester film, this works best for covering a whole section rather than just a small area, although it can be cut out to cover a patch. The film can be tinted using spray applied airbrush acrylics to match surrounding spangles and can be attached to the galvanised steel substrate using Paraloid® B72 spray adhesive as shown in Figure 7.

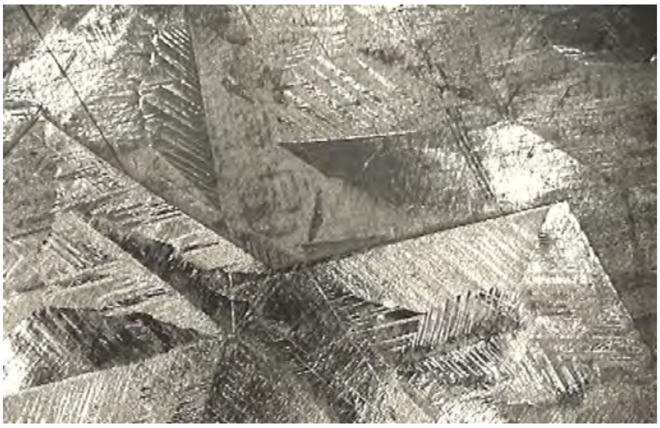


Figure 7. Join of holographic film (top right) and uncoated galvanised steel (bottom left) under magnification. Note the edge was cut to fall along the line of the spangles.

The process of sputter coating aluminium could be applied directly to a cleaned flat area of galvanised steel. For larger works with substantial losses this may be effective but requires further investigation.

Electroplating has not yet produced good aesthetic effects and involves cyanide-based solutions (Lins 2005). Soldering with zinc-based alloys is carried out in industry, although its application method and safety implications exclude it from most conservation uses.

Conclusion

Despite concerns by Judd (Temkin 2004) about coatings interfering with the relationship of the artwork and the viewer, it was shown that coatings on HDGS can be practically invisible, even to museum professionals, and that some offer a greater level of protection over no coating. In this study, tests revealed that Regelrez offered potential for further investigation as it saturated the surface, performed well in identification of coatings tests and provided some interesting EIS results.

Spangle recreation needs further exploration with aesthetic results so far proving less than ideal. In light of this, preventative conservation is essential and typical handling guidelines are recommended (Nagy 2004). For new HDGS artworks being accessioned, an artist interview discussing their attitude towards the conservation and coating of their artwork is essential.

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Materials

Mill Hot Dipped Galvanised Steel Samples
Fowle & Co Ltd, Menzies Road, Hastings, East Sussex
TN38 9BQ, UK
Telephone: +44 (0)1424 444666

Mica Pigments
Merck Chemicals Ltd, Boulevard Industrial Park, Padge
Road, Beeston, Nottingham,
NG9 2JR, UK
Telephone: +44 (0)1202 785309

Polyester Galvanised Film
Steven Schwimmer Shops in Paper Corp, 50-05
Metropolitan Ave, Ridgewood, NY 11385, USA
Telephone: +1 718 417 3333

Regelrez
Talas, 330 Morgan Ave, Brooklyn, NY 11211, USA
Telephone: +1 212 219 0770

Paraloid B48N and B72, Rennaissance Wax, Frigilene
Conservation Resources UK Ltd, Unit 2 Ashville Way, Off
Watlington Road,
Cowley, Oxford OX4 6TU, UK
Telephone: +44 (0)1865 747755

Golden Artist Colours™ Acrylic Gloss Medium
Addington Conservation Supplies, Addington Studio,
The Old Bakery,
Marshwood, nr Bridport, Dorset DT6 5QF, UK
Telephone: +44 (0)1297 678247

Aluminium Powder
Stuart R Stevensons, 68 Clerkenwell Road, London
EC1M 5QA, UK
Telephone: +44 (0) 20 7253 1693

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Derek Pullen is head of the sculpture conservation section at Tate UK supporting exhibitions, displays and acquisitions programs at Tate's five UK sites. The section is responsible for three-dimensional artworks in all media ranging from traditional materials, such as marble, to ephemeral media installations. His conservation interests include the technology of modern materials, sculptors' studio practice, and design for art in transit. He also acts as a consultant to several UK public bodies, is a trustee of the Public Monuments and Sculptures Association (PMSA) in the UK, and a member of the steering committee of the International Network for the Conservation of Contemporary Art (INCCA) in Europe. Email: Derek.Pullen@tate.org.uk

David Greenfield received a PhD at the Corrosion and Protection Centre, University of Manchester Institute of Science and Technology, UK. His PhD research was carried out as part of the Organic Coatings and Cathodic Protection Group within the Corrosion and Protection Centre. His research considered the role and importance of interfacial processes in the failure mechanisms of blistering and delamination of organically coated mild steel. Since joining the Centre for Corrosion Technology in 2000, Dr Greenfield has continued with his interest in organic coatings alongside the development of a suite of scanning electrochemical techniques held in the centre. Email: d.greenfield@shu.ac.uk

Q & A SESSION

Paper Not Presented

Caring For Outdoor Cultural Heritage

Chair: Shelley Sturman
Panelists: Tony Rajer, Patty Miller, Joe Sembrat, Lyn Wilson, Ali Davey

Tim Foecke: Specifically with regard to the canopy here. First of all congratulations on being able to arc-weld wrought iron. Ordinarily that's impossible because you melt the slag and coat everything with glass and nothing sticks to each other, so you did a good job! For a surface clean that is much more aggressive than what I've seen in the other presentations like this. One thing you might want to consider is shot peening with something that chemically matches what you are peening, because you get some other advantages that you didn't get into, for example shot blasting to the point of putting a compressive stress on the surface, that is actually called 'shot peening', and it cuts down fatigue cracking but also if you put a large compressive stress on the surface you are going to cut down corrosion considerably because it gives an extra energetic bump that has to be overcome by any corrosion process. And if any embedded material would be the same chemically as what the substrate is your patina is probably going to look just the same sort of thing also. I had a more general question based on probably some of the terrible things that I've done to artifacts in the past… when it comes to cleaning this and also it came up with the Hunley with the bolts. Does anyone use thermal shock as a way to get encrustation or coatings or whatever off of substrates? When I had hull samples from the Arizona that had an adherent encrustation – I dumped it into liquid Nitrogen and then put it into a desiccator so that it would dry without forming frost on it. One thermal cycle given that the ceramic is ten times the thermal expansion coefficient of the substrate – both the interfaces lose. I also did the same thing with rivets recovered from the Titanic. They were completed encrusted, dunk them in and the encrustation came off in one piece. Even the crevices on the iron were clean. Is this anything that anybody uses or is it just simply too brute force?

Ian MacLeod: Yes I published a paper on this technique for deconcreting marine iron artifacts and it works very well. I've been able to get rock-hard concretion from totally mineralized sardine tins and you can even see the mineralized sardines inside the remains! There is nothing left of the tin, but you can keep the contents, and then freeze-dry it. But we've used it on delicate artifacts from Historic Scotland – they used it for deconcreting a composite hilt on a sword from the wreck of the Swan – one of that mongrel Cromwell's shipwrecks. He is a mongrel because he killed 651 of my clansmen in the battle of Worcester, but that is another story!

Unknown Name: Ian, how long is the object submerged in the liquid Nitrogen?

Ian MacLeod: Basically put it in until it stops going 'Pshhhhh'… and so it depends on the size and the mass of the object. So you basically put it in until it gets cold. And what I then do is I plunge it into water and if you've got something like a big cast iron anvil you can put your tongue on the artifact – I did it to prove it to the archaeologists –after deconcreting the anvil I put my tongue and lips on it and it wasn't cold and yes, I've still got my lips, so…!

Randall Heath: From a commercial point of view, I've used liquid Nitrogen to recover forged aluminum parts that have rubber vulcanized to them. Put it into liquid nitrogen, leave it for a few minutes and then put it in a plastic container. Tap it with a mallet, it shatters and you get your part back. Also I did a demonstration at a military facility where they are decommissioning nerve agent – very poisonous type things. I was there to take coatings off the floor. They were going to decommission the entire facility. I was there to demonstrate dry ice blasting, because they are very worried about secondary waste with all the toxins they have out there. But something I just did kind of as a test was I took a bucket of dry ice and poured it on the floor that I was going to demonstrate and the coating just peeled up, it erupted like a volcano! And I removed the stuff – they didn't need any dry ice to remove that coating, or any blasting. Just the dry ice!

Unknown Name: Did you get the contract?

Randall Heath: They are doing it themselves!

Paul Mardikian: One word of caution about liquid nitrogen, I mean it doesn't work on everything ok. And you need to have still an interface somewhere near the original surface. Because otherwise you will blast or destroy your artifact completely – I've done that! So we have to be aware that this might work in some cases but if you have one single artifact that you want to clean – and if you have tons of them, then you can play with them, right, a cannon ball or.... But if you have one single artifact and there is no technique that would work, you might be tempted to use this technique! But you need to understand that if it doesn't work you might create a lot of damage.

So…just several comments about the papers: It was really bright and so interesting. About Joe's paper: what I love about your paper is the fact that you are putting together the industrial world and what basically people do for their living is to repaint structures – and you adapt that as a conservator, aware of the artifacts and aware of their flaws and problems and that's what I like about your approach here on the artifacts so I was really happy to see that. And at the same time you use the standards and you adapt them the way you can to have this quality and control, which is really nice, we need this. One word about reversibility or retreatability: when you said Joe, that you could basically remove any kind of coating – well, I would say it's probably possible on most of the artifacts, but when it comes down to artifacts that we work on that are extremely porous, that have slag and deep crevices and all of that, removing a coating from a fragile surface can be extremely difficult and I think that in some cases we have to really differentiate what we're working on. But when it comes to objects that have suffered extensive corrosion particularly on the seacoast and artifacts made of wrought and cast iron, I think that it could be very difficult to remove some of the hardest coatings. So it was just one word about that, thank you.

Joe Sembrat: If I could comment on I guess the first point. First of all thank you for the compliment, but getting back to coatings. This is an industry that billions of dollars are spent in researching technology in regards to surface preparation and to the coatings themselves, and to application and so on and so forth, that there's no sense in us reinventing the wheel for a lot of what we do, but as you said, to know the limitations of what industrial technology offers us and tailor it to conservation. And getting back to this developing of a standard, we should pick it up, and it is not developing a standard that this is how you should treat a cannon, or this is how you should do something. I think it's developing repeatability and understanding what the results are and the tests that we are doing so the simple thing of just measuring the thickness of a coating I think is critical so that if we are doing work here in the United States and you're doing something in France and someone else is doing something in Australia, we can compare apples to apples and we're not talking about one coat, because my one coat can differ significantly from yours. And once again as you saw in some of these ASTM standards, these things are really thought through, I mean these are top people in the field who develop these protocols for testing and so forth. So, I think it's really something that we need to look at and adopt and although these techniques that we are using for monitoring coatings for large, outdoor industrial artifacts, they're also relevant to archaeological artifacts also. That continuity tester can be utilized in a much smaller way, it's a very simple thing and the tools are not expensive either. And they're the difference between a successful treatment and a not successful treatment because ultimately your coating is the last and the first barrier to getting to your artifact. And reversibility; Malcolm Collen and I were having this discussion on treatments and so forth, I completely agree with you, I would not use epoxies on archaeological artifacts and so forth, but I think the issue needs to be addressed. Once again, I think we hold onto a term and it's applied across the board for everything, and people don't tend to look beyond a certain statement or a saying, so that's my two cents.

Virginie Ternisien: I've got a general question: because we're talking about outdoor heritage, I'm just thinking if you took into consideration direct impact of the environment on your object because, maybe the particular location of your object, maybe of the shape, you could have, I guess some parts which could be more exposed to the environment, and so, which could react differently, and so…..

Patty Miller: I will just speak very briefly about some of the research we did before we worked on either of the Saturn V projects, which was, we actually got a lot of the climatological data, it's all available on the internet for purchase, these different climatological data's for the area, and it not only gives you your range of all of your environmental information for a year or multiple years, it also can give you contaminations in the atmosphere, so they have collecting stations nearby. It happens to be that since we were at JSC there was one very close by, we were at Johnson's Space Center and they are always measuring and testing the air quality of that area, so we had excellent information knowing that the amount of aerosols and other contaminants in the…because there they are actually surrounded by many, many chemical factories and refineries, so again, and you only have to go 20 miles away and they're also testing the air quality and all of that sort of swells and sits right around where that rocket was before we put the building over it, and is one of the reasons it was an excellent idea to put a building over it. We did the same thing in Alabama and at that location, it was sitting down in a valley and it was right next to Redstone Air Force base where they also fire off ordinances and all sorts of things, and they also have environmental data, contamination data, you know atmospheric data. So, its available in a lot of the places if you know where to look for it, and I think it is usable and we kept it in terms of what sort of protection the coatings should have to provide. But obviously on those two projects they went for a period of time outside coated and then had, one was moved to the interior, actually it was physically moved, but its something that we keep in mind every time we are doing and planning these outdoor projects.

Peter Northover: Comments for Lyn and Ali on an area of welding. I was very glad to see some microstructures because you do need that monitoring on what you're planning to weld so that you can choose the weld so that you don't produce an inappropriate microstructure. I've recently come across two things, one was we were looking at an electron beam weld on a race car, part of a race car transmission, and the robot had not stopped in the right place and it had re-heat treated part of the weld to pure martensite. So the first time the car went out it broke. So, you do want control of the microstructure. And I'm at the moment looking at a very elegant and delicate medieval Islamic brass, openwork hanging lamp, very delicate, and at some stage quite some time ago it had been repaired with a copper phosphorus brazing alloy, and sufficiently long ago that the braze is corroding. But those alloys are actually rather brittle and that is totally inappropriate for fixing very delicate thin sheet, because, you know, bits are just breaking off. So you do have to really pay attention to the microstructure when you're welding some of this historic material.

Lyn Wilson: We actually found that the microstructural analysis was the most useful part of the suite of tests that we carried out, both the optical and the scanning electron microscopy, so thanks for that, it is certainly something to think about.

Peter Northover: Metallurgists are sometimes useful people!

Adam Jenkins: I have a handful of questions for the panel, but also some of these are for the floor. The first one relates to the use of ultra high-pressure water. We found that when we used it, the machine itself sprays out quite a lot of oil from the actual unit on your object, and I'd like to hear how people have cleared that oil in practice, because you end up with a very reactive surface when you clean it under that much pressure and then adding the oil to it that just adds more steps that could complicate further the cleaning process.

Joe Sembrat: That did happen in certain instances, but there's a problem then with the gaskets in the unit, that was addressed when that happened the first time and it did not happen again after that. Basically the oil should be nowhere near the nozzle rotation, but yes, I would imagine that would be a mess, contaminating your surface. But are you talking about actually in the water flow or coming from the rotation of the nozzle, because I noticed in Tony's paper that they had a UHP gun but there was not a rotating head on it and it was just a fan tip.

Adam Jenkins: It's related to the spinning of the nozzle.

Joe Sembrat: OK, there's probably an issue related to the nozzle because these guys are working in nuclear reactors, I mean they are even much more stringent than we are in regards to contaminations and so forth. So I would think maybe in that one case it's related to probably a faulty unit.

Adam Jenkins: Thank you. The second question was for Lyn and Ally, did you record the energy densities when you laser cleaned the samples?

Lyn Wilson:: Sorry, did we record what?

Adam Jenkins: The energy densities when you did your laser cleaning?

Lyn Wilson: No, well actually it was just a very quick test that was kind of added on at the end of the suite of experimental methods simply because we had the facility available for stone cleaning, but certainly now that I know that there's a lot more literature out there and people have cleaned metal with lasers very effectively I'll look info that further now.

Adam Jenkins: With higher-powered lasers with higher energy densities and very short pulse lengths you can clean rust very effectively.

Lyn Wilson: Thank you.

Adam Jenkins: My third question is for Tony – I'm still not completely clear about the function of the red layer below the zinc chromate primer.

Tony Rajer: We put the red layer on because French had originally specified that and I wanted to maintain the artistic integrity as much as possible. That's why.

Adam Jenkins: So why add the yellow layer on top of it?

Tony Rajer: There was a lot of discussion about this and I would have preferred to put the gold on top of the red layer, but it was felt that the intensity of the gold would be more magnified by having a substrate of the yellow.

Adam Jenkins: Thank you.

Philippe de Vivies: I have a comment on what Joe just said before about not re-inventing the wheel and we know there is a system that exists for coating and anti-corrosion and it's interesting to use it, but what Joe didn't say is about the warranty time of the system. I work in France on a metallic structure where I apply three different layers of that corrosion system and paint, and then after that the warranty they gave was 7 years on it. And so I think it is interesting as a conservator to remind that….I mean we had a discussion about coating and we are hoping to apply one thin layer of coat and it will last at least our time as a conservator. After retirement is fine but at least we hope that we can keep that until that time. But you see in the industry they have a really good layer and a good system and people spend billions of dollars to try to find the right thing, but the warranty that they give is minimal, so we need to keep that in mind. It's not a forever thing and we need to think when we as a conservator apply a system and coating, we need to remind the owner that they need to keep going and that layer is not forever. And that was just a [comment] to add to the discussion we had the other day.

Patty Miller: Warranty questions do come up and mostly we have the discussion on warranties with coating manufacturers in order to placate the client knowing that they are getting something, but also for us to have a relationship with the coating manufacturer and understand any changes that we do aren't going to affect that warranty, because one of the things working on coatings on these deteriorated [materials] where materials have been significantly altered, surfaces have been significantly altered due to corrosion, to follow their stringent primer methods and to use all of the undercoat layers as specified by the topcoat manufacturer. So I know when we were choosing our coatings they said to us if you don't use our primers, we are not going to warranty your topcoat and mixing can happen with conservators I think a lot and you have to be very aware of it because they may have a warranty on the topcoat but if you don't include whatever they say should be in the primer then you're out of luck.

Philippe de Vivies: And the way you prepare the metal before you put your layers on. And I have one other question about, sorry, I missed part of the paper because I had to go to the airport, but about the wrought iron welding. Did you do any analysis on the amount of phosphorus you had in your wrought iron because I mean this time period is where the puddle iron, such as the one that is used by Eiffel in this era, is really difficult to weld. I mean you can weld it and I did welding and then I did metallographic [analysis] but there was no diffusion in between the new steel and the old part. So I just wanted to know if you had done characterization of the elements of your wrought iron.

Lyn Wilson: Yes, we did an SEM analysis and an EDX mapping of the wrought iron, the control sample and there was a low amount of phosphorus – phosphorus was present but it was quite low. So perhaps that was why we were able to carry out the welding.

Philippe de Vivies: OK, thank you.

Carol Grissom: I was involved in a project on silver coatings that was presented by Nicole Grabow at Metal 2007, and this is more of a plea along the lines of Joe's paper, for people to please report the thicknesses they use on coatings. We were concerned about whether our coatings and tests replicated what conservators actually used and we found almost no publications either in the testing literature or in the more practical conservation literature about what the thicknesses were of coatings. We did try to test some coatings on objects but of course it is very difficult to do that because you don't have such a flat surface and if you have any corrosion it ruins your measurements. I don't know how many people have thickness gauges but they are not terribly expensive or terribly rare so I think it would be great if people reported that kind of thing when they do treatments as a sort of matter of course.

Tom Chase: I have two different comments; one was the question of particle velocity and blast media. When Nick Veloz and I did our work about glass bead peening etc., we did some measurements of particle velocity. We were collaborating with someone at the National Bureau of Standards (NIST) and it was very useful and interesting, he had some good equipment to measure particle velocities. I don't know what's happened in the last 20 years in terms of that kind of thing, perhaps we could find something that would be even cheaper and easier to use and then we could all measure our particle velocities, because I think that is a very important thing to measure.

The other question was for Tony. Tony, you chose a traditional gilding method; some other people have used epoxies. I want to go back and look at your paper, but I think it would be nice to try to collect what everybody has done within recent memory about gilding so that we've got it recorded so 20 years down the pipe we can say 'Oh yes, that epoxy lasted really good, or the traditional method was better than the epoxy'. I think it would be very useful to collect that information.

Tony Rajer: I think it would also Tom, and I tried to collect as much data, comparative data, as I could, from interviewing conservators in Italy and France as well as in the United States from the other projects that had taken place. And Arthur Beale was also very helpful because of his connection with helping to spec the conservation of the Sherman monument in New York, but I would agree because I had difficulty finding data, comparative data and I went with that traditional approach because it seemed to be the consensus among the conservator's that I was interviewing.

Shelley Sturman: Tony how many years were there in between when you did your initial [conservation work] and then when you went back and had to do the falcon clean-up?

Tony Rajer: It was approximately 14 years.

Shelley Sturman: And what was the condition way up there at the top?

Tony Rajer: You know, I tell you Shelley I was surprised at how well it had held up, and I think part of that be because in Wisconsin we have little or no industry, so there's no real pollution you know in the environment, and I looked at it with the telescope, in fact I just looked at it with the telescope just a few weeks ago before I came here and I was surprised how well it was holding up considering the exceedingly harsh winter we have in Wisconsin. In the paper there is some statistical data about the weather conditions too, because I went to the weather bureau to get them.

Shelley Sturman: So, Tom there is your first data point, and then find an equivalent epoxy gilding.

Joe Sembrat: Tom, I don't know if you know Mike Kramer from Maryland, from the Gilders' Studio? He's done a lot of research into gilding and I think is the head of the Gilders' Studio, but has done a lot of research, now we can't use zinc chromate any longer since Tony's treatment so that is another primer that's out, but there's a lot of butyral primers, pre-treatments and things that Mike has used, and he is probably the most knowledgeable person I think in the US in regards to outdoor use of gilding so that would be a good contact.

Shelley Sturman: Joe would you repeat that name?

Joe Sembrat: Mike, Michael Kramer spelt with a K, from the Gilders' Studio and he's in Olney, Maryland.

Lyn Wilson: Tony could I just say that at Historic Scotland we carry out a lot of outdoor gilding as well and one of my colleagues is actually currently on-site re-gilding a project that he only carried out 8 years earlier. He uses traditional methods as well, red lead primer and the gold size and then gold. It's a fort near the sea, a very aggressive environment and he's currently on-site re-gilding after only 8 years, so you must have a very good environment in Wisconsin because it doesn't last that long in Scotland unfortunately.

Tony Rajer: We just got electricity!

Eric Nordgren: I just have two brief questions, one is on the experiments repairing cast iron with welding techniques and if you tried or thought about preheating the piece before the weld or if you found that might help or be necessary or not. And another one for Joe and Patty which is more about how do you monitor the effectiveness of the water jetting or other techniques in the confined spaces and how well you have been able to get clean corrosion in those spaces and also as far as the coating efficiency, whether it's using a corrosion inhibitor or perhaps a paint coating system inside those confined spaces, just how you monitor that in there.

Lyn Wilson: The cast iron was preheated, I should have mentioned that in the presentation, because we're trying to assess the potential for in-situ cleaning, it was heated using a blow torch so perhaps it wasn't a completely even heating but we certainly did give that an attempt in advance of the welds.

Patty Miller: You can use a borescope, there are also these other confined spaces that we worked in that were inter-tank sections where bulk heads come together very tight and we had them cleaning inside of there, and you can take the run off of entrapped water and check that. Within those very tight spaces there was the use of the borescope, a lot of those stringers where we were cleaning were totally torn away so you could really see, plus we are doing a lot of repairs which included removing some of the materials that had failed, so doing mechanical cleaning right down to removing corrosion product.

Eric Nordgren: Is there any sort of industrial technique or standard for monitoring, such as looking for the holidays using the equipment for more accessible spaces for coating effectiveness, that has been designed for more confined spaces?

Joe Sembrat: For the inside perhaps of pipes, is what you're asking? To finish up on your last question, I think for those locations it requires physical inspection, you have to know what you're looking for and not solely rely on a piece of equipment. Also, in those areas where we just couldn't get in, those areas we used Cortec products again for either fuming or dusting inside that they have long-term storage materials for that emit vapor phase corrosion inhibitors over a period of time, but once again, that relies on somebody going back and following up to ensure that it is still functioning at that point. I have to look into to see what they do on the inside of pipelines and so forth, I know that they have monitoring equipment, but I'd have to check to see if there is a holiday detector for doing that. Generally there are not coatings on the inside of most pipes, but there are inspections, so it is a good question.

Joe Sembrat: Shelley, I had a question for you. Am I right or wrong, did you treat a Calder with a stealth fighter paint at some point in the past. I thought I heard a talk about it? I was just wondering how that held up, was that some nanotechnology paint or something?

Shelley Sturman: The Object Conservation Department at the National Gallery of Art, Washington, has been working with the United States Army Research Laboratory for over ten years to adapt military paint for use on outdoor sculpture. We are trying to bring this product to market and make it available for conservators and artists. After years of artificial and natural aging on prepared coupons of the military paint and several commercially available paints, we felt ready to apply our adapted paint on a test case sculpture. Working closely with the Calder Foundation to determine the appropriate color and gloss, (if anyone has treated a Calder you know they want a very, very matte surface), *Tom's,* a monumental black sculpture was selected as our first test case. In addition to working with the Calder Foundation, we're also consulting with the Tony Smith Foundation, to identify (and quantify) the right color and gloss level for Smith sculptures. As you may know when you have a matte surface you have very little binder plus a very high amount of pigment and extenders which means that when these paints are exposed outdoors they are going to fail very quickly. So, just like in many of the talks we heard this morning, people don't want to go to the expense and trouble to repaint a sculpture with a product that will certainly fail within a year or two, especially in some of those remote sites pictured in the talks. Likewise, the Army doesn't want to repaint their bridges or water tanks too frequently, hence the push to develop more durable, matt coatings; we are fortunate to be collaborating with them. *Tom's* has been painted for seven years, we check it every few months with a gloss meter and a color meter and it still looks beautiful - the surface is very mar resistant (especially compared to the coatings traditionally used to repaint outdoor Calder's), if the surface has bird droppings or debris we can wash it off, and the surface remains intact. To date, we are happy with the performance of the adapted paint. We are trying to get the paint to the market, but there are still several hurdles to cross, so we're not there yet. Most recently we began investigating making pigmented matte coatings using the same technology. The most recent publication about our research on these paint systems, co-authored with Katy May, Abigail Mack, and John Escarsega, was in the Preprints for the ICOM-CC meeting in New Delhi.

Joe Sembrat: I forgot who asked the other question, if it was Philippe or not, but they have fluorescing admixtures that can be added to prime coats that you can then go back and do detection with an infrared camera and they will fluoresce and show you where the flaws are in your coating. I think Sherwin Williams produces one of those it is actually on the market and can be utilized.

Karl Knauer: I really liked Tony's comment about the safety factor with the extra gold sheets, and since you all had to deal with contracts, bidding or calls for tender, I was wondering if you had any other brief comments or observations or practical advice about factoring in surprises and eventualities in cost overruns, especially since all of your projects were pretty big?

Tony Rajer: Well, as you know it certainly helps to interview absolutely everybody on earth before you make the decision, and I did not make the decision as to who the sub-contractors would be, I produced the statistical data and made the recommendation. We did have one local firm in Wisconsin, and they felt that they were qualified but it didn't appear that they were on paper, and when they didn't get the contract you know then all hell broke loose, as it usually does. All I can say is do your research and attempt to work with your contract officer who generates those contracts and make them as tight as you can.

Patty Miller: What we have been doing lately is if we are writing specifications, and what we have been seeing coming through lately for some of these large contracts, is adding to the treatment report a very specific maintenance plan. The maintenance plans are not just 'if you see it failing, repaint it' kind of thing, we are getting right down to the very specifics of how you should visually and quantitatively test and monitor on a yearly or maybe every 3 or 5 years depending on their budget and what they know they can do and work with them on developing these sorts of maintenance plans and moving them into documents which say that when you are going to do this project you have to provide the maintenance plan at the end. As a conservator I think you should work with them and know what their own staff is able to do and then also know what they have to contract out and the museums that we've worked with and the city and State governments that we've worked with are really asking us what is my responsibility after you do this 50, 70 or $100,000 treatment that I have just paid for, am I going to have to spend another $20,000 in 3 years or 5 years, what can you project?. That is what we are trying to work towards is trying to help people project what to expect in the future.

Molly Carlson: In the approach to the Snow Squall's cleaning using the dry ice dusting technique, one of the things I wanted to think hard about was what was going to be the effect of a cold temperature drop on a piece of brass sheathing that was as thin as what we have on the ship. To that end, Randall and I designed a little experiment that tested a couple of parameters, and one of them was the cold drop. He put a thermocouple on the back of the sheathing and in five different trials for one minute, we found that a drop of 81°C in one minute, which is about 147°F. Then I was curious, because it was very thin metal, is there an effect of the cold for cold stress cracking? That sheathing as it is applied on the ship is overlapped and through-nailed to the next layer so I was working up to how could we design a way to measure the shrinkage of that metal. We measured the sheathing temperature off the ship realizing also that if the dry ice dusting technique had been applied to the ship, there is going to be a layer of jute and a layer of wood insulation on the back side, and probably we wouldn't be dwelling for 60 seconds in one spot. One of the effects we did see was there was some damage when we purposefully over cleaned certain spots. David Scott looked at the pieces of metal metallographically afterwards and he wondered if it was an effect of the vortices of a particle in an air stream, and we wonder if it's an effect of cold stress cracking off the corrosion layer. So I just wondered of anybody had a comment on that.

Tim Foecke: FCC [face center cubic] metals like brass don't undergo a ductile to brittle transition even down to liquid nitrogen temperatures generally. There could be some rate effects, but effectively what you are doing by cooling down the plate is it will shrink and it will pull laterally on those lap joints that are nailed together and if you put some stress on it you might tear one of the holes out. If you want to keep track of what the stresses are you can simply install a string gauge on the backside, which is just glued on, and you monitor the resistance and it will tell you what the lateral strain is. I have a feeling if you have that thin layer of metal on such a huge thermal mass like the wood and stuff behind it you're not going to have any issues.

Rozemarijn van der Molen: Another comment on that subject, in Germany there has been more research on the effect of these cold temperatures for dry-ice blasting on metals and this has been highly debated and people were not able to reproduce results. I think the string thing [the string gauge mentioned by Tim Foecke] would be very useful. I would just like to say that we should look into the literature because it's there and I am very happy to send everyone my literature list. Also, there has been some research in Germany on using very cold temperatures on organic layers on furniture and paint which has also been published.

Tim Foecke: This is about measuring particle velocities. If the particles are metallic you can actually use what is called a velocometer which looks like a pair of television rabbit ears, but much easier is just to use a high speed camera and do photogrammetry against some kind of a background. If anybody really wants to be able to do that amongst my playpen, I have a 1000 frame per second camera and if you want to schlep all of your equipment up with the caveat that I will not allow anyone to do measurements simply for a commercial endorsement, if you want to bring the stuff up, we can probably do some measurements if you really want to know what your particle velocities are.

John Scott: Since we were talking about the gilding and people mentioned epoxy and so forth, I think it is really important to remind ourselves that environmental and maintennace factors can have a huge amount to do with the survival and condition of gilding, especially when things are accessible to birds and also for maintennance. I would recommend to anyone who is in New York to go see the Sherman Memorial monument which is at the south east corner of Central Park and look at the condition of the gilding, it is in terrible condition and yet it was regilded in a much vetted and planned system by a nice company that's near New York, that I won't mention who they are. They used an epoxy coating on the bronze and then they used their traditional oil based red over that because you needed that red. The reason for red in gilding is to adjust your tone so you get a warmer tone underneath your gilding that's what its for. Then they used the regular oil size and then they put on their gold. A completely high quality treatment but the birds, and as far as I can tell by intermittently looking at this as I am in the New York area, I believe the indiscrimate application of the same kind of maintenance procedures, other than applying wax, that are used on sculptures in the rest of the park is one of the reasons [is causing damage]. For instance, the use of water blasting, not ultra high or anything like that. Between this and the pigeons all over the piece and the intermittent maintenance has had an eroding effect on the bronze gilt surface.

Joe Sembrat: We've looked at that monument, the birds are definitely a problem, when worked for Centrral Park Conservancy, that was one of the maintenance issues, but the pigeons are all over the top. If you look on the underside it also has extensive chloride problems, it's right in that traffic square, there is deicing salts that wash up on it. Which gets back once again to surface preparation. I read the report that the firm wrote about it but there was no testing of soluble salts so even the most durable of coatings are not going to stand up to a surface that's contaminated with soluble salts.

Ian MacLeod: First of all I would like to say thank you to all of the presenters, obviously I am the 17th person to ask a question or pass a comment in this panel discussion session, and that's a record for the conference so far, so well done Shelley. It's really an observation about the use of holiday detectors. I had spent 6 months desalinating the interior of the boat the *Australia II,* the one that took the America's Cup away, for a litte while, and our former Director had said that the syndicate could go and take the boat out of the Museum, back to Cowes to sail in the 150th anniversary of the America's Cup. I was dead against it, I was overruled, and I said, 'well you can have it on condition – that you do a holiday detection all around the boat, and make sure every holiday found is repaired and so it left Australia absolutely complete, and because there were no holidays and they had to be very careful in sailing it, except for when they came back drunk after winning a race and smashed it into the pier, but after that repair had been done, there were no new holidays. So all I can say is if your objects do have to go out and take extraordinary service, if you've done your preparation work, and you have in your conservation report that there were no holidays detected, then at least you know that the wretched chlorides are going to have a real battle to get back into the object.

Shelley Sturman: Well that was a perfect ending comment, thank you Ian, I think it brings us to a very high note. One of the final points that I wanted to make is I think this panel and these papers, in addition to all of the amazing technology and the beautiful collaborations with industry, and government, and universities and museums and so on, is that they have pointed out to us yet again the very high ethical standards that everyone here is maintaining. When Tony talked about the gilding by the former contractor, there was no one up there to check on what the person did, or if it hadn't been for Joe and Patty constantly going behind the contractors, or with Lyn and Ali doing all of that testing to find the best [conservation practice]. We are doing these things because we want them to be right and it'd not because anyone else is looking over our shoulder, I think in most of your cases there was no one overseeing you, you were it, and it was because you knew it had to be right. It's like what Ian just told us too, he had to make sure that boat was right before he let it go so I think that we can all feel good about that and I guess I will close from a line from the Ghostbusters 'if you are ever faced with one of those, who ya gonna call? - right there, we've got them.

ENGINEERING AND 3D TECHNOLOGY IN CONSERVATION

Session Chair: Ian MacLeod

TREATMENT OF THE DAMAGED BRONZE OF RODIN'S *THE THINKER* FROM THE SINGER MUSEUM IN LAREN, THE NETHERLANDS: AN INNOVATIVE APPROACH

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Abstract

This paper will discuss the innovative treatment of a severely vandalised bronze sculpture, The Thinker *by Auguste Rodin, from the Singer Museum in Laren, The Netherlands. It gives a step-by-step account of the practical work undertaken to restore the sculpture, as well as an insight into some of the technology used. Additional aspects of this complex treatment, such as decision-making and documentation are also discussed. A variety of analytical techniques were employed to identify the materials and casting method of this well known bronze. These methods ranged from X-ray fluorescence (XRF), X-ray diffraction (XRD) to tensile strength testing of the alloy. The paper concludes with an evaluation of the complex treatment and gives recommendations for similar future treatments.*

Keywords: Rodin, 3D scanning, 3D printing, stereo lithography, vandalism, bronze powder, epoxy, cold cast bronze.

Introduction

On January 17th, 2007, seven bronze sculptures were stolen from the sculpture garden of the Singer Museum in Laren, the Netherlands. Of these missing bronzes, only *The Thinker* by Auguste Rodin[1] was recovered. The thieves attempted to cut the Rodin bronze into pieces in order to sell the metal for its scrap value. As a result, the bronze had several saw cuts, a distorted left upper arm and the right lower leg was missing. The museum approached the University of Amsterdam to research possible treatments for the sculpture. Several options were presented and after much consideration the museum opted for a novel approach involving 3D scanning and 3D printing[2].

The decision making process

After much consultation and deliberation, the museum formed an expert committee consisting of museum curators, art historians, material scientists, conservation scientists and conservators to investigate the options for restoration of the damaged bronze. The primary aim was to return the outline of the sculpture to its original appearance as accurately as possible. However, a treatment could only be carried out under certain conditions that were set by the museum; namely that any additions to the sculpture would be reversible and identifiable, that no (heat) treatment would alter the patina or metal structure and that any added surface would be directly derived from a surface modeled by Rodin. The only permissible alteration to the sculpture would be to return the plastically deformed areas to their original position. The sculpture will also not be placed back in the sculpture garden but will be exhibited inside the Singer Museum.

Once these conditions were established by the committee, the metals conservation programme at the University of Amsterdam (UvA) was enlisted to research the viability of potential treatments. All possible treatment options were considered and evaluated. These options ranged from traditional techniques to very innovative ones. Because most of the traditional techniques involved heat treatment and an unacceptable loss of surface detail, a process like rapid prototyping became an attractive alternative. Rapid prototyping has been used in the cultural heritage field but mainly for making reproductions (Podany 1992, Travis 1992, Accardo 2004).

Damage assessment

The physical damage inflicted on the sculpture by the thieves was unusual compared to what is usually found

Figure 1. Damaged statue from different angles and close up of the head, before treatment. (copyright M.Svenson)

on vandalized objects. There were few distortions such as bent or broken parts because the thieves used an angle grinder in their attempt to cut up the sculpture for scrap metal. As a result, most of the damage consisted of saw cuts and missing parts, with only minimal plastic deformation and a loss of patina (see Figure 1). The first step was to document the damaged bronze in its present condition by making a detailed damage assessment (see Figures 2a, 2b) and a 3D scan. Analyses of the alloy using XRF and of the patina using XRD were also performed[3].

3D Scanning

By taking 3D scans[4] of both the damaged bronze and an undamaged copy, it was possible to determine the differences between the two versions very precisely

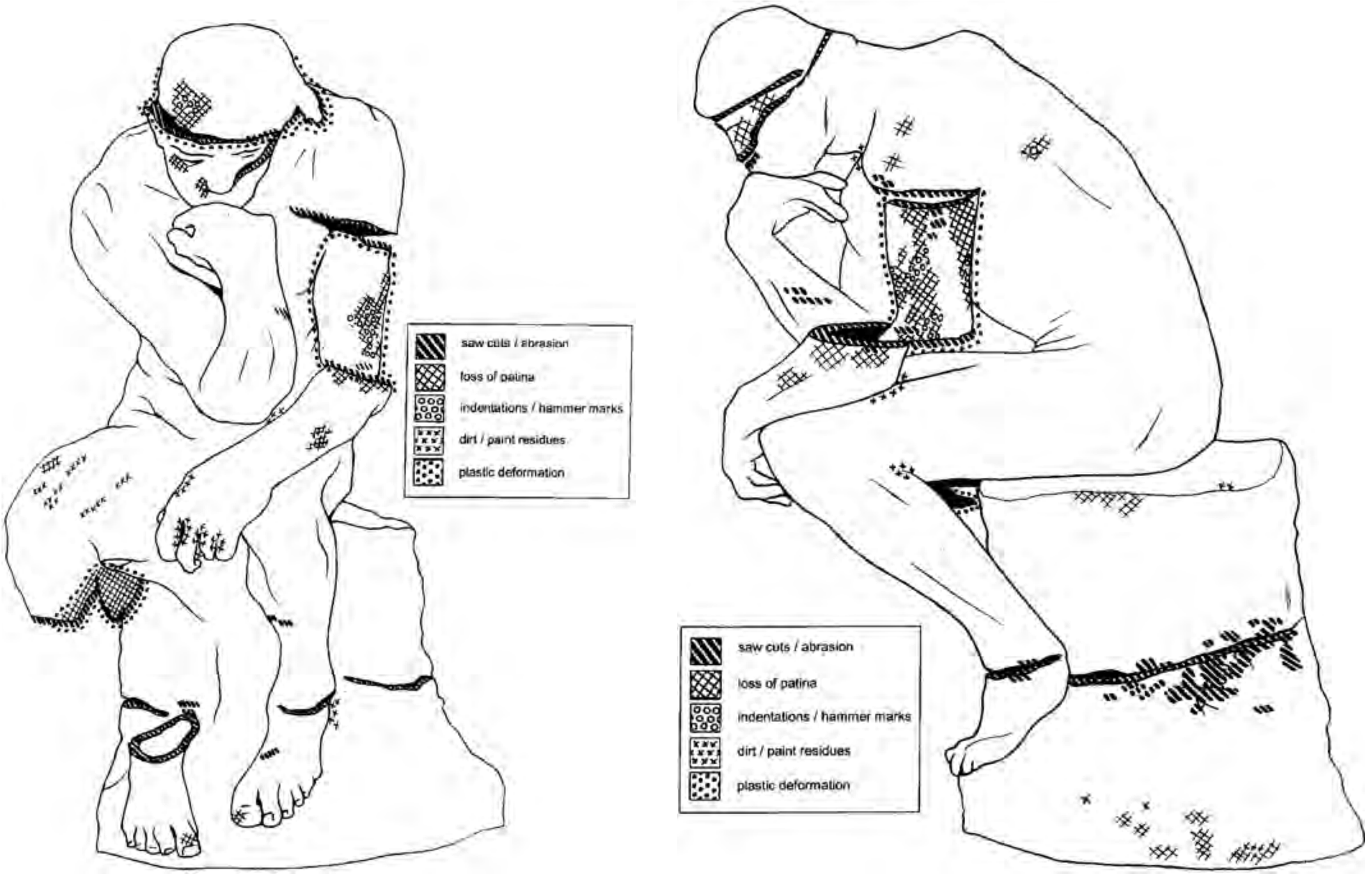

Figure 2. Damage assessment drawing of the bronze (front and proper left side) indicating the different types of damage. (copyright T. Davidowitz)

by superimposing the two scans digitally. The Rodin Museum at the Villa del Brillants in Meudon, Paris[5] was approached regarding the possibility of scanning one of their early plaster models of *The Thinker*. The sculpture owned by the Singer Museum was reportedly cast in bronze using the sand casting method[6], and as the Rodin Museum still owns some of the original plaster foundry models, this exciting opportunity became possible. The damaged sculpture from the Singer Museum was brought to Meudon to compare with several copies in their museum collection. An interesting line-up was arranged, consisting of the four available plaster models, a later bronze copy, and the damaged bronze (see Figure 3). Of the four plaster models assessed, two were true foundry patterns[7], the other three having been derived from casts. After a careful examination and comparison of the details and measurements of the damaged bronze and the plaster patterns, one plaster[8] matched the bronze from the Singer Museum exactly.

Figure 3. The damaged bronze amongst plaster models and patterns in the Rodin Museum in Meudon, France. Third from the right is the damaged bronze from the Singer Museum and second from the right is foundry pattern S.2840.

The Rodin Museum in Paris was approached about the possibility of scanning the original plaster foundry pattern. They agreed, and a 3D scan of the plaster was made. The 3D scans of the damaged bronze and the plaster were digitally superimposed, and the scan of the bronze had to be digitally enlarged slightly (1%) to compensate for shrinkage during casting (see Figure 4). By overlapping the scans, it became possible to ascertain the extent of the damage, as well as the precise dimensions of the missing parts (see Figures 5 and 6). With the 3D working models of these scans it was now possible to produce replicas of the missing parts using the process of stereolithography, a form of 3D printing[9].

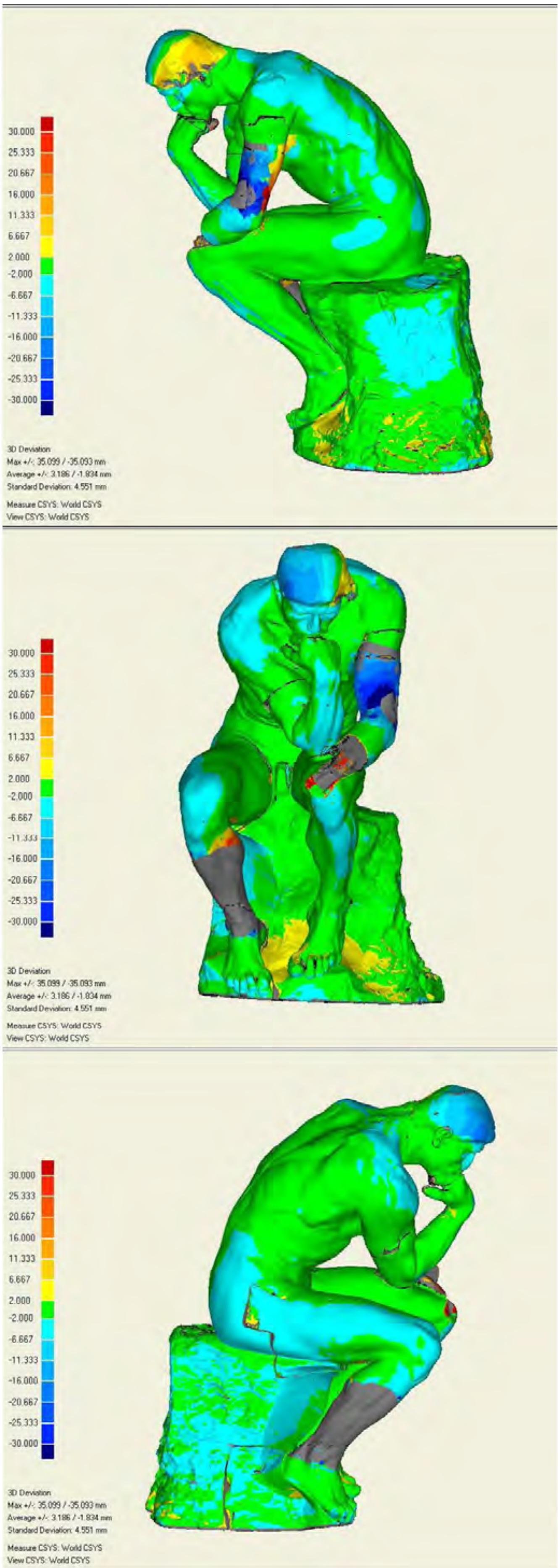

Figure 4. 3D scan of the damaged bronze from the Singer Museum and plaster S.2840, superimposed with colour indicating deviations. (copyright Introtech)

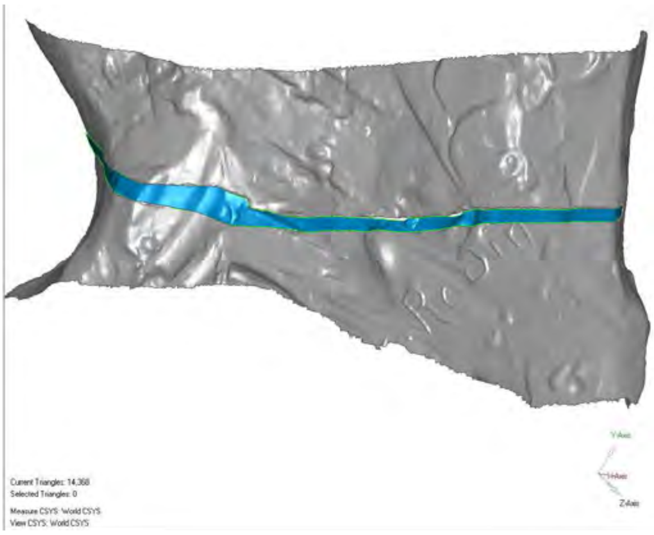

Figure 5. Virtual image of infill in saw cut in base of the sculpture. (copyright Introtech)

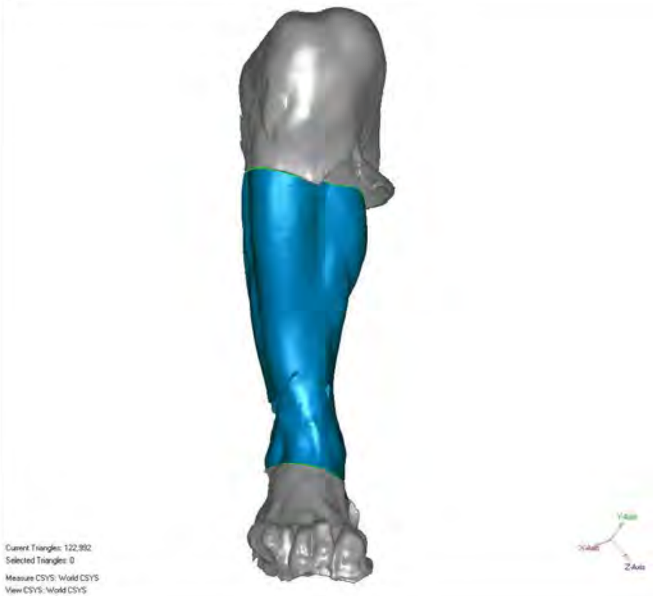

Figure 6. Virtual image of missing right lower leg of the sculpture. (copyright Introtech)

Epoxy tests

At this point the question arose of what material should be used to fill the missing sections? The following materials were considered:

- Bronze: very stable, properties identical to original, difficult to work.
- Epoxy: limited lifespan, properties differ from original, easy to work.
- Epoxy with bronze powder: limited lifespan, properties close to original, easy to work.

Practical tests were carried out to see how the different materials performed.

These tests focused mainly on the epoxy filled with bronze powder, as this material has a relatively short history of use in conservation compared to bronze (Evers 1971, Gilroy 1976). Three epoxies were selected based on their long-term stability and good casting properties: Hxtal Nyl-1, Fynebond, and Araldite 2020. Several grades of bronze powder were tested as well, in a variety of grain sizes and colours[10]. Silicon rubber moulds were taken from the 3-D prints (three-dimensional positives) of the saw cuts. These moulds were subsequently used to cast replicas of the missing areas in the various mixtures of resin and metal powder. The slow curing epoxies, Hxtal Nyl-1 and Fynebond, did not perform very well. This was due to the longer setting times which allowed the bronze powder to sink, and cause a layer of bronze powder to form on the bottom and a clear epoxy layer on top. While this could have been prevented to some extent with a filler such as fumed silica, adding too much fumed silica had a negative effect on the casting properties. The best results were obtained with Araldite 2020, in a weight ratio of 1:9 epoxy resin to bronze powder. When the epoxy casts were cured and removed from the silicon mould, they had a very detailed, yet plastic, appearance. This was due to the unavoidable very thin outer layer of pure epoxy that forms at the surface. This layer was easily removed by very light brushing or polishing with a fine brass brush, revealing a very convincing metallic surface. This metallic surface could even be patinated by chemical means, using copper nitrate applied cold and left to dry (see Figure 7).

Figure 7. Epoxy with bronze powder test casts: unfinished as cast (*5, 6, 7*); polished (*8*); and patinated with copper nitrate (*9*).

To counteract the separation of bronze powder in the epoxy, the silicon mould was adapted to allow the epoxy to be poured from more than one point and with a very large casting head. These tests showed that epoxy with added bronze powder was a convincing alternative to bronze as a filler material. The epoxy with bronze powder is easier and quicker to cast as well as giving greater detail. The epoxy is also easier to work, allowing a cast to be reproduced much faster than with bronze. The disadvantages of using epoxy are that it has a shorter lifespan[11] than bronze and is more brittle. As a result of these tests, it was decided that the gaps caused by the saw cuts would be infilled with casts made from the epoxy and bronze powder material. As the saw cuts are long and thin, it would have been difficult to cast these infills in bronze, and very time consuming to make the bronze infills fit precisely into the saw cuts. For the missing leg, however, bronze was a more suitable infill material, as the missing part had to be fixed to the sculpture with an internal support. This required a stronger material capable of holding an internal clamp fixed into the new leg with screw threading and a pressure fit. The shrinkage of the various cast materials was not a concern because the virtual model of the 3D print can easily be digitally scaled up to compensate for the shrinkage.

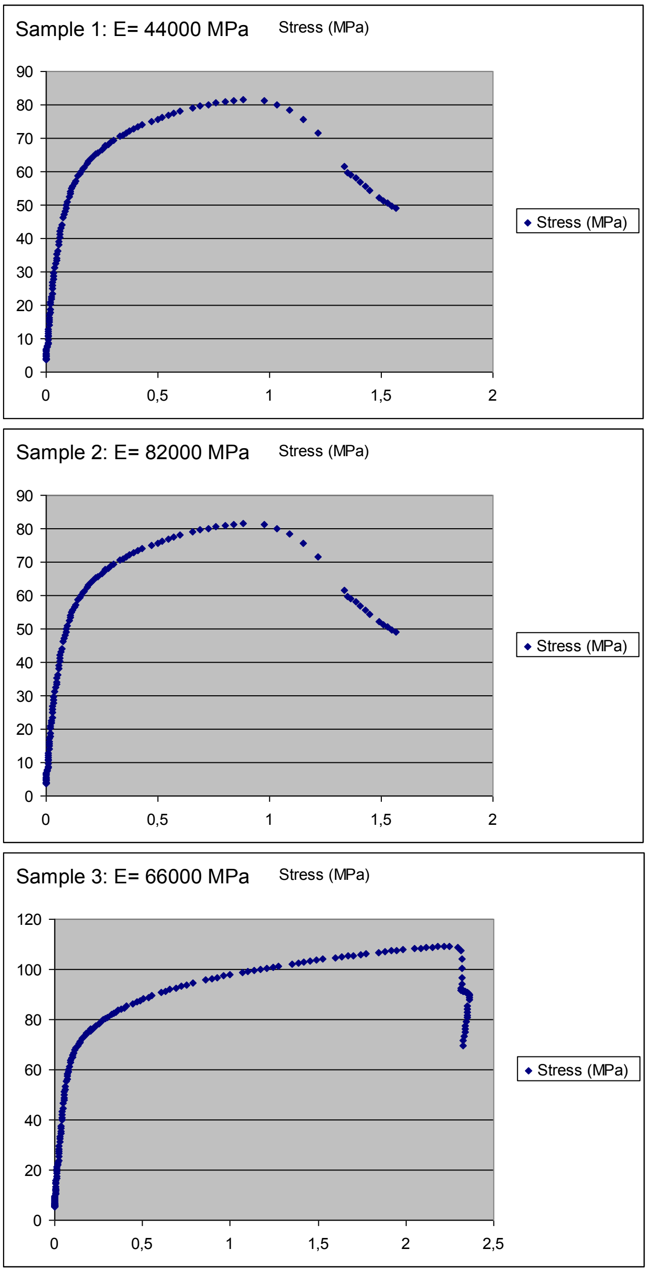

Figure 8: Tensile strength test results of three test rods of the same alloy as the bronze statue of the Thinker by Rodin. (copyright Corus)

Reshaping

Before most of the saw cuts could be scanned it was necessary to shape the deformation back to its original position. Prior to the reshaping, it was necessary to determine whether additional plastic deformation would pose too great a risk of fracture to the bronze. This was established by tensile strength testing of the alloy. Test rods were cast in the same alloy as the damaged bronze and subjected to tensile strength tests[12] The conclusion of this testing was that the alloy was brittle but that controlled plastic deformation would be possible to a degree (see Figure 8). Controlled deformation was achieved by making custom-built clamps which were fixed to the distorted areas and the surrounding area of metal. By gradually tightening the screw mechanism, pressure was applied in a very controlled manner and was closely observed, preventing additional damage. For the damaged left upper arm, an additional device had to be constructed. This tool, which expanded upon tightening a screw mechanism, was placed inside the dented arm to remove the dents from the inside out.

Creating the missing parts

Once the distorted areas were shaped back to their original position, a 3D scan could be made, and in turn, the missing parts could be printed using the stereolithography process. The fills for the saw cuts were printed in a UV-curable photopolymer acrylic resin[13] Sanding is required to remove the stepped surface texture with most of the larger 3D prints. This so-called ‘stair casting’ can be reduced by slowing down the printing process, causing a build-up of thinner layers of the resin. A careful choice of polymer can help as well. In this case, the treatment of the outer printed surface had to be kept to a minimum, and it was important for the layer build-up to be very fine. Silicone rubber moulds[14] were made from these 3D prints, which were subsequently used to cast the epoxy and bronze powder mixture. Once cured, these epoxy fills were removed from the silicone mould (see Figure 9). As the resin prints were made slightly wider than the gap they needed to fill, they had to be filed down by hand to allow for a perfect fit (See Figure 10). Although the saw cut fills were already held securely in place by pressure fit, they were also adhered with Paraloid B-72 as an extra security measure. The replacement leg was printed directly in an acrylate suitable for burn-out[15], which was then used for casting in the lost wax process. The 3D wax model was invested in plaster and then burned out to create a mould in which to cast the bronze[16] (see Figure 10). An armature was also fitted inside the leg to make it possible to attach the replacement leg to the main sculpture. A similar construction was also used to fix the left upper arm in place (see Figure 11)

Figure 9. Infills for the saw cuts: the 3D print (bottom) and the cast of this in epoxy with bronze powder (top). (copyright of the author)

Figure 10. The newly cast replacement leg in bronze with casting sprues and runners still attached. (copyright Paul Kramer)

Patination and retouching

One of the conditions stipulated by the Singer Museum was that the patination of the new bronze additions would cause no damage to the original patina[17] Therefore it was decided that the retouching of the bronze fills would be done with light-fast acrylic paints. In order to give the patination depth and a good base, the fills were patinated with copper nitrate before being attached to the sculpture. Once placed on the bronze, they were retouched with acrylic paint to blend in with the sculpture's patina (see Figure 12).

Future replication

Because of the limited lifespan of the epoxy inserts (expected to be at least 30 years), a solution was needed

Figure 11. Statue from different angles and close up of the head, before retouching, with new additions in place. (copyright of the author)

Figure 12. Statue from different angles and close up of the head, after treatment. (copyright of the author)

to prevent a repetition of the costly 3D-scan and 3D printing[18] It is realistic to assume that with constantly changing technology it will be difficult to use today's software or storage media in thirty year's time. One cannot depend on the museum to update software or storage media for the next generation(s). Therefore it was decided to make silicone rubber moulds of the 3D-prints of the saw cuts in silicone that can withstand high temperatures[19] These moulds were then used to cast an alloy of tin, which provides very good detail and is very stable. These tin alloy casts were placed together with a CD of the treatment report inside the hollow sculpture. Also placed inside the bronze is a second CD containing a copy of the 3D-scans and STL files used for the 3D printing.

Conclusion

Following the theft and recovery of Rodin's *The Thinker* from the Singer Museum, several options were considered to restore the visual appearance of the damaged bronze without affecting its fragile condition. These options were based on the decision to display the bronze indoors. An invasive but reversible treatment was sought and ultimately found using innovative 3D scanning and 3D printing techniques. Although relatively costly and time consuming, these modern techniques offer exciting new possibilities in the field of conservation/restoration. The sculpture is now on permanent display inside the Singer Museum.

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Endnotes

[1] Le Penseur, 1889, bronze, height 72cm, signature A.Rodin, foundry mark Alexis Rudier / Fondeur Paris, Singer Museum inventory number: 56-1-412, earliest documentation 1930. This bronze was on display during a visit to the Ateliergebouw at Metal 07 in Amsterdam

[2] The 3D scans were performed by a commercial firm, Introtech, on location in Amsterdam and Meudon. The 3D prints of the inserts of the saw cuts were performed in Leuven, Belgium, by the firm Materialise, the 3D print and casting of the leg were performed by Proto*Metals* in Zwijndrecht, the Netherlands.

[3] The alloy used for the sculpture was analysed by XRF as an average of 94.5% Cu, 01% Zn, 4% Sn and < 0.5% Pb. XRF analysis was undertaken by Luc Megens (ICN), and Hans van der Weijde (Corus). The composition of the metal and the metal powders were analysed using the Bruker Tracer III-V with a rhodium tube operating at 40 kV and 2.2 uA with a 0.0012 Al/ 0.0001 Ti filter in the primary beam and a Si-PIN detector. Quantification was performed using the S1PXRF software.

[4] A Steinbichler COMET 5, 4MegaPixel, C400 system was used for scanning. The COMET 5 sensor is a white-light projection system that consists of one camera and one projector. These two components are screw-mounted on an aluminium bar at the appropriate position for the measuring field. A black and white line pattern is projected on the object using the projector. The camera, offset slightly from the pattern projector, looks at the shape of the line and uses a technique similar to triangulation to calculate the distance of every point on the line. A Field of View (FOV) of 400 (400x400mm) was used to scan *The Thinker*. Several FOV options are available: 100, 200, 400, 800, allowing a broad range of applications, from the size of a coin up to a car. System accuracy is 0.025mm (25micron) with FOV400 and 0.005mm with FOV100. This accuracy is verified after each calibration. A calibration is generally done after system transportation or after temperature changes. This calibration is done within 10 minutes. Individual 'scan shots' are stitched together using unique overlapping features in the shots.

[5] The Rodin Museum, housed in the Villa de Brillants in Meudon, on the outskirts of Paris, is where Auguste Rodin lived from 1895 till his death in 1917. Rodin also worked in Meudon, and in his former studio the Museum preserves a vast collection of mainly plaster models inherited from Rodin. The collections of the Rodin Museum are housed at two sites; the Hôtel Biron in Paris, which exhibits the finished marbles and bronze sculptures, and the Villa des Brillants in Meudon

[6] A sand cast is usually made by pressing a solid plaster model, referred to as a 'pattern' (positive form), into the two halves of a two part sand mold. The pattern is then removed, and the metal is cast in the cavity created when the two parts of the sand mould are put together again without the pattern. When a hollow figure needs to be cast, as in the case of *The Thinker*, a core of pre-baked refractory material is used. This can be sand, clay, plaster, loam or mixtures of these materials.

[7] A pattern for sand casting cannot, generally speaking, have undercuts and therefore foundry patterns of a complex shape with undercuts like *The Thinker* are usually built up from various parts. In the case of foundry patterns from the Rodin Museum in Meudon, it was possible to remove the left arm and right leg.

[8] Museum inventory number.S2840 . To date, research has not been able to exactly date this pattern; the Rodin Museum thinks it dates from the 1930"s. Personal communication with curator Francois Blanchetière.

[9] The 3D scan is converted into a working file (STL file) which is programmed into the stereo lithography 3D printing machine. STL stands for Surface Tesselation Language or Standard Tesselation Language whereby the

surface is divided up in triangles. Stereo lithography is an additive manufacturing process using a vat of liquid UV-curable photopolymer "resin" and a UV laser to build parts a layer at a time. On each layer, the laser beam traces a part cross-section pattern on the surface of the liquid resin. Exposure to the UV laser light cures, or, solidifies the pattern traced on the resin and adheres it to the layer below.

[10] 54880 Bronze powder, dark, Kremer Pigmente GmbH & Co. KG: Around 400 grit gives the best result. Cu89/Sn12 (wt%) (XRF analysis).

[11] Several conservation departments of various Museums were asked about the condition of early fills where epoxy and bronze powder was used. These institutions replied that the fills were still in very good condition even after thirty years. Personal communication with Norman Tennent and Ian Macleod.

[12] The alloy used for the sculpture was analysed by XRF as an average of 94.5% Cu, 01% Zn, 4% Sn and < 0.5% Pb. XRF analysis Tests performed on an Instron draw bench, draw speed 30 MPa/sec, Draw rod DP5; the test rods were 10 mm diameter and 200mm in length.

[13] Polyjet, Materialise HQ

[14] Elastosil M-4600, Wacker Chemie AG

[15] VisiJet® SR 200, 3D systems, Inc.

[16] The replacement leg was cast in an alloy close to the alloy of the original bronze: Cu 94.4, Zn 0.9, Pb 0.2, Sn 4.8 as determined by XRF

[17] The main constituents of the green patina are brochantite and some antlerite; determined by X-ray Diffraction using a Siemens GCCS with GADDS Bruker-AXS Tracer III-V using Bruker AXS S1PXRF software

[18] A full 3D sculpture scan this size cost € 2000, converting to STL-file € 1000, 3D-print of one saw cut fill cost € 200, 3D-print leg of the in wax acrylate plus casting in bronze cost € 1600

[19] Elastosil M-4470, Wacker Chemie AG

Materials

Fynebond (epoxy resin)
Fyne Conservation Services
Airds Cottage, St. Catharine, Loch Fyne
Argyll
Scotland
PA25 8BA

Hxtal NYL-1 (epoxy resin)
Restorers Supplies Inc.
PO box 112200
Naples, Fl 34108-0137
United States

Araldite® 2020 (epoxy resin)
Huntsman International LLC
5121 San Fernando Road West
Los Angeles CA 90039-1071
Tel: +1 8185070167

Bronze powder:
Kremer Pigmente GmbH & Co. KG
Hauptstrasse 41-47
88317 Aichstetten
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Tel: +49 756591100

Polyjet
Materialise HQ
Technologielaan 15
3001 Leuven
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Tel: +32-16396611

Elastosil M-4600 (silicone rubber)
Wacker Chemie AG
Hanns-Seidel-Platz 4
81737, Munich, Germany
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Elastosil M-4470 (heat resistant silicone rubber)
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VisiJet® SR 200, 3D systems, Inc.
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Rock Hill, SC 29730 U.S.A.
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Hauptstrasse 41-47
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Copper Nitrate
Fisher Scientific
2000 park Lane Drive
Pittsburgh, PA 15275
Tel: +1-800-766-7000

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Authors

Tonny Beentjes was originally trained as a goldsmith and silversmith in the Netherlands. This was followed by a degree in metal conservation (Antwerp) and soon after he started teaching metalwork conservation at West Dean College in England. He currently holds a position as the Programme leader in metal conservation at the University of Amsterdam where he also conducts PhD research into historical goldsmithing technology.

Rozemarijn van der Molen studied design at the Rietveld Academy in Amsterdam (BA 2005) and subsequently studied conservation of historic and ancient metals at the Netherlands Institute for Cultural Heritage (ICN), graduating in 2009. She recently graduated from the master's programme in Metals Conservation at the University of Amsterdam and works as a conservator in private practice. Email: rooz@metalsconservation.nl

Tamar Davidowitz completed her Bachelor's degree in Art History at Leiden University, in combination with Graphic Art at The Royal Art Academy in The Hague. She has just finished her Master's in Metals Conservation at the University of Amsterdam, having written her thesis paper on the paint layers found on the 'der Merkelsche Tafelaufsatz' by Wenzel Jamnitzer. She is currently a postgraduate student at the University of Amsterdam. Email: tamardavidowitz@gmail.com

Q & A SESSION

Ian MacLeod: I think that's one of the most fine statements of understatements what Tonny and his team have done is really quite simply superb and it almost brings tears to your eyes when you see the rejoining of those elements.

Philippe de Viviés: Wonderful work, really impressive. I have a question regarding the technique you used. You made a 3D molding of the missing part – you did a print of the missing part and then you made a mold of it. Is that true?

Tonny Beentjes: Only in the case of the in-fills that went into the saw cuts. That was those tiny slithers. With the bronze leg, it was printed directly in a material that could be used for the lost wax casting process. So the acrylate they use can be burned out straight away.

Philippe de Viviés: Because I was wondering why you used a filling with copper if you were going to paint on top of it – and why you didn't use the 3D printing you had directly.

Tonny Beentjes: We considered that, definitely, but we felt we needed a material that was closer to the bronze itself. Also with the retouching, you have a good ground layer that already is dark and looks natural, and maybe with subsequent handling, some paint is rubbed off and you still have a natural looking material underneath.

Paul Mardikian How did you realign the pieces? I understand that you've tried to press them back in position but when did you know that it was right?

Tonny Beentjes: I did two things: it's a pity that I don't have a slide of that in here, a 3D scan is basically an image of the outside, so really the 'skin'. So what I did was, I asked the firm that did the scanning – we didn't do all of the work ourselves, we used an industry firm because the scanner is 300,000 euros, and the printing machine is also a similar amount of money. What they did they printed a form that you could actually put on the outside, like a 'chablon' - a cut-out shape that locks into place when everything is in the right place.

Paul Mardikian: A sort of control.

Tonny Beentjes: And then we had to follow up to confirm that it was actually in the right place – we had another scan. But because the scans are about 2000 euros every time, you don't want to have them 5 times coming back before it's in the right place! So we made those tools, but it actually worked really well.

Paul Mardikian: Ok, and my second question is - I'm not sure I understood… the infills were made of epoxy – but how would you put the epoxy within the cut. You need to have some kind of silicone rubber, right? To put in shape so it really fits well into the cut. Can you just tell me again how you put the infill into the cut? And how it fell in place? I wasn't clear about that.

Tonny Beentjes: So what you see here [shows image], this piece is actually now solid. It actually just slides in there. Although we made it sometimes slightly slightly bigger, so we had an absolutely perfect fit. But that was the advantage again – if you would have used bronze, the amount it would take to just only take off a tiny bit whereas we could just slide it in. Some of them were actually such a good fit that we didn't even need to actually glue it in place.

Paul Mardikian: And it is true that it is a cut, so…

Tonny Beentjes: Well, as it is the angle-grinder, it can never really make an undercut type of groove, but I must say, one thing is some of the saw cuts almost went right around the base of the sculpture – really big and we had to break [the inserts] in order to fit them in there.

David Watkinson: Thanks Tonny – a very interesting talk. You had an ethical committee and obviously you ranged over every possibility for the statue. I just wondered whether there was discussion around the idea that society might be being robbed of a historical event by you actually putting the statue back to what it was. Thinking of – well, not parallels, because everything is contextual – but in archaeological terms, if you come across a Viking hoard where the silver and gold has been bent out of shape and you've got a whole range of unique objects, you don't reshape them and put them back to what they were. I just wondered how this fits in with the history of the object. Do you see yourself making the history of the object by undoing this event?

Tonny Beentjes: I only mentioned it briefly, but it was a huge discussion and probably when the sculpture is revealed it will come up again. I wasn't personally involved with that part of the decision-making. That was really the museum and some of the museum curators. The museum felt very much that this was a piece bought by the founder of the museum and they loved the piece so much and it was really an icon for that museum, and they were suddenly robbed of that. I think you can justify to quite a large extent the treatment we did, because except for only the distortions we brought back, all of it is very reversible. If you give me a few hours I can bring it almost back to the stage it is now. The other thing is that the whole process is extremely well recorded. I don't know of a project that has recorded its objects so well. We've done even x-ray, we've done thermal camera imaging, all to record. The only thing there was a bit of a disappointment with – we hoped that the retouched areas would actually come up in UV light. That would have been very nice, also maybe in the gallery, to put a UV light on there, but that didn't work and we thought about putting a UV marker in there. However we weren't absolutely sure about long-term stability of UV markers with the retouched areas.

David Watkinson: Thank you. It might be something worth revisiting later with the panel. Not with your panel, the panel that Ian convenes at the front, because I'm sure there are lots of different possibilities and views on it.

Tonny Beentjes: A lot of alternatives have been suggested to make another cast, of its current state, for example. Or just a new cast, or make a 3D print of the entire damaged sculpture. So there are plenty of possibilities. The museum is very open about the restoration because the exhibition I was telling you about in January, is mainly about the treatment we did.

Bruno Pouliot: I wondered if you'd had a chance to do any corrosion studies with the epoxy with the bronze or copper alloy powder in there? We've had several instances where, particularly if the epoxy has not cured completely the curing agent can react quite severely with the copper and cause rapid corrosion. It's something that was observed but we've never really studied. But in my discussions with Richard Wolbers he seemed to indicate that indeed the curing agent for most epoxies can be quite corrosive to copper. So I know that you put the B-72 barrier between the actual sculpture so it would be mostly the corrosion that occurs within the film material that you created. So did you investigate any further as to what will happen?

Tonny Beentjes: We wanted to know long-term stability of epoxies with metal powders. So we contacted Ian [MacLeod] and Norman Tennant about early uses of this. We actually found quite early use of epoxy-metal powder, bronze powder mixtures, even in the '70s people have been using it. We asked certain people to revisit the pieces in the museum and they reported they were still fine. We've got a piece in the Rijksmuseum, the Verrocchio candlestick [and that is still fine].

Aaron Shugar: Great presentation. The advancements in 3D printing in the last 5 years have been enormous and in the past stepping sizes were too large to do stuff like this. Did you discuss the use of 3D printing in granulation? So you could make an instant bronze piece to slide in?

Tonny Beentjes: We thought about it. As you said, developments go really quickly. Even we looked at laser sintering. We decided that it wasn't at the stage of using for this sculpture, but we definitely looked into that. And I must say – what you said with the visible layers – the stair-casing, that we had quite some trouble finding firms that could actually work to the definition we wanted. We couldn't have done this 5 years ago I must say.

Robert van Langh: Tonny, great talk thank you. Just a remark actually to what David was saying earlier, and also a discussion to bring up perhaps a little bit livelier and a little bit later. Unfortunately in the Netherlands people cut up paintings, set paintings on fire or cut up bronzes like these. Unfortunately that does happen. In 2009 we had the Bartholomeus van der Helst, which was set on fire a very large painting – 5 meters. I think. Being one of the members of the advisory committee, the ideas that we had about that: as long as you know what the object looked like before it was damaged – let's call it that – and you have a clear idea as to what the possibilities are – can you bring it back to that state that it was in before, is one of the options for the treatment, yes or no? I'm just mentioning this as to the line of thinking that was used for that. Because so many things all around it – from the Rodin museum in Meudon - that in the beginning they said 'no, this is gone'. Whereas, when we said 'well, this is what we want to do with it' or 'could be doing with it' and each time in the process we always said 'guys, it might be possible that we are not going to do anything at all'. Know that we can always pull back, but let's see what the possibilities are. And I think, what Tonny has already indicated from the technical point of view: also from the philosophical or ethical point of view was really – was really always open-minded and saying 'are we going to do this? Why should we be doing this?' and each time rethinking about that process. Indeed that takes time, and especially when you have a committee of 14 people but I must say the discussions were always robust and intense.

Tonny Beentjes: Yes, very heated discussions! Especially about the use of the epoxy and bronze.

Robert van Langh: Yes, but that's for later! But I must say, that really the fact that you know what it looks like before it was damaged, and that's the difference of course for instance with the archaeological finds – you don't know what they looked like before they were damaged, or maybe. But in this case we had clear evidence, we had so many pictures, we knew: this is what it was. Whether it's good or bad, that's for everybody themselves to decide – there is no good and bad, I think in this case, but this is the result and the result - Tonny, Rozemarijn and Tamar – that was really done excellently. Thank you.

Arlen Heginbotham: Just some very informal research we did at the Getty looking at epoxies and copper alloys, which just might be of interest; we were trying to do some experiments to see what epoxy we could use under a certain circumstance and my colleague Jane Bassett got about 35 different epoxies and put them all on copper alloys and tried to observe what happened over a long period of time. We still have them 10 or 15 years later and it is very variable between the epoxy-types as to what happens. The worst reactions we had were with epoxies that are designed to adhere copper alloys because they have etchants in them and that are intended to etch the metal.

DIGITAL DOCUMENTATION OF HISTORIC FERROUS METAL STRUCTURES: 3D LASER SCANNING AS A CONSERVATION TOOL

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Abstract

Digital documentation via 3D laser scanning is rapidly becoming a tool of choice in heritage recording. Traditional survey of historic ferrous metal structures can be particularly difficult due to the complexity of their construction, and laser scanning offers a highly accurate, objective and informative method of documentation. The authors outline the process by which such recording is undertaken and then present the results of three recent case studies that highlight the potential of this technique as part of a conservation tool kit.

Keywords: Digital documentation, 3D laser scanning, historic conservation, ferrous metals

Introduction

Three-dimensional (3D) laser scanning for digital documentation of heritage structures is increasing in popularity due, in part, to its advantages over traditional survey methods (see for example Lerma et al. 2010, Meneely et al. 2009, Pritchard et al. 2009, Ruther et al. 2009). Scanning offers a faster, objective and more accurate method of documentation, and is particularly suited to historic ferrous metal structures. 3D laser scanning provides an additional dimension to conservation recording of traditional metalwork. This technique, used in combination with existing conservation science methods is proving to be invaluable for Historic Scotland. This paper will present three case studies from Scotland on the conservation and digital documentation of historic ferrous metal structures, each featuring different applications of the scanning technology.

3D Laser Scanning

3D laser scanning is a completely non-destructive, non-contact survey method. Scanning systems generate a 3D 'cloud of points' that can be manipulated to produce the desired output, such as architectural drawings or 3D models and computer animated visualisations. Historic Scotland owns and operates four high-definition laser scan systems capable of recording detail down to sub-mm level at very high accuracy. The terrestrial scan systems vary in the range they can capture, from a few meters distance from the target to 250 meters. Our state-of-the-art scanning hardware comprises two long-range time-of-flight pulsed instruments capable of recording 500,000 points/second (Leica ScanStation C10 and Leica ScanStation 2), which are ideal for recording as-built architectural heritage in its environmental setting. We have one mid-range phase-based scanner (Leica HDS6100), which has very high accuracy and is best for capturing interiors and architectural features. Finally, we have recently acquired an ultra-high resolution triangulation-based micro-scanning system (Perceptron Infinite II Arm and V5 Scanner) used to record carved or cast details at sub-mm detail.

Historic Scotland works in collaboration with colleagues from the Digital Design Studio (DDS) at the Glasgow School of Art to translate the raw point cloud data into photorealistic 3D models and animations, as well as 2D architectural line drawings. DDS owns and operates a Leica ScanStation 2 laser scanner, which was used for digital documentation of the projects detailed here.

Applications

Digital documentation by 3D laser scanning has many important applications in the conservation of historic ferrous metal structures:

- To provide an accurate and objective survey record of the structure or monument prior to and after conservation.
- To aid condition monitoring of the structure.
- To assist with conservation and reconstruction in combination with conservation science research.

- To create 3D models and animations to aid visitor interpretation and understanding of the structure and its construction methods. An important part of Historic Scotland's remit is education and outreach, and the authors are rapidly finding that interactive 3D graphical displays of traditional architectural forms, based on highly accurate three-dimensional data, are an effective means of interpretation.

- To produce exact scale model replicas of small objects.

- To create a digital archive of heritage structures should they be lost to catastrophic events.

Methodology

A standard laser scanning methodology was adopted for each site. Scans were carried out from a number of vantage points around each structure, ensuring full coverage from all angles and considerable overlap between scans. Scan resolution was determined for each specific project and all scans within that project were carried out to this pre-determined level of detail. Individual scans were tied together via a process known as registration using one of two methods: a) target registration (surveying targets scanned in multiple scans and used in registration software to align scans), b) cloud-to-cloud registration (whereby common points are used to tie adjacent scans together. This method produces accurate registrations on point clouds where there are sharp edges and easily identifiable common features). For these projects, the registration software used was Leica Cyclone (Leica Geosystems (2010)). Leica time-of-flight and phase-based laser scanners carry out a self-calibration check at start-up. To further ensure the accuracy of the resultant scan data, Leica Cyclone software generates a Quality Control report following registration, allowing the operator to quantify the accuracy and error of the registered point cloud.


Figure 1. 19th Century hotel entrance canopy in poor condition. Isle of Bute, Scotland.

The Bute Canopy

This rare and elaborate 19th century Scottish cast iron entrance canopy located on the Isle of Bute came to the attention of Historic Scotland in a state of disrepair (see Figure 1). Situated adjacent to the seafront and exposed to high levels of salt, a lack of maintenance had resulted in cracking and peeling paint. Aggressive chlorides from sea spray had caused active corrosion on all surfaces of the ferrous substrate.

As an integral part of the Historic Scotland-funded program of conservation, Digital Design Studio (DDS) was commissioned to laser scan, model and visualise the canopy in 3D prior to its dismantling for repair. The aim was to provide an accurate and objective digital documentation pre-conservation, and to produce architectural drawings of the structure to aid dismantling and reconstruction. A traditional measured survey was also carried out on the canopy to allow comparison of accuracy with the laser scan survey.

By moving the scanner around the canopy, the entire structure was digitally recorded in just eight hours at 2mm resolution, using a Leica ScanStation (see Figure 2). A total number of 30 million points were collected. Individual scans were registered off-site, which allowed the raw point cloud data to be viewed in 3D (see Figure 3).

Point cloud data can be exported to architectural drawing packages, such as AutoCad. By aligning to an appropriate coordinate system, the objective point cloud data can be directly utilised to generate detailed survey drawings. While there is still a human element


Figure 2. 3D laser scanning of the Bute Canopy.

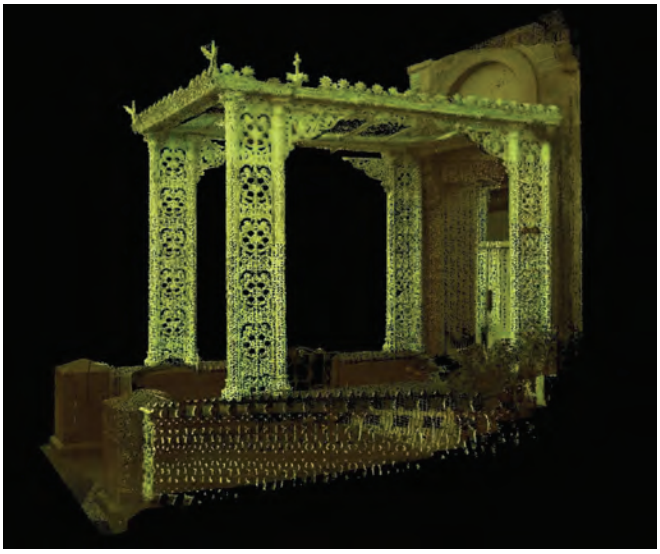

Figure 3. Screenshot of 3D point cloud data of Bute Canopy (developed by DDS).

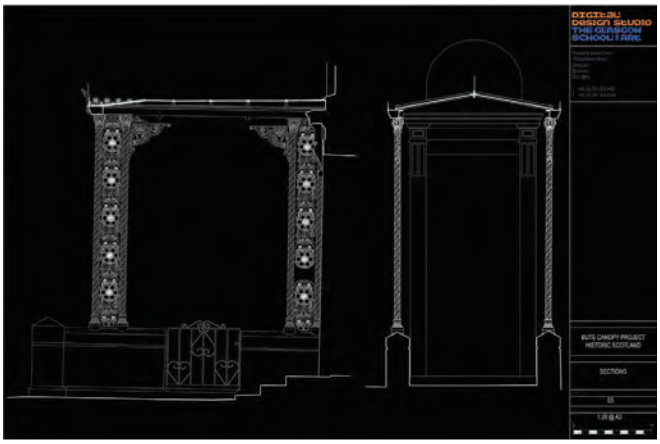

Figure 4. 2D architectural line drawings generated from 3D point cloud data (developed by DDS).

to choosing the points to use in AutoCad, the process is assisted by the fact that AutoCad can 'snap' to points. Also, the data generated by our scanners is 'clean', i.e. there is not as much surface noise as early scanners produced. The AutoCad technician draws lines on the basis of cloud density, taking the densest point groupings and identifying them as features. For the Bute Canopy, 2D architectural line drawings were requested by the contractor involved in the conservation programme (see Figure 4). These were of particular benefit to the contractor who could use them to take precise measurements of the structure off-site: a process that would not have been possible using, for example, digital photography.

It is possible to 'burn' high-resolution digital photographs of the structure of interest directly onto the point cloud allowing production of highly photorealistic 3D models (see Figure 5). This can be achieved in Leica Cyclone software by aligning specific points in the point cloud to specific points on the photograph. A minimum of seven common points are required to wrap each photograph onto the surface of the point cloud. Another way this can be achieved is through texture mapping onto meshed point cloud data in software packages such as Polyworks (Innovmetric 2010). Such models can be animated, providing an innovative visual record of the canopy in its original form. Finally, from the 3D model, an axonometric projection (or 'exploded' view) of the canopy was extrapolated, which allowed the component parts to be easily identified and catalogued prior to repair.

Aided by the digital documentation package, conservation of the canopy proceeded. It was reconstructed *in situ*, following cleaning, repair and re-painting (Wilson et al. 2010). The 2D architectural drawings produced from the laser scanning were relied on heavily during reconstruction. In comparison with the

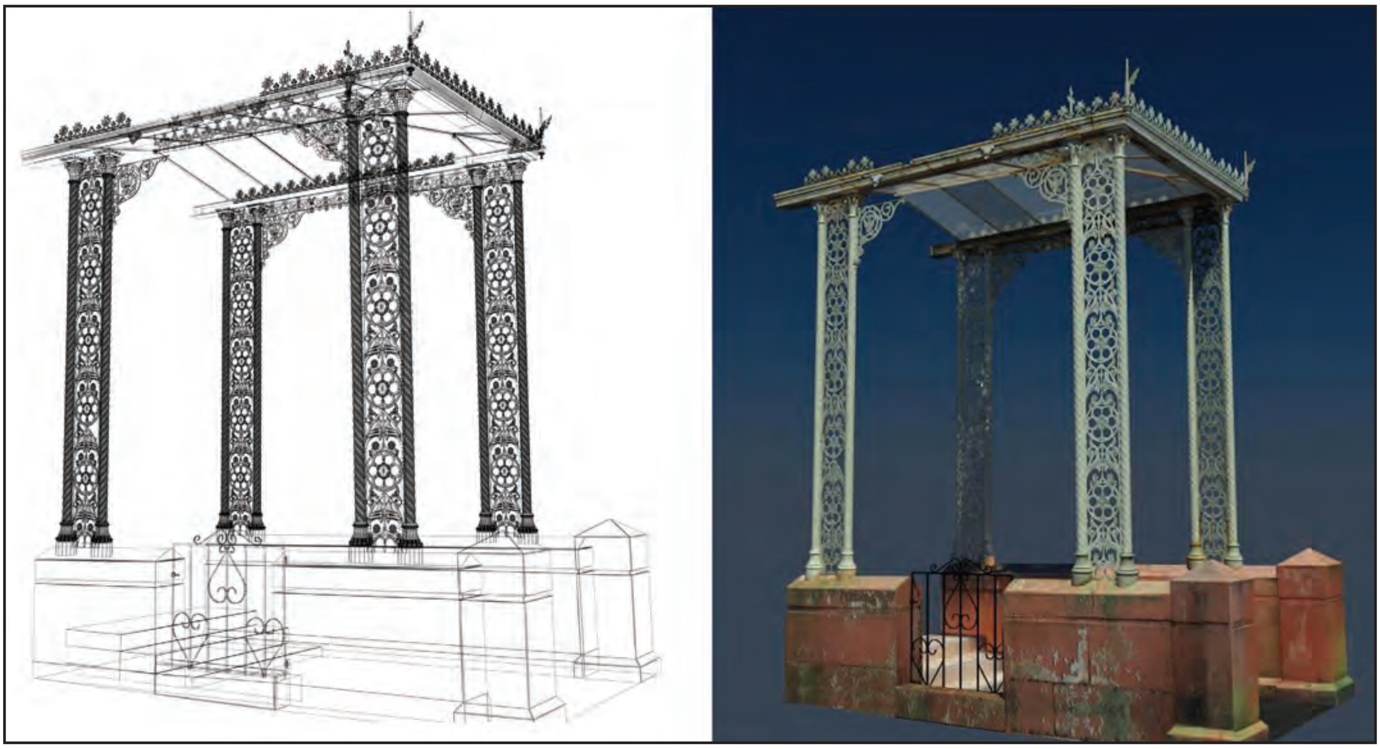

Figure 5. Screenshot of wire-frame and photo-realistic 3D models of Bute Canopy (developed by DDS).

traditional measured survey, the laser scan data proved to be more accurate in addition to being considerably faster to obtain.

Linlathen East Bridge

The Linlathen East Bridge, near Dundee, is the oldest surviving iron bridge in Scotland, dating to c.1804 (Paxton 2007). It features both wrought and cast iron elements. However, its historical importance has not protected it from the ravages of time, traffic, the environment, and even fire (see Figures 6-7). In 2008, Dundee City Council committed to a program of conservation that began with a laser scan of the bridge and its surroundings. As with the Bute Canopy, the aims of digital documentation were to accurately and objectively capture the current condition of the bridge and to produce 2D architectural drawings that would inform the conservation process.

Again, resources of DDS were commissioned by Dundee City Council to digitally survey the bridge. Laser scanning over a 10-hour period was performed using a LeicaScan Station long-range scan system. As in the previous case study, the scanner was moved around the site in order to document the bridge in its entirety from nine vantage points. The scanner was even placed in the river to allow digital documentation of the bridge's underside. A total of 64 million points were collected at a resolution of 2mm.

Once the registered point cloud was generated (see Figure 8), accurate 2D architectural line drawings were produced (see Figure 9). For conservation treatment, the bridge will be dismantled and repaired off-site before later reconstruction *in situ*. To assist and inform the contractor during dismantling, the laser scan point cloud data was converted into a 3D block model (i.e. a very basic representation of the scanned object based on meshed point cloud data without photorealistic texturing), which could be digitally dismantled and its component parts identified (see Figures 10a-f). Conservation work is expected to begin on the bridge project in spring 2010.


Figure 6. View of Linlathen East Bridge (c.1804) during 3D laser scanning.


Figure 7. Close up view of damaged Linlathen East Bridge.

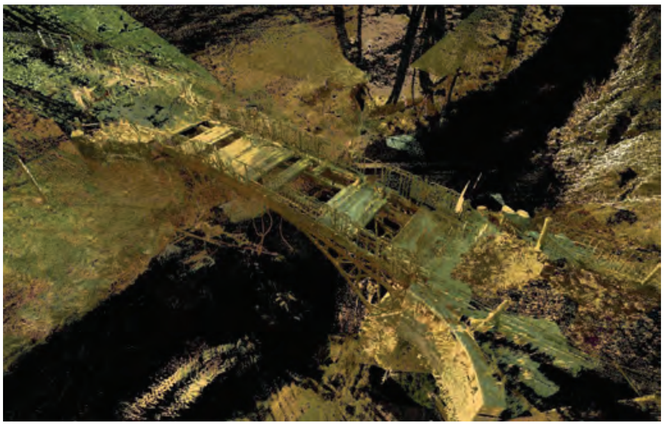
Figure 8. Aerial view of registered point cloud of Linlathen East Bridge (developed by DDS).

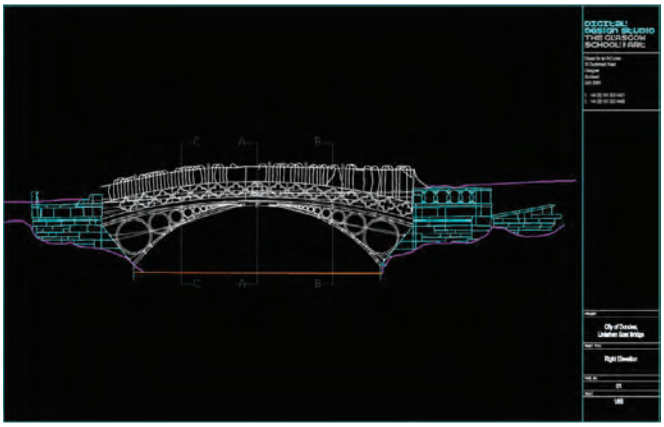

Figure 9. 2D architectural line drawings generated from 3D point cloud data (developed by DDS).

The Grand Fountain, Paisley

A spectacular 19th century painted cast iron fountain stands in the neglected Fountain Gardens park in Paisley, West of Scotland, which is currently the focus of an urban regeneration program by Renfrewshire Council. The fountain, constructed by George Smith and Co.'s Sun Foundry, Glasgow, in 1868, was gifted to the people of Paisley by Thomas Coats, a wealthy and well-travelled industrialist (Scottish Ironwork Foundation 2010). Its design reflects Coats' travels, with life-size walruses, herons, dolphins and other exotic creatures adorning the structure (see Figures 11-12). Even the apparent stone surround is fabricated entirely from cast iron. Historical records show the original paint scheme was devised by Daniel Cottier, the Scottish-born aesthetic designer credited with introducing the Aesthetic Movement in the U.S. and Australia. The fountain and its story form an important part of Scotland's rich ferrous metalworking heritage and it is Historic Scotland's role to ensure

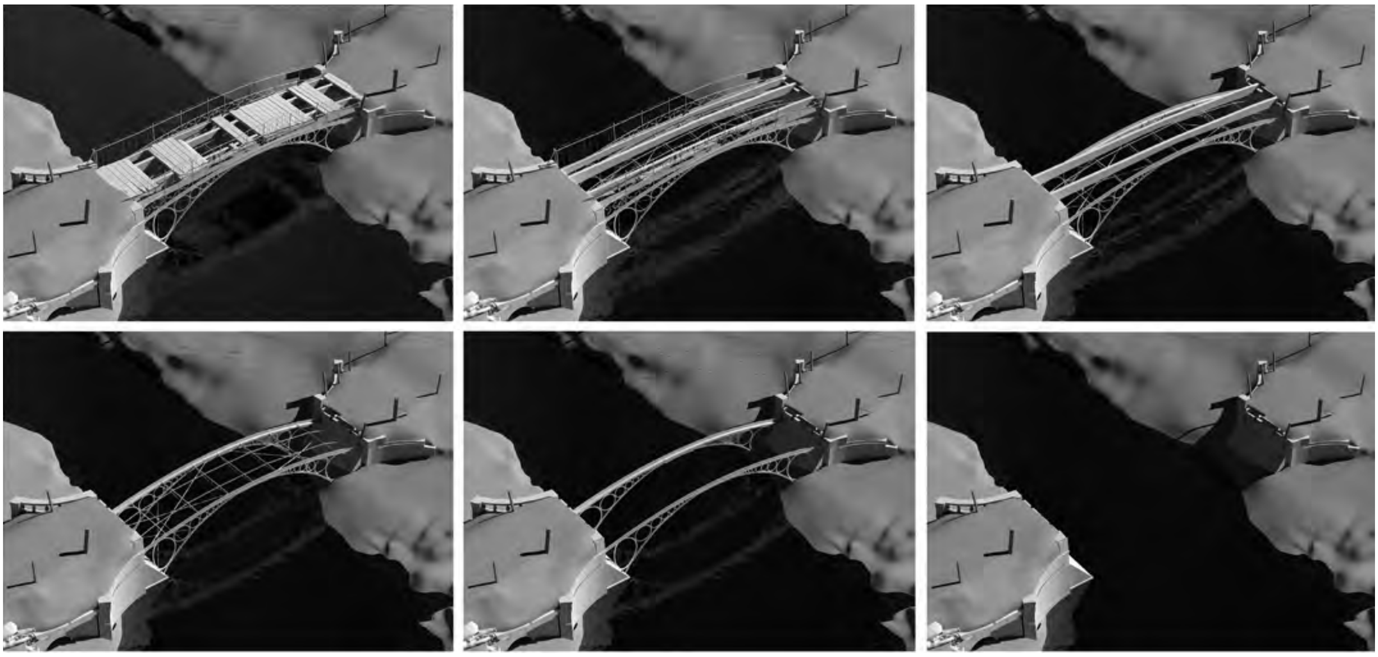

Figure 10. Screenshots of 3D block model of Linlathen East Bridge and its digital dismantlement (developed by DDS).

Figure 11. Photograph of the Grand Fountain, Fountain Gardens, Paisley (1868), showing current derelict condition.

Figure 12. Photograph of the Grand Fountain, Fountain Gardens, Paisley, showing detail.

its longevity: one route to achieving this is via digital preservation.

DDS was commissioned by Historic Scotland to laser scan, model and visualise the fountain in 3D. Over two days, a digital survey of the fountain and the surrounding park was undertaken using a Leica ScanStation 2. Eight scans were needed, including three from a scaffold, to accurately capture the upper sections of the fountain. In this instance, a total of 31 million points were captured at 2mm resolution. After registering the 3D point cloud the fountain could be visualised at a few mm accuracy (see Figure 13).

Differing from the previous two case studies, the aims of laser scanning the Grand Fountain combined 3D digital documentation with scientific investigation. Historic Scotland paint scientists and conservators sampled original paint layers throughout the fountain and identified the pigments from mounted cross-sections (see Figure 14). The historic paint scheme was then mapped onto the digital 3D model, which allowed an accurate and objective virtual reconstruction of the fountain as it looked originally, and how it could appear again post-conservation (see Figure 15). Typically, historic paint schemes are represented in flat 2D drawings, but 3D models and animations allow the colors to come alive. Even the lustrous finish of an original shellac coating, discovered through analysis, is represented in the 3D reconstruction, but would have been very difficult to depict by traditional methods. As a conservation tool, the novel combination of analytical data with 3D visualisation is highly effective.

In its present condition, several cast components of the fountain are damaged or missing. Creating new wooden patterns to re-cast these features would be an expensive and lengthy process. However, laser scanning offers an innovative method to circumvent this problem. Using an ultra-high resolution micro-scanning system, existing components could be documented at sub-mm resolution with very high accuracy: 24μm measurement accuracy throughout the entire field of view (Exact

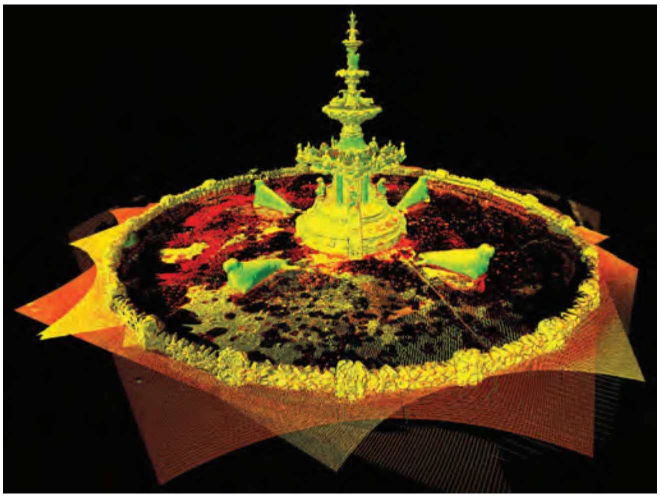

Figure 13. Screenshot of registered 3D point cloud of Grand Fountain (developed by DDS).

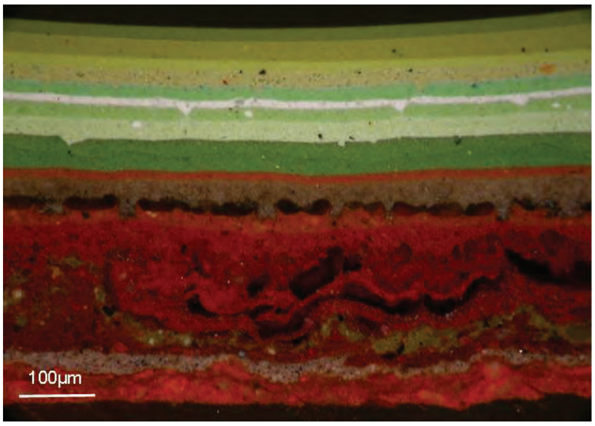

Figure 14. Detail of paint Cross-section of historic paint scheme from the Grand Fountain viewed under an optical microscope. The first paint was a red-lead primer, followed by a grey ground for bronze painting; later layers are confused due to paint stripping. Scale = 100µm.

Figure 15. Screenshot of 3D model showing virtual reconstruction of historic paint scheme on the Grand Fountain with shellac lustre (developed by DDS).

Metrology 2006). Areas where no data was collected (such as undercuts and voids) would be filled by careful manipulation of the software meshing package. Via a system known as rapid prototyping, the laser scan data can be exported as a format that can be read by 3D printing systems to directly produce physical and dimensionally accurate replicas of missing sculptural components.

In practical terms, generation of a 3D replica of a cast iron metal component via laser scanning could be achieved by producing a duplicate in a 3D print medium (e.g. resin or nylon). The 3D print could then be used instead of a traditional wooden pattern: inserted into a green sand mould, removed while allowing the mould to retain the shape of the 3D print, then the molten metal poured into the mould box and allowed to cool. The relative cost of this method is comparable to traditional pattern making techniques, plus the 3D print will be more accurate and truer to the original than a fabricated pattern.

This process has successfully produced replicas in the engineering world, for medical applications such as prosthetics and in museum contexts (e.g., Pieraccini et al. 2001, Shuxian et al. 2005, Willis et al. 2007). Historic Scotland has produced 3D replicas of Pictish carved stones from laser scan data for museum presentation**.** This has facilitated strong interaction from the public, from helping visually impaired visitors understand the carvings, to allowing children to touch and create drawings from the replicas (Muir 2010).

The fountain has not been operational for many years and as a result is a target for graffiti and vandalism. It is hoped that via education and community engagement, facilitated by the 3D (laser scan) animations and models, the fountain will soon be restored to its former splendour and once again be a focus for community pride and enjoyment.

Conclusion

In each case study, the authors have demonstrated that 3D digital documentation by laser scanning has significantly assisted the conservation and documentation process, from inception to completion. In comparison with traditional survey techniques of historic iron structures that may take weeks or even months to complete due to the complexity and corrosion of the ferrous metal, laser scanning can produce more objective and more accurate results in a fraction of the time. The potential is even greater when laser scanning is combined with conservation science methods, such as paint analysis. The ability to replicate missing components from laser scan data has important ramifications for conservation. Combined with the educational and interpretative aspects of 3D models and animations, the authors believe laser scanning soon will become an integral part of the conservation toolkit.

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Q & A SESSION

Ian MacLeod: For discussion later on if people want to know the symbol, which was the coat of arms of Glasgow of a fish with a ring in its mouth, I'm sure Lyn will tell you the story of how St. Mungo saved the reputation of the queen of Strathclyde, but that's for another time. But clearly Glasgow is flourishing and one of her finest gems has just presented a glorious picture for us.

Tim Foecke: Another aspect of this technology and I've seen it used just a little bit at the Federal Highway Administration – if you can make an architectural drawing, you can convert it to Pro-E. If you can go to Pro-E, you can go to any number of finite element packages. For example, instead of just virtually taking the bridge apart, you can run a series of simulations to find out, 'if I take it apart this way, is it going to fall down mid-process?'. Or if something has been damaged, do a quick scan of it, even an elastic model of it to find out 'is this thing really in trouble and that I don't know?'.

Lyn Wilson: I'm really interested to find out more about that from your talk hopefully.

Paul Mardikian: Lyn, this is wonderful. It is such an illustration of what we can do with this technique and it is good to see the end product. My question about the end product is the cost of the end product and how much time it takes for instance to do the Bridgeton Umbrella canopy – how long for instance would it take to do that or the bridge?

Lyn Wilson: Obviously the cost varies depending on the particular deliverables. If it's a 3D virtual reality animation, that is kind of the high-end output of this. I think that animation took the specialist 4 days to produce.

Paul Mardikian: So from the time you are on site, how long does it take to do on site? Everything included? I'm not interested in the cost really, I'm more interested in the man-hours or days.

Lyn Wilson: We were on site for 2 days. The man-days on the Bridgeton Umbrella project: 2 days on site, 1 day for data processing and 4 days for the production of the animation.

Paul Mardikian: Wow, it's very short.

Lyn Wilson: Yes.

Stéphane Lemoine: For the large metallic structure that you have shown – is it possible to add to the 3D files special applications to calculate, for instance tension, compression, stress of the different elements involved in the structure in static or dynamic cases?

Lyn Wilson: I think it probably would be. I think the finite element modeling is something that the next speakers will talk about. I think that is the best way to approach this, including this type of work.

Peter Northover: The collection of the data is extremely accurate and with the digital photography, that could be accurate too, although it will slightly depend on the camera optics. Then you have the processing of the data– depending on what you want to do with an architectural drawing – eliminating perspective and then you're depending on the algorithm. Obviously you do that as accurately as possible. So do you have any comments on the process – particularly on the process of eliminating perspective?

Lyn Wilson: Yes, it is as objective as you possibly can be but there are still human elements involved in the processing stages. We worked with the visualization specialists when we started the process. They would model things from their head essentially. But coming at it from a historical perspective we wanted them to model exactly what was there. So we've now moved them away from the sort of computer games realm and everything that is modeled now is exactly as it was on the point cloud. If there is an area missing that we haven't scanned then that will be filled in, in a different color so that we can show that we don't actually have the data for that.

Peter Northover: Would you normally physically measure some dimensions on the structure as well?

Lyn Wilson: Not as a rule of thumb because we know how accurate this is.

Peter Northover: Right, I was just thinking in terms of checking on the rendering in the drawings and so on, it would be a check. The only other thing I'm involved with this at all at the moment is the research on the famous statue of the Griffin that belongs to Pisa Cathedral. What we're really hoping with that is that we can overlay a laser scan on the photographs on the CAT-scan and get the inside 3D as well of something that's hollow and you can't get everywhere inside with the endoscope. So we try to put the two together.

Lyn Wilson: The CAT-scan is a fantastic piece of technology. I think [putting the two together] that would be possible. There are software packages that can do all of those things.

Benjamin Rennison: On that last comment: there is actually some research at the University of Bern who are actually combining CAT-scan data with 3D. I've just got a couple of questions: the first one is at the Schöobrunn Palace in Vienna, how did you actually scan the reverse sides of the exterior structure? Because there is glass on there.

Lyn Wilson: That one has taken a long time. Scanning a glass box is not the easiest thing to do and it has taken a long time to cut out all the reflections from the glass. But we scanned everywhere – inside and out and then combined the interior and exterior point clouds using targets so we were able to do that. But there has been a lot of editing of the data in terms of cutting out the reflections.

Benjamin Rennison: Thank you. And the second one is: for your texture mapping of the 3D data – do you actually create the blueprint and then texture map the photography on to there or do you texture map straight on to the points? Additionally, if so, do the points actually have color or is it the matrices that have the color?

Lyn Wilson: We texture map directly on to the point cloud. We always keep a copy of the point cloud in its original form intact and then we make a copy of it and texture map the high resolution photographs on to that. So the points do actually take on the RGB value of the camera.

Benjamin Rennison: And the last question is: do you have any benchmark analysis? So if you need to return, you can be sure that your first, second and third survey are all accurate.

Lyn Wilson: Yes, it depends on the particular site. If they let us put in permanent ground markers then we do. That then lets us go back and rescan at a later point; again, if we are allowed to put in the permanent ground markers we would take out our GPS system as well so that we have a really accurate record of where those points are. On some of our sites, we're just not allowed to do that, so it varies, but where we can, we do that, so yes.

Benjamin Rennison: Thank you, that's brilliant.

Kate Cuffari: Thank you that was a stunning presentation. I was wondering if you could tell us a bit about the scale of data with respect to storage of data for different scales of projects and for an institution like the one in Vienna that is looking for a facilities management tool – what the requirements are then for software, hardware and implications for ongoing maintenance of that dataset with technology transfer.

Lyn Wilson: Yes. The higher resolution the scans are the bigger the dataset and it is an ongoing issue that everyone involved in laser scanning is working on at the moment. To give you an idea of scale: the Palm House from the Schönbrunn Palace was approximately 100 GB. It increased probably to about 200 GB once we'd mapped on the photos. We can decimate down the point cloud to make that more manageable. We do try to keep things – for instance if the palace management wanted to use this – we can reduce the file sizes to a sufficient level so that they can work with them. But it is an ongoing problem and we have external servers here, there and everywhere and storage off-site. But that is something that the laser-scanning community needs to work on – we need central facilities for these types of data.

AN INTEGRATED STRUCTURAL HEALTH MONITORING SYSTEM FOR THE PRESERVATION OF THE HISTORIC FIREBOAT *ALEXANDER GRANTHAM*

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Abstract

The structural integrity of a metal artifact is always of concern to conservators and curators, particularly if the object is very large and intended for permanent display outdoors. Being the first vessel preserved as a historical relic in Hong Kong, the Fireboat Alexander Grantham was lifted from the sea and has been on public display since 2006. Given the unfavorable, yet uncontrollable outdoor environment, the fireboat will inevitably suffer from degradation and perhaps structural failure, which may not be easily detected or identified at an early stage through visual inspection. For the sake of her long-term preservation, the Central Conservation Section in Hong Kong has pioneered the development of an integrated Structural Health Monitoring system to monitor the structural stability of the vessel on exhibition. This paper will discuss the conservators' experience in devising the system and the preliminary findings obtained from the program to illustrate the merits and limitations of its application on historic vessels.

Keywords: integrated structural health monitoring, extreme events, structural behavior, strain, hull convergence, historic vessels

Introduction

Being the largest in the fleet of local fireboats during her service, the Fireboat *Alexander Grantham* (AG) was an icon embodying the achievements of the fire service as well as the glorious history of the shipbuilding industry in Hong Kong. With the objective of preserving this unique piece of cultural heritage, the Leisure and Cultural Services Department, the Government of the Hong Kong Special Administrative Region, undertook to fund and lead the Fireboat AG project. As soon as the fireboat was decommissioned in 2002 after some 50 years of service, she was given a series of intensive restoration treatments to arrest specific preservation problems, to ensure her structural well-being for the lifting operation onto dry land, and to provide protection against weathering and possible damage when she was set for open display (Tse et al. 2008). The fireboat is perched on the waterfront of the magnificent Victoria Habour in Hong Kong, with a small gallery built around her hull showcasing Hong Kong's sea salvage history of the past 100 years.

Overview of the structure

Constructed in the 1950s, the Fireboat AG is a steel twin-screw diesel driven vessel for fire-fighting and sea salvaging operations. The hull was constructed from Lloyd's grade-A steel plates (Hong Kong & Whampoa Dock Co., Ltd 1950) supported by 67 transverse frames with watertight bulkheads also made of grade-A steel. The steel plates were butt-welded in non-critical areas and complemented with traditional riveting at all the seams and frames. The bulkheads not only increase the overall structural rigidity, but also divide the hull into various functional compartments, such as engine room, pump room, etc.

As the boat is displayed on land, it is now supported by a cradle system (see Figure 1), which was designed with input from cross-disciplinary professionals, including architects, structural engineers, marine engineers, ship-builders and conservators. All factors, such as her static load distribution, dynamic load to be imposed by visitors and the wind load effect were considered in the cradle system's design. Nevertheless, structural systems are inevitably subject to age-related deterioration, causing concerns over their stability, maintenance, public safety, and environmental and cost implications. The fireboat is no exception. Therefore, the role of conservators is to manage the possible changes incurred upon the fireboat and to prolong her life for future generations.

Figure1. Cradle system supporting the Fireboat *Alexander Grantham.*

Current inspection practice for ships

As a general practice, structural assessments of ships are conducted by professional surveyors to assess functionality. The survey is normally a process of visual inspections, sometimes with supplementary thickness measurements and Non-Destructive Evaluation (NDE) for specific areas, such as welds and joints (Wang et al. 2008). Although these techniques reveal structural information, the process can be time-consuming and costly over a long-term, especially when many of the structural members are normally covered by wall panels and machinery (Salvino and Collette 2009). Moreover, these assessments are basically on-the-spot surveys and targeted for ships that are still serviceable to identify their fitness for continued use as a floating structure. Current monitoring techniques, primarily related to operational safety and stability, are not applicable to the fireboat as her use has now been significantly altered. Given her current exhibition status, a proactive, rational, and integrated approach is warranted to monitor the structural integrity of the whole display. With this approach, monitoring is more than a visual inspection as it requires that continuous structural checks are performed. With technical advice from various experts, a structural health monitoring (SHM) system has been developed for the fireboat that involves monitoring various parameters in order to integrate and evaluate all the findings for data analysis and interpretation (Rizzo 2008). The principles of SHM are based on the SHM program for fixed land-based structures, such as bridges. By collecting and analyzing data over time, the conservators hope to assess the prevailing condition of the display, and project the likelihood of any structural failures prior to their development into significant issues that threaten the integrity of the structure.

Concept of integrated SHM

The concept of SHM has been widely researched in the past few decades for its potential to reveal the structural stability of road facilities, bridges and high-rise buildings. It is aimed at providing accurate and in-time information concerning structural stability and dynamic behavior. SHM monitors for unusual behavior that may indicate a malfunctioning structural condition. When detected, the unusual behavior necessitates a detailed inspection and diagnosis/prognosis of the structure, and typically calls for immediate maintenance to rectify the failure (Glisic and Inaudi 2007). Core activities of the integrated SHM program for the fireboat include (Wong and Ni 2009):

- risk assessment and setting monitoring scopes
- identifying representative monitoring parameters
- designing integrated monitoring systems and the sensor network
- data acquisition, processing and interpretation

Risk assessment and setting monitoring scopes

In adoption of a risk-based approach[1] (Serratella et al. 2008), the following potential risks to the structure of the fireboat are identified to determine the scope of the program and the areas to be studied include:

- Failure of the structural components due to degradation will lead to the collapse of the fireboat. It is necessary to understand her structural behavior under various service patterns and weather conditions
- As the fireboat is now established as an accessible collection for public visitation, the dynamic load applied is significantly different from what she was originally designed for. Therefore, it is desirable to identify the anomalies in her load distribution and other dynamic behavior in order to assess the possible damages that may have incurred
- Although natural disasters have not been a real threat to Hong Kong, there are a number of typhoons every year. The severity of the damage is often difficult to establish without appropriate assessment means. Therefore, it is essential to evaluate the structural integrity immediately after the occurrence of extreme events.

The result of adopting this approach will allow resources to be focused on the structural components where they are most needed. The integrated SHM program can provide the necessary information and analytical tools for planning, evaluating and designing a long-term inspection program and effective maintenance strategies, and hence re-direct the maintenance from a corrective to a preventive approach.

Selection of monitoring parameters

Load pattern of the fireboat

In the past, the fireboat was supported by water buoyancy pressures and therefore her static and dynamic loads (e.g. vibratory loads from machinery) had been duly spread over the frames. With the vessel now mounted on land, all loadings are shared by the cradle members. Therefore, any change in the load pattern of the vessel could have a direct effect on the structural reliability of the cradle, which in turn affects the structural behavior of the whole display.

Deformation of the hull structure

The cross section of the hull can be regarded as a tunnel and its geometry has a direct relation with the structural reliability of the ship. Therefore, it is necessary to measure the hull convergence, which would be calculated as the degree of hull deformation.

Tilting and acceleration

During extreme events, such as a typhoon, the fireboat will be subject to severe external forces that may affect her overall structural stability. The related changes in stability parameters can be duly reflected by the measurements of overall tilting and acceleration.

Foundation settlement

The fireboat is now sitting on a stretch of reclaimed land that was not intended to take massive loads. Though piles were embedded in association with the construction of a foundation plinth for the fireboat, differential settlement may still take place and affect the reliability of the data gathered from the SHM program, particularly the change of load pattern. Therefore, settlement measurement is essential for data verification.

Wind speed and direction

To differentiate the readings caused by damage due to variations in environmental conditions in data normalization, environmental parameters such as wind speed and direction also are logged (Farrar and Sohn 2000).

Description of the monitoring system

With reference to the proposal of the engineering consultants, an integrated SHM system has been developed in phases to measure the identified parameters. Except for the strain gauges that were installed in March 2006, extensive instrumentation has been deployed as per the system requirements for implementation of the program in March 2009. The current setup (see Figure 2) can be categorized into three sub-systems:

- Continuous monitoring system — vibrating wire strain gauges, anemometer, accelerometer, tiltmeter
- Periodic monitoring system — reference points for tape-extensometer,
- settlement markers
- Data acquisition management system — devices for continuous logging of data from sensors.

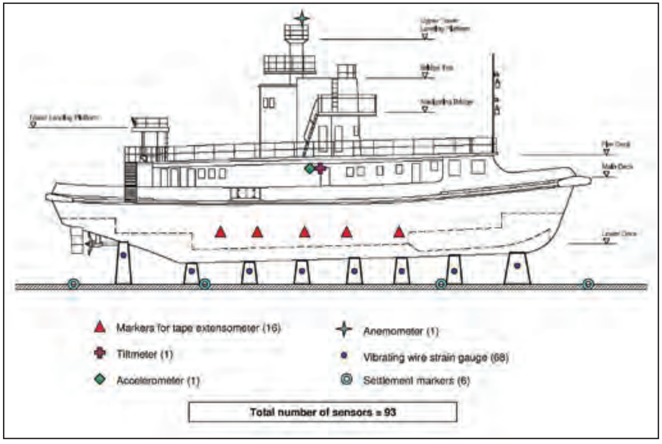

Figure 2. Location of monitoring sensors on the Fireboat *Alexander Grantham.*

Vibrating wire strain gauges

Sixty-eight sets of vibrating wire strain gauges, Gauge Technique model TSR/5.5/T, were installed onto the cradle before the installation of the fireboat. The gauges measure the strain/stress levels acting on each cradle member at hourly intervals so that the change of load pattern of the fireboat can be determined through engineering calculations.

The Anemometer

Installed at the highest point on-board, the RM Young 05106MA anemometer (see Figure 3a) will capture the data of wind speed and direction acting on the vessel and will not be affected by the turbulence transferred from the shipboard structures. Data has been logged at 5-minute intervals and the anemometer has been connected to the accelerometer and the tiltmeter in order to over-ride their pre-set sampling frequency during extreme events.

The Accelerometer

The accelerometer, Kistler 8330A3, mounted to a structural member inside the pump room casing (see Figure 3b) is used to measure the dynamic movement across the vessel. It normally takes readings hourly but will sample at 10Hz when the 5-minute mean wind speed is greater than 40 km/hour.

The Tiltmeter

The Durham Geo Slope Indicator EL Monopod tiltmeter (see Figure 3c) is deployed to measure changes in orientation of the vessel caused by deformation of her structure, wind load effect or differential settlement of the foundation slab. The frequency of data sampling is the same as that obtained by the accelerometer.

Reference points for tape-extensometer

Due to the arrangement of machinery and superstructures on-board, hull sections within the main engine room and the pump room are more susceptible to deformation. Therefore, 16 sets of reference points have been installed onto frames inside these compartments for repeatable measurement with tape extensometer. Apart from the regular measurements to be conducted monthly, supplementary measurements will also be carried out within two days of the occurrence of extreme events for rapid condition screening to provide, in near real time, reliable information on the overall integrity.

Settlement markers

Six settlement markers have been installed on the foundation slab to assess differential settlement that may affect the structural stability of the fireboat and the readings collected by other on-board instruments. Optical surveying techniques (see Figure 3d) have been deployed for the assessment, using a Leica NA3003 digital level, once every three months.

Data management system

The data management system is composed of three categories of equipment, namely data acquisition units (for collection of data from the sensors), data transmission units (the cable network for transmission of signals) and storage device (for temporary storage of data until retrieval). The data is then downloaded to a computer and the project Structural Engineer deals with the analysis and interpretation.

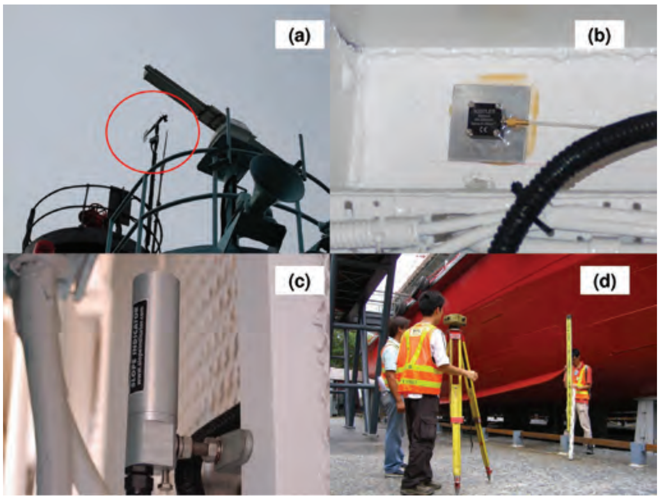

Figure 3. (a) The anemometer is fixed on top of the fireboat; (b) The Kistler 8330A3 accelerometer measures dynamic behavior of the fireboat especially during the occurrence of extreme events; (c) The tiltmeter is installed inside the pump room casing; (d) An Optical surveying technique has been deployed for settlement measurement.

Preliminary findings

Change of load pattern

The load pattern measurements obtained between March and July 2006 are shown in Figure 4. Measurements of the force acting on the cradle member supporting frame 21, the heaviest part located at the centre of the vessel, show a change after the installation of the fireboat in March 2006. The drop of force over time depicts a compressive force generated by the static load of the vessel acting on the cradle. This force gradually increased from the end of March apparently because the fireboat had started to sag. Continuous monitoring has been conducted over the past few years, and readings on the same cradle from April 2007 until December 2009 (see Figure 5) illustrate that the change of strain was within 3-5%. This result is within the instrumental and measurement error, as determined by the project structural engineer, and thus considered as insignificant. This implies that the sagging of the fireboat largely settled at an early stage before April 2007. The strain gauges were installed with an individual temperature sensor and therefore all the readings were corrected for temperature effect. Readings on the same cradle in 2009 (see Figure 5) illustrated that the change of strain was almost insignificant, which implied that the sagging of the fireboat has largely settled.

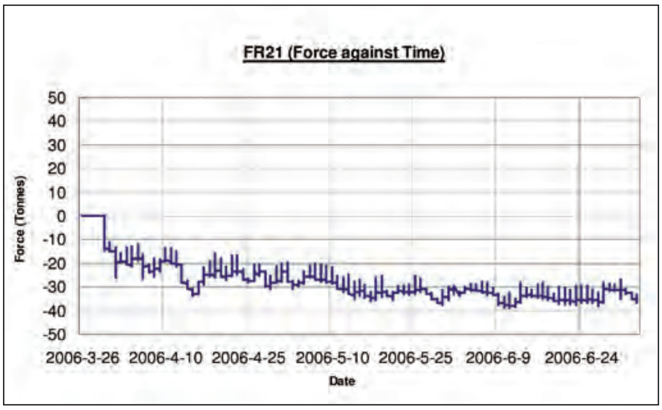

Figure 4. The amount of force acting on frame 21 during the period from 26 March 2006 to 4 July 2006.

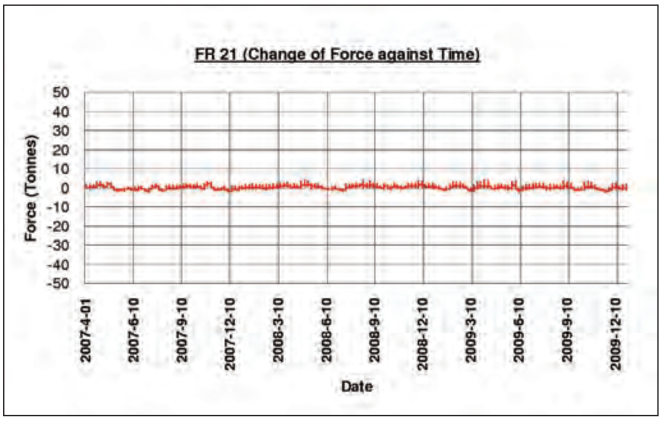

Figure 5. Change of force acting on frame 21 during the period from 1 April 2007 to 10 December 2009. The readings along the zero level indicate that the change of force acting on the cradle was almost insignificant over the period.

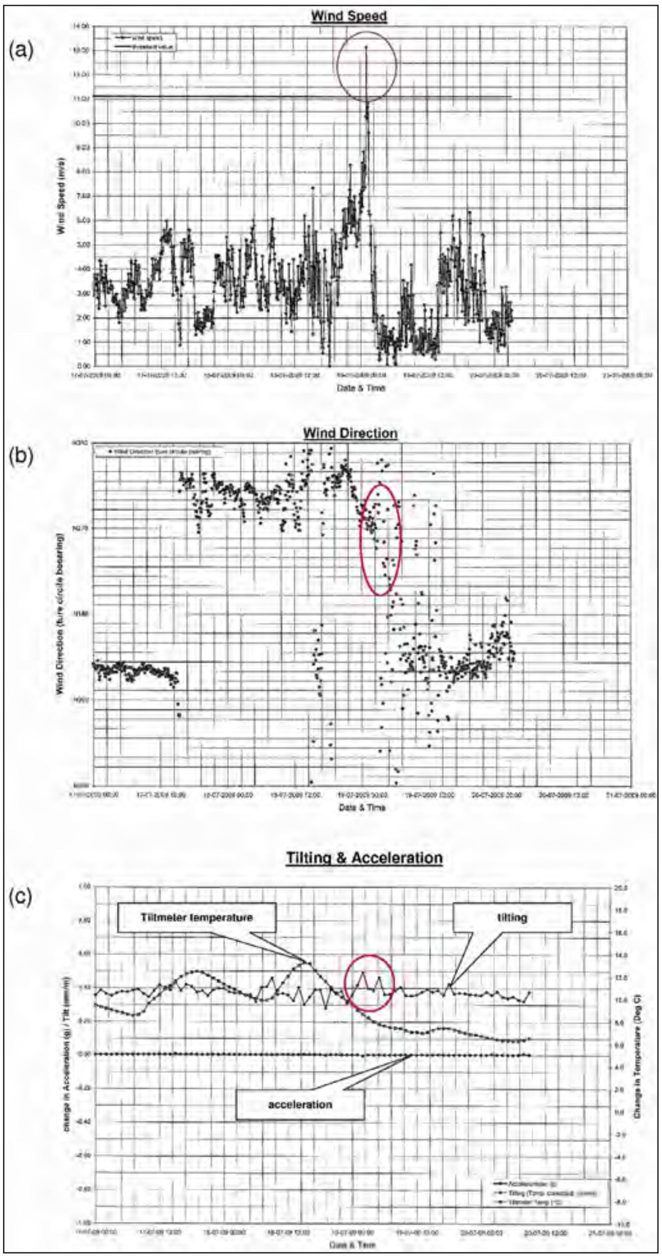

Figure 6. (a) The wind speed plot indicates the maximum wind speed that was recorded after midnight on 19 July 2009; (b) The wind direction changed from west to south-west during the period with highest wind speed; (c) The maximum transient tilt was recorded during the period with maximum wind speed, while acceleration was negligible.

Tilting and acceleration

The impact of a typhoon is illustrated in Figure 6. A maximum wind speed of 13m/s (see Figure 6a), with direction from west to south-west (see Figure 6b), was recorded around 1 a.m. on July 19, 2009, while the typhoon signal no. 9 was in force[2]. It is evident from the chart that the maximum transient tilt of Fireboat AG was also detected simultaneously. Fortunately, the event did not lead to any permanent tilt and the reading resumed to normal shortly afterwards (see Figure 6c). Therefore, the wind load effect was not very significant. This can be explained by the phenomenon that the wind direction was almost parallel to the fireboat, which is aligned in an east-west direction, hence only a small part of the vessel was subject to the wind load. The acceleration recorded was negligible, which implied that the tilting movement had been relatively slow.

Hull convergence and foundation settlement

Up to January 2010, data collected in the program indicates that hull deformation and foundation settlement are both insignificant, but continuous monitoring will be carried out.

Limitations and future challenges

Though the SHM technique has been well developed for assessing the condition of new structures, its use for assessment of the Fireboat AG is, in fact, a pioneering attempt to apply the system to an historic vessel. The difficulties or challenges to be overcome include:

- While the Finite Element Modeling (FEM) is a typical component of a SHM programme for predicting the behaviour of new structures, lack of available information for the Fireboat AG meant that an FEM was not feasible. (Clemente and Buffarini 2009)
- The mechanical properties of historic structures may vary, due to workmanship, obsolete techniques, deterioration and corrosion
- There may be significant changes in the constitution of structural elements in the course of time, a consequence of the object's past service history (Lourenco 2001).

In most cases, an observational approach has been adopted in this project to determine the thresholds of the readings that give an early warning regarding the integrity of the fireboat and her cradle. Apart from the useful results, the project has provided the conservator with a good opportunity to assess the potential of applying SHM as a monitoring tool for the long-term preservation of historic vessels or large metal artifacts. Moreover, further studies on the following aspects will need to be carried out so that a more sensitive system with structural evaluation and appropriate diagnostic and prognostic capabilities can be developed. Future areas of interest are:

- The use of fiber optic sensors to provide more sensitive measurement, especially concerning the structural deformation;
- Development of a FEM to further verify the structural stability of the vessel, and to determine the life expectancy of the whole display
- A real-time monitoring system be devised so that the structural behavior of the fireboat can be evaluated instantly, especially during extreme events
- Statistical models to be developed to differentiate undamaged features from damaged structures so that algorithms can be implemented to quantify the degree of damage of the vessel.

Conclusion

Display of objects in an outdoor environment is always difficult and metal objects in these situations are subject to degradation that will inevitably reduce their long term structural stability. A corrective approach, which is based on structural health monitoring that incorporates periodic inspections, and at times, instrumental tests or non-destructive analysis, was recently previously adopted to preserve the historic Fireboat *Alexander Grantham* in Hong Kong. After several decades of research and development in the engineering field, structural health monitoring is now considered a proven process for damage detection in structures. Providing adequate information on the structural performance over time ensures the overall safety and stability of the structure. Having pioneered this technique for the preservation of the Fireboat *Alexander Grantham*, conservators in Hong Kong believe that it can bring a new dimension to the inspection, maintenance, and repair strategy for other historic structures.

Acknowledgements

The authors are grateful to Dr. CHAN Chin-Wing for his altruistic contribution to literature research on the subject, which sustains the content of the paper.

Endnotes

[1] Risk-based approaches to inspection, maintenance and repair (IMR) strategies originated in the nuclear industry in the 1970s and have progressively migrated into other industries over the years, including the shipping industry for marine and offshore structures. It is a proactive approach and gives a balance between risk and inspection effort by including risk assessment of the asset coupled with the understanding of degradation mechanisms and consequences of failures for development of an optimum IMR programme.

[2] In accordance with the Hong Kong Observatory, typhoon signal no. 9 indicates the sustained wind speed is between 63-117 km/h, the gusts may exceed 180 km/h, and the wind strength is expected to increase significantly.

Materials

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Q & A SESSION

Tim Foecke: You've definitely identified the difficulties of structural health monitoring which is basically teaching your system. So far where you have put the sensors are pretty much a scientific wild guess and you don't know if those are necessarily going to pick up anything if anything goes wrong. I'll give you another example: the 35W Bridge collapsed in Minneapolis a few years ago and they rebuilt it. It is the most instrumented transportation structure in the world. It has fiber optic sensors, it has everything. The civil engineering department of the University of Minnesota is responsible for monitoring the bridge, and I asked the guy who is monitoring it - who used to be my professor - 'how do you know when you have a problem?' And he said: 'if the fiber optic signal stops we know it fell down again!' So what you need to do now as the next step, make even a simplistic finite elemental model to find out where your stress hot spots are. Are your sensors in the right place? And then see if there is something you can do to the boat in a controlled fashion that you can also model to see if your sensors respond the way the model does. What the Federal Highway Administration does is they have an 80 ton truck that they close a bridge, they have a model of it, they put the truck in various locations on the bridge and measure deflections using however it is instrumented. It is a long arduous process and it may never get to the point of success but you have a relatively compact system that is fairly well characterized. I think you've got a pretty good chance at it.

Jonathan Tse: Yes, we need to confirm. For example, we need to do some more things, how to optimize the location of the sensors in order to reflect the true data. For example there are problems in identifying the placement of a sensor. For example where to place the accelerometer and the tiltmeter, it's quite critical. If you put your sensors on secondary structures because as you can see, we've got some other structure on top of the deck. If you put a sensor on those areas, yes you will have a reading, but is the reading true to reflect the actual performance of the boat – these are questions. So the other thing I want to thank Tim for his suggestions is: we need to do some more control samples to see whether our sensors are very useful or really applicable for our study, thanks Tim.

FINITE ELEMENT ANALYSIS OF THE *H.L. HUNLEY* SUBMARINE: A TURNING POINT IN THE PROJECT'S HISTORY

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Abstract

Conservation efforts for the 40-foot-long H.L. Hunley *submarine (1864) have now reached a point that requires mechanical rotation of the vessel's hull. This new course of action has raised a number of important questions regarding the submarine's structural integrity. In response, project scientists have developed a finite element numerical model of the hull in its current state in an attempt to answer these questions. Data for the numerical model was obtained from archaeological documentation, as well as analytical data from non-destructive evaluation and metallurgical studies. Although finite element analysis is commonly used for structural analysis in many fields of engineering, its application to a historical structure such as the* H.L. Hunley *brings significant challenges. In particular, the exact degree of deterioration and the heterogeneous nature of the corrosion create uncertainty in identifying material properties. The finite element analysis provides conservators with a theoretical framework to assess the impact that rotation of the hull's original orientation might have on its overall structural integrity and provides a basis for conservation-related decisions.*

Keywords: *H.L. Hunley*, conservation, structural integrity and analysis, finite element analysis.

Introduction

On August 8, 2000, the American Civil War-era submarine the *H.L. Hunley* (1864) was successfully raised from the bottom of the ocean. In order to preserve the stratigraphy of the interior sediment, the submarine was raised in the exact orientation in which it was discovered; approximately 45-degrees on its starboard side. Recovery was accomplished using a steel truss fitted with a system of tensioned slings and cushioned bags for support and stabilization (see Figure 1). After its recovery from Charleston Harbor, the *Hunley* was immediately transported to Clemson University's Warren Lasch Conservation Center in North Charleston, South Carolina. The submarine was placed in chilled water under an impressed current cathodic protection (Mardikian 2004).

Analysis of the hull began using endoscopic examination and ultrasonic techniques. These techniques were followed with X-radiography and gamma-radiography to help define a protocol for access to the interior of the submarine for excavation. Investigation revealed that the submarine was constructed from sections of rolled plates, riveted together with two expansion strakes to form a hull that was roughly elliptical in profile with tapered ends comprised of riveted quarter plates and castings. To facilitate access to the submarine's interior, four semi-hemispherical riveted plates, located above the crew compartment between the two conning towers, were removed. In addition, two riveted quarter plates positioned above the fore and aft ballast tanks were removed to gain access to the ballast areas. To remove these plates, several hundred rivet heads were partially drilled out. During the following nine years, 11 tons of sediment, more than 1,400 individual artifacts, and the remains of all eight crewmembers were excavated from the interior of the submarine.

After almost a decade of excavation, forensic study, technical analysis and documentation, the *Hunley* project has reached a turning point. Rotation of the submarine's hull from its current 45-degree tilt to the 12-o'clock upright position, allowing the vessel to rest on its keel, represents the next logical step for the long-term preservation and final display of the submarine. The removal of the concretion layer that formed during burial is the key to the long-term stabilization of the submarine.

Rotation of the hull and removal of the sling system will facilitate the deconcretion of the hull and maximize the effectiveness of the stabilization treatment.

Figure 1. *H.L. Hunley* resting in its current support system at the Warren Lasch Conservation laboratory after its recovery (Copyright Friends of The Hunley, Inc. 2001).

To assess the impact that rotation of the hull will have on the submarine's structural integrity, project scientists have developed a finite element numerical model of the *Hunley* as a predictive tool. The input for the model was refined using the three-dimensional archaeological site map and analysis from non-destructive evaluation and metallurgical studies of the hull. Although finite element analysis (FEA) is a numerical technique commonly used for simulated structural analysis in a variety of engineering specializations, its application to a historical structure like the *Hunley* brings unique challenges. The complex design of the submarine, the heterogeneous corrosion of the hull, and the structural modifications made to the hull for the interior excavation are major challenges in developing a finite element numerical model that can be used as a predictive tool for the rotation of the *H.L. Hunley* submarine.

The Pre-Recovery Structural Analysis of the H.L. Hunley

Prior to the *Hunley's* discovery in 1995, the only available information about its construction was from historical records, including: a painting by Conrad Wise Chapman dated to 1863; sketches from 1872 by James R. McClintock, chief designer and engineer of the *Hunley*; and a 1903 magazine article containing a sketch by William Alexander, first officer of the *Hunley*. While Alexander's sketch detailed some of the internal structures of the submarine, Chapman's painting and McClintock's sketches provide more accurate descriptions of the hull (Mardikian 2006).

In 1996, a year after the discovery of the *Hunley*, an assessment of the site conducted by the National Park Service revealed that the hull was relatively intact and filled almost entirely with sediment (Murphy 1996).

In order to devise a plan to safely recover the *Hunley,* project engineers began looking for specific construction details, including the total weight of the submarine and residual strength of the hull. Unfortunately, this information was lacking, and in fact, 'very little factual data [was] available for the development of a structural analysis as only the rivet pitch and size [was] known' (Oceaneering January 2000). The rivet pattern on the exterior of the hull was recorded during the site assessment in 1999, using underwater molding techniques. Attempts to measure the thickness of the hull using ultrasonic techniques failed due to the corrosion of the hull. Instead, the hull thickness, approximately 3/8" (0.95 centimeters), was measured from a rivet hole in which the rivet had completely disintegrated allowing measurement through the thickness of the hull. The weight of the submarine was perhaps the most critical unknown factor and was estimated from historical records at 58,000 pounds (26.3 tons). The actual weight at the time of recovery was 47,000 pounds (21.3 tons), as measured by Oceaneering's equipment. The difference between the estimated and the actual weight was because 'transition sections on the bow and stern were much more tapered than depicted in the historical drawings' (Oceaneering, November 2000).

The first three-dimensional (3D) mathematical model of the *Hunley* was developed by engineers from Oceaneering based on measurements from James R. McClintock's sketches. Properties of the hull were assumed to be the same as wrought iron and the interior sediment of the submarine was assumed to have the same weight as wet sand. Results from this model indicated that stress concentration would be greatest along the longitudinal rivets and assisted the engineers in choosing a conservative approach for the recovery. In particular, it was concluded that a sling-and-bag system with a rigid structural truss would provide the best support during recovery. On August 8, 2000, the *H.L. Hunley* was recovered intact after nearly 140 years on the bottom of the ocean.

Finite element analysis

The finite element method (FEM) is a numerical technique used in many fields of engineering to simulate the behavior of a structure under a given load. The finite element analysis, which is the practical application of the FEM, consists of a computer model of a material or structure that is stressed and analyzed for specific results. In order to develop a FEA, four pieces of information are needed: (1) a numerical model of the geometry of the structure, (2) the mechanical properties of all materials, (3) the interaction properties of parts in contact, and (4) the loads applied on the structure. If accurate information is entered into the model, FEA can provide valuable data, such as the distribution of stress and location and value of areas of highest stress in a structure. This analysis can provide a direct indication of potential structural damage and failure. FEA also can provide information about structural deformation and is a valuable tool for structural monitoring and design.

FEA has occasionally been used in historical conservation projects, such as the prediction of future deterioration of the hull of the USS *Arizona* (Russell et al. 2006). FEA is also used in archaeological applications to predict structural failure due to transportation, seismic loads, changes in environmental conditions, and accumulation of degradation over time (Murphy and Russell 2002). The validity of the FEA output is directly dependent on the user's input in terms of accuracy and reliability of the four aspects mentioned above. In historical conservation projects and in the case of the *Hunley* submarine, an emphasis on non-destructive sampling often complicates the collection of data sets, presenting significant challenges for the engineers due to the lack of available information. Therefore, engineers working with the FEA must make important assumptions and conduct parametric studies[1].

Creating the geometry of the model

The 3-D numerical model of the structure's geometry shown in Figure 2 was created using the dimensions of the hull. The model is composed of shell surfaces for all plates, backing plates, bulkheads, strakes, and regions of riveted connections. All other parts, such as the bow, stern, conning towers, hoops, and ballast blocks are modeled with solid 3-D elements. Because interior and exterior appendages, such as the crank shaft, flywheel, propeller, and dive planes, are considered added weight, they were removed from the current model. This is considered a conservative measure since they are assumed to add stiffness and strength to the structure. The geometrical model is then divided into more than 300,000 finite elements creating a 3-D computerized mesh of the submarine (see Figure 2). Since adequate thickness measurements cannot be taken until after de-concretion of the hull, entering the original thickness of the wrought iron plates (8 mm to 10 mm) into the model as a variable parameter, instead of a fixed thickness, proved useful in accounting for the effect of corrosion during the simulation. Parametric studies incorporate the variable thickness of the hull, ranging from moderate to extreme loss of material at key structural locations on the submarine.

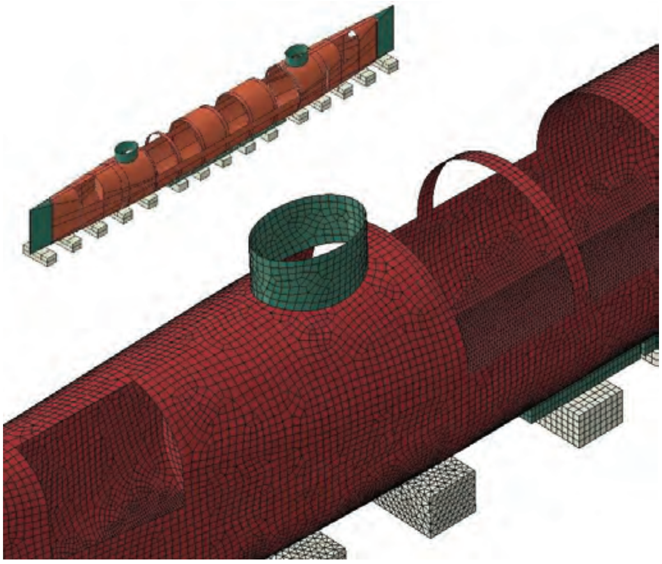

Figure 2. Finite element model of *H.L. Hunley* in vertical position.

Mechanical Properties

The key to creating an accurate FEA is combining a representative model of the geometry with a complete analysis of the physical and mechanical properties of the structure's elements. To analyze the structural behavior of the *Hunley*, the three major material properties required are density, stiffness, and strength. These property values are given in Table 1 and discussed below:

- Density controls the gravitational loads applied on the structure. Density values were measured from material samples of the *Hunley*, namely wrought iron rivets and pieces of concretion.
- Stiffness of the metal is defined by the modulus of elasticity in tension and shear. Metallurgical studies of cast and wrought iron components from the *Hunley* were conducted to determine the chemical constituents and microstructure of the *Hunley's* iron components[2]. Testing of the wrought iron samples yielded results, but due to sampling constraints, testing of the cast iron was impossible (Mardikian 2006). However, it should be noted that the heterogeneity of the corrosion noted throughout the submarine's structure does not permit assessment of a single stiffness value, as would be possible with freshly cast or wrought iron. Given the uncertainty of the analysis, elastic properties are estimated to vary within the range of values described in Table 1.
- The strength of the metal, which is necessary to predict the risk of failure, represents the upper stress limit that the metal can withstand before permanent deformation occurs. Metallurgical studies[2] from the *Hunley* showed a relatively high level of silicate slag in wrought iron components, which generally provides added strength (Mardikian 2006). By direct comparison with a reference database[3], the strength of the iron was found to be comparable to today's wrought iron (Mardikian 2006)."

Interaction properties

The hull of the *Hunley* is constructed from nearly 100 different parts riveted together. Several parts, such as the compression hoops and the keel blocks are in contact with the hull. Since recovery, the submarine has been supported by a set of movable slings and cushions that are in surface-to-surface contact with the hull. These interactions represent an important aspect for the reliability of the numerical model. Consequently, the contact friction coefficient is considered as a parameter (see Table 1).

Applied Loads

Gravity loads from the hull and appendages such as the dive planes and the propeller are defined throughout the structure as concentrated loads. Additional, concentrated loads are applied to account for staff members climbing at specific locations on the structure during examination and conservation work. Finally, the reaction forces applied by the supports are the most detrimental loads. These reaction forces depend on the stiffness of the cushions, as well as the relative positions of each support with respect to the other supports and the hull.

Property	Unit	Nominal Value	Minimum	Maximum
Density of iron	kg/m^3	7,430	-	-
Density of concretion	kg/m^3	2,160	-	-
Modulus of elasticity of wrought iron	GPa	200	170	210
Modulus of elasticity of cast iron	GPa	150	100	200
Modulus of elasticity of cushions	GPa	0.001	0.0002	0.01
Strength of wrought iron	MPa	180	-	-
Strength of cast iron	MPa	120	-	-
Plate thickness	mm	9.5	4.0	9.5
Friction coefficient at contacts	-	0.95	0	1

Table 1. Physical and mechanical properties.

FEA results for the *Hunley*

After constructing the model based on these parameters, several FEA simulations were conducted between 2007 and 2009 using the commercial software ABAQUS (by Simulia). These FEA simulations were used to assess the stress level in the structure and the potential risk involved with the removal of individual slings and submarine elements. Those results were used to confirm the intuitive approach of the conservators and guide them during the removal of the two ballast pumps (Watters et al. 2009). This model was further developed to build a more efficient risk assessment tool to assist the conservators with the rotation of the submarine. The model showed that, since the design of the hull in the bow and stern regions differ significantly from the central portion of the hull, these sections respond differently to hull supports (see Figure 3).

When handling objects, most conservators intuitively aim to evenly support the object, but with the *Hunley* this paradigm must be questioned. Perhaps the most important piece of information that FEA can determine is the amount of force that should be applied to the submarine by each of the supports to ensure that stresses are minimized. The force applied by a support is directly controlled by its vertical position with respect to the hull as the sandwiched cushion is being compressed. The higher the position, the more it pushes upward on the hull and the more weight it carries; this is called the 'reaction force'. Three scenarios were analyzed with the FEA, each with a different vertical position for the central supports.

Figure 4 shows the reaction force at each support position (from 1-15, *bow to stern,* as shown in Figure 3) for the three scenarios. Figure 5 shows the corresponding deformation and stress distribution for the same three scenarios. In scenario 1, the vertical position of the central supports is the highest and the distribution of the reaction force most uneven, while scenarios 2 and 3 show a more uniform distribution of reaction forces. However, these results show that scenario 1 would be less detrimental to the hull since it has the lowest maximum stress levels (see Figure 5).The notion that a more uneven load distribution results in a lower overall stress level is counterintuitive and underscores the complexity of working with large objects such as the *Hunley*. This example demonstrates the critical need for a FEA numerical simulation in reducing the risk of structural failure.

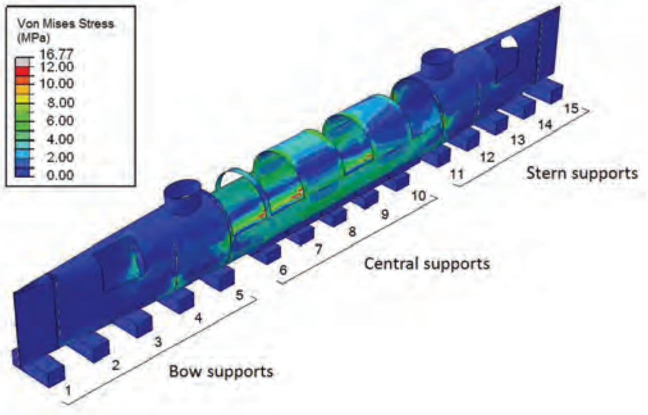

Figure 3. Stress distribution due to gravity for the submarine in a vertical position.

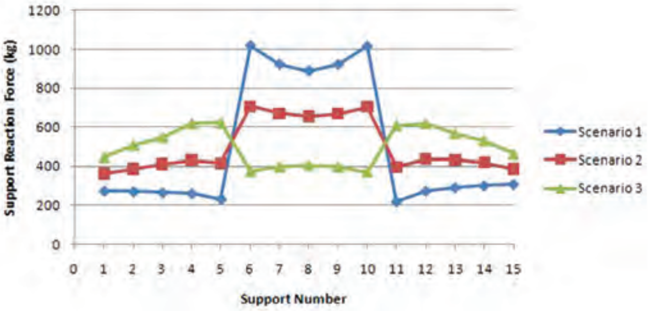

Figure 4. Three different distributions of support reaction forces based on the vertical position of central supports: high (scenario 1), average (scenario 2), low (scenario 3).

Scenario 1: Maximum stress = 16.8 MPa

Scenario 2: Maximum stress = 18.0 MPa

Scenario 3: Maximum stress = 23.8 MPa

Figure 5. Deformation and stress distribution for the three scenarios of Figure 4 (deformation is amplified by a factor of 500).

Rotation of *H.L. Hunley*

The FEA modeling is essential in refining a plan for rotation of the *H.L. Hunley*. The goal of the FEA is to enable project engineers and conservators to identify all of the theoretical stress that the rotation of the hull will put on the structure, and then refine the approach to minimize stress as much as possible. Based on the results obtained to date, the preferred rotation technique

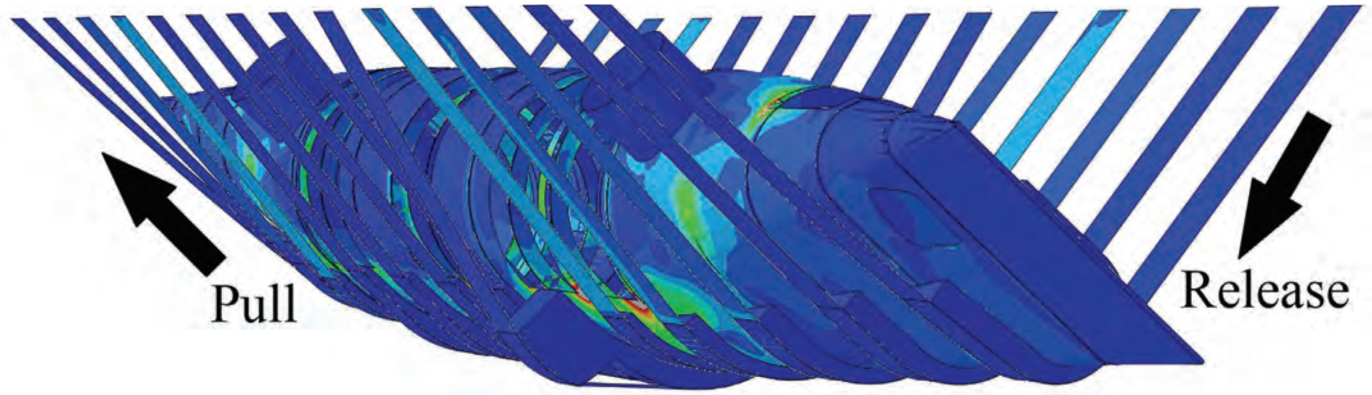

Figure 6. Stress distribution due to gravity for the submarine in its current sling system before rotation and diagram of the 'pull and release' action that will drive the rotation.

consists of using turnbuckles connected to individual load cells to pull the starboard sides of the slings while simultaneously releasing the port side (see Figure 6). FEA is used to simulate the quasi-static motion and associated deformation and stress on the hull and assess the appropriateness of the method of rotation. The main difficulty with the rotation of the hull is due to non-uniformity of the hull profile. The bow and stern regions have a very different hull profile, weight distribution, and local stiffness compared to the center of the submarine. Therefore, in order to prevent torsion and bending of the hull, the amount of pull and release that is required for the rotation will vary according to the position of the slings on the hull.

The FEA model for the *Hunley* will be used not only to simulate and predict the effect the rotation will have on the submarine, but also to calculate the exact pull and release values for each individual sling. The FEA allows these values to be calculated and then modified according to the amount of deformation of the hull that is generated from the modeling. The FEA model will also predict the changes in the tension of the slings during rotation. The predicted values will be compared to the measured tension on the slings during the rotation to safely monitor the process.

Conclusion

Since the *Hunley* was raised in 2000, intense efforts have been made to analyze and evaluate the structure of the submarine. Motivated by those early experiences, a comprehensive FEA was undertaken to model the structural behavior of the submarine under various scenarios. The results of the modeling are currently being used by conservators and engineers to plan for the safe rotation of the submarine. Although the accuracy of the model is affected by unknown factors related to the deterioration of the structure, the FEA represents a valuable risk assessment tool that will continue to assist the conservators. After the rotation, FEA analysis will be used for the next steps of the project, including the transportation of the submarine, after conservation, to its long-term display site.

Endnotes

[1] A parametric study consists of studying the effect of a selected parameter (such as plate thickness, stiffness of iron and position of supports) on specific outcomes (such as stress level and maximum deformation) by varying the value of this parameter while maintaining all other parameters constant.
[2] All metallurgical studies were carried out by Tim Foecke and Steve Banovic from the National Institute of Standards and Technology (NIST). Three samples from the *H.L. Hunley* were tested; a wrought iron rivet (HL-3036) from quarter plate FTP2, a small sample (S#4905) removed from the northwest corner of wrought iron quarter plate ATP2, and a fragment (S#4906) of cast iron collected from an area immediately adjacent to a large hole in the stern.

[3] Reference database compiled from NIST's work on other shipwrecks contemporary to the *H.L. Hunley.* Metallurgy Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA.

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Q & A SESSION

Molly Carlson: How has the removal of the iron plates affected the stresses on the ship?

Vincent Blouin: Dramatically. Drastically. Enormously. Basically if the submarine had been kept intact, if somehow it would have been possible to remove the sand and everything that was inside and leave it closed as a tube, it would have been significantly stronger. We haven't done an actual analysis of this scenario because basically it would be a simple exercise. But definitely, all the stress concentration, if we go back to all those images you can tell that the stress concentration occurs at the corners, which are basically where the plates were removed. Each time there is a shape change, like a corner, this is where stresses are going to concentrate. So obviously if the whole thing was closed up we would have basically this [shows image] type of stress distribution. Now you can notice, however, that the maximum stress occurs right here, which is below the hull. So it would probably not prevent this maximum stress occurring right here. But at least this whole region would not have that much stress. Right now it is around 15 megapascal. I suspect it would be less than 10 or even 5 megapascal in this area if it was closed.

Paul Mardikian: What you have in the paper that you don't have in the presentation because it's only 20 minutes, is the rationale behind rotating that submarine. Because you may want to know why are we rotating that submarine. You are conservators so you would not want to do something that is not necessary, right? The main reason for rotating this submarine is because we need to stabilize the hull. The hull is currently being supported by slings and those slings are tightly against the surface of the submarine. Therefore, the treatment that we are going to use to diffuse out the salts from the structure is going to be extremely slowed down [if the supports remain in position]. So what you want to do is to minimize any point of contact against the hull and still be able to support the submarine. Remove the slings, remove the truss, so the submarine can be completely deconcreted and then stay in the treatment solution as supported as possible. This is why we got adjustable keel blocks supports and those keel blocks are going to be moved around during treatment. That is the first point. Then the display of the submarine is also important, because when you ask the people 'how do you want to see the submarine in the future?' 'do you want to see it in the truss supported by its slings?' they say, 'no we don't want that'. So at one point we would have to rotate the submarine for display purposes anyway. But as far as I am concerned I am more concerned about the treatment of the hull than the final display. So you've got a dual goal here. The second thing I wanted to say is that the excavation of the submarine took a number of years and 10 tons of sediment were removed. Eight people [remains of the crewmembers] were in that submarine and therefore you can imagine the complexity of the task. But there would not have been a way to not alter the structure of the submarine to complete this excavation. We could have used the conning towers to get inside the submarine and do some kind of analysis of the sub, but you cannot imagine an archaeologist, going through the conning tower and excavating the interior – it would have been impossible! So we had to remove a number of top plates. So this is why you've got that submarine right now opened up like a convertible.

Aaron Shugar: Paul, you answered part of my question. A couple of questions: one was how much weight was the soil that was inside before you excavated? The question that leads from that is: when you originally put the slings on, that was a solid structure. Now you've excavated with, I assume the same tension on those stringers. How has it changed, removing that much tonnage from the structure as it is? It's a question that might be addressed in the future to see how it's already changed since it's been here for several years. The second question: issues related to the input parameters – I have to commend Paul and his team for doing excellent materials analysis of the hull – I'm curious to know if you've altered those parameters with regards to the thicknesses and strength of the metal that is left behind. Because that's a huge factor involved.

Vincent Blouin: For the first question, actually I think Paul maybe you could answer that better than I can. What I would like to say is that, first there is no real way of telling whether or not the structure changed drastically before the sediments were removed and after. For sure, before when the whole submarine was filled with sediment that would have created a pressure on the inside. Any kind of motion would have been absorbed by the sand, the sediment. So I suspect that when it is full, it would have been stronger than when it is empty. Now obviously the sediments would add stresses to it. But somehow I would say that before it was opened, and now it is in a much more vulnerable position – that's the way I see it. But there is no real way of telling whether or not there is a significant change because now it is done. Also we have tried to monitor the stresses over time with strain gauges. There are all kinds of constraints that we haven't mentioned in the paper and in this presentation that deal with how we can actually work on the submarine. Paul can talk about this. Basically we only have a few hours – windows of a few hours to access the submarine which makes it almost impossible to successfully attach strain gauges to the hull. Ideally you need 48 hours to have a good bond between the metal and the strain gauge, then you need to waterproof the whole system. The main thing is that the metal is so corroded and so impregnated with chlorides that actually it prevents a good bond between the strain gauges and the metal. So basically the monitoring over a long period of time has not been successful. I hope that answers your first question.

The second question was about the material properties. Yes, the material properties are as good as we can get them in terms of micro-hardness testing for the modulus of elasticity of the wrought iron and cast iron; and then some of the riveted connections – this is kind of a guess number. So to be able to somehow still make intelligent decisions – the only way that we deal with it is by making parametric studies, by varying those values and seeing what the effect is on it. Then we see the trends and make decisions based on those. Knowing that those numbers have a very large amount of uncertainty, but we have to make decisions. Those numbers are extremely important because this is the strength of the iron. Basically that is the stress level. If you reach 130 megapascals, for sure the metal is going to deform plastically, so we don't want to reach this. Obviously, as you see in some of the pictures, we reach only something like 17 megapascals at most. We are far from that number, but still there is so much unknown, that we use a very large factor of safety. I think it is safe to say that we use a factor of safety of roughly 10, to make sure that if there is a crack somewhere, we don't want the crack to propagate. This 17 megapascal that we came up with, we know that it is only a number that has uncertainty to it. We want to minimize that number more than trying to reach a maximum target. So we try to find a scenario that will reduce that number as much as possible.

Joe Sembrat: I was wondering if there was any thought about putting the plates back on and reattaching them temporarily to make the move? And two: whether you could potentially use airbags inside and try to right it with water in the tank, and then drain the water and set it down on blocks, possibly?

Vincent Blouin: Those are interesting questions that we keep asking ourselves. For the first one, I don't think there is any plan on putting those plates back. My point of view is that it would have to be done very carefully to add those rivets the way they were.

Joe Sembrat: More bolts I was thinking – you could temporarily bolt it in place rather than rivet in place.

Paul Mardikian: We thought about that but there is too much risk.

Vincent Blouin: Yes some of those holes for the riveted locations are so corroded, that putting some load on it from a fresh new bolt, may induce more stresses around it. There would be I feel as much risk to put them back on as not having them. So we adopted the option of making sure that we work on the forces that are applied from below to maintain the cradle position as much as possible. So we talked about adding reinforcements, bars and reinforcements on those corners where there is stress concentration. Each time we came up with the conclusion that it might be just as risky by adding more reinforcements – it is not the option that we are taking at this point.

FINITE ELEMENT ANALYSIS OF CORROSION-INDUCED PROGRESSIVE COLLAPSE OF THE WRECK OF THE USS *ARIZONA*

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Abstract

A finite element model (FEM) is a computer-based engineering model that calculates theoretical stresses, propagation of force, and shape changes to a structure under loads using thousands, or even millions, of individual elements whose individual responses are well understood. An FEM of an 80-feet long (25 m) midships section of the USS Arizona site was created to analyze archaeological site formation processes on the sunken battleship, in particular to determine the current condition of the wreck and predict its future strength and structural integrity as it continues to corrode. The FEM incorporates findings from other key components of the USS Arizona Preservation Project, such as steel-hull corrosion rates, structural surveys of the vessel, sediment compaction studies, and analysis of the concretion that covers the ship's hull, into a single tool to predict how the wreck will degrade.

Keywords: Finite Element Analysis, maritime archaeology, corrosion analysis, site formation processes, USS *Arizona*, Pearl Harbor

Introduction

The *USS Arizona*, which sank during the bombing of Pearl Harbor on December 7, 1941, is symbolic of America's entry into World War II and contains nearly 500,000 gallons of fuel oil within its corroding hull. The USS *Arizona* has been designated a National Historic Landmark — the highest level of national historic significance in the United States — and is administered cooperatively by the National Parks Service (NPS) and the U.S. Navy. It is among the most recognized and visited war memorials in the United States.

Of vital interest to the custodians of the wreck is knowledge about the physical stability of the structure. In particular, how the progression of corrosion affects the structural integrity, which could lead to a potential environmental threat due to the amount of residual oil contained in the wreck. To this end, a detailed analysis of the stability of the wreck of the Arizona was undertaken using the finite element method. A finite element model (FEM) of an 80-feet long (25 m) midships section of the Arizona site was created to analyze archaeological site formation processes on the sunken battleship, in particular to determine the current condition of the wreck and predict its future strength and structural integrity as it continues to corrode. The FEM incorporates findings from other key components of the USS *Arizona* Preservation Project, such as steel-hull corrosion rates, structural surveys of the vessel, sediment compaction studies, and analysis of the concretion that covers the ship's hull, into a single tool to predict how the wreck will degrade (Johnson et al. 2000, Makinson et al. 2002, Storlazzi et al. 2004, Storlazzi et al. 2005, Johnson et al. 2006a, 2006b, Russell et al. 2006).

Beginning in 2001, the National Park Service's Submerged Resources Center (NPS-SRC) designed the USS *Arizona* Preservation Project to be multi-year, interdisciplinary, and cumulative, with each aspect of the project contributing to overall research questions. The primary project focus was to acquire requisite data for understanding and characterizing the complex corrosion and deterioration processes affecting *Arizona*'s hull, internally and externally, and to model and predict the nature and rate of structural changes resulting from corrosion.

Because of the USS *Arizona's* national significance, any oil containment solution must incorporate a minimum-impact approach so that long-term site preservation is not compromised (Delgado 1989, 1992, Linenthal 1991, Vesilind 2001). Unnecessary disturbance to *Arizona*'s hull is likely to be seen by many as more problematic than the limited oil release now occurring. In addition, all research and monitoring operations were conducted with the respect due to an American war grave and with minimal impact to the site consistent with NPS principles of stewardship and preservation (Russell and Murphy 1997). In practice, this means that divers do not enter the ship, which is effectively a tomb for more than 900 sailors and marines who died during the attack, and we have very limited access to the interior spaces of the sunken vessel.

Finite Element Analysis

The FEM mathematically divides a complex solid into many thousands of smaller components called *elements*, each of which can be one of numerous simple shapes. Each element is given a location, a proximity to other elements, its own mechanical properties such as strength and brittleness, details about how it is connected to its neighbors, how it is allowed to deform and move, and how it transmits stresses to adjacent elements. Properties for the material of each element are input into computer software that describes the element's behavior between its end (or finite) points (for example, mechanical properties, heat flow, density, etc.). The end points of each 'finite' element are called *nodes*. Once the structure is built of these elements in the computer, conditions are set regarding how nodes connect to one another, and loads and fixed points (known as boundary conditions) are added to the model to restrain movement. As each individual element changes under different boundary conditions, it transmits a slightly changed condition to neighboring elements, which adjust in response, and so forth through all the elements of the model. The results of the model are predictions of the deformations and deflections that will result from that loading, as well as predictions of the stresses that each element, and thus each piece of the body, will experience. These results are displayed as plots of displacements of nodes and calculated stresses in the structure at all points. Taken in the aggregate, the displaced nodes and stresses of all the elements in the FEM offer a predictive model of stress and change under different conditions for an entire structure.

There are particular difficulties in applying FEMs to shipwrecks, however. Geometry is constantly changing due to ongoing corrosion, loads can be very complex, and loads and corrosion interact in such a way as to increase the complexity of the model (for example, from processes such as stress corrosion cracking). There are ways to overcome these difficulties, but accurate data based on direct measurements and observations are of primary importance. For the model to be representative of actual conditions, input data such as structural dimensions and connections, corrosion rates and loads must be as precise as possible.

Predictions about current status and future collapse resulting from the FEM will vary in accuracy depending on the detail of the input data, crafting the correct boundary conditions, and by simplifying assumptions. For the first issue, the greatest deficiency in data in this case was the knowledge of the current thickness and conditions of hull features of *Arizona*, both internally and below the present harbor bottom. The present conditions could not be directly measured like the external portions of the hull above the harbor bottom. All other assumptions and simplifications have a much smaller effect on the results of the model than these data. The boundary conditions — the external constraints that limit the scope and extent of the FEM — were similarly difficult, as the hull is supported by a water-saturated, semi-solid harbor bottom that moves relative to the hull.

If monitoring change in *Arizona*'s structure over time conforms well with changes predicted by the FEM, researchers will have confidence in extending the model's predictions to areas of the ship that are difficult to access directly for monitoring purposes, such as the lower decks. If monitoring changes does not accord well with the predictions of the FEM, the disjunction between real and predicted behavior will alert researchers to modify the FEM, gather new data that may have been overlooked in the initial model, or both. Over the course of this investigation (and afterwards), a dynamic give and take between the FEM and ongoing research is anticipated.

Building the Model

For initial modeling, a baseline FEM of USS *Arizona* was developed by modeling an 80-feet long (25 m) cross-section of hull structure amidships, between frames 70 and 90. The *Arizona* was built with frames on 4-ft. (1.2 m) centers, numbered beginning at the bow and moving aft — thus, frame 70 is 280 ft. (85 m) aft of the bow. This particular section of hull was chosen for three primary reasons. First, this hull section represents the stern-most intact portion of the ship affected by the blast that sank the vessel during the bombing of Pearl Harbor on December 7, 1941. In addition to blast damage, this portion of the ship's hull was engulfed in fire for nearly three days subsequent to the ship's sinking — an event that changed the structural characteristics of the ship's fabric. Applying an FEA to this section of the ship will give a conservative estimate of overall hull deterioration, because corrosion in this area is likely highest due to its proximity to the massive explosion that sank the vessel and the subsequent fire. Although each area of *Arizona* is different from others, this region of the ship is primarily composed of engine spaces below and working spaces above and it is free from massive structures, such as main gun barbettes that would make the results of the FEA more difficult to generalize for other regions of the ship. Finally, because FEA has not been applied to corrosion and deterioration of an historical shipwreck before this study, this preliminary model allows the refinement and testing of methodologies before developing the more complex and costly overall model required for predicting present and projected structural strength of the entire hull.

The first stage of the FEM process was to create a detailed, three-dimensional mesh of the 80-feet long (25 m) amidships section of *Arizona*'s hull in an original, as-built state. To do this, original construction plans and blueprints were used to make the *Arizona* FEM as accurate as possible. Unfortunately, several pieces of information regarding the internal configuration of the ship, particularly the detailed placement of floor beams, wall columns and their dimensions, were not found in the drawings.

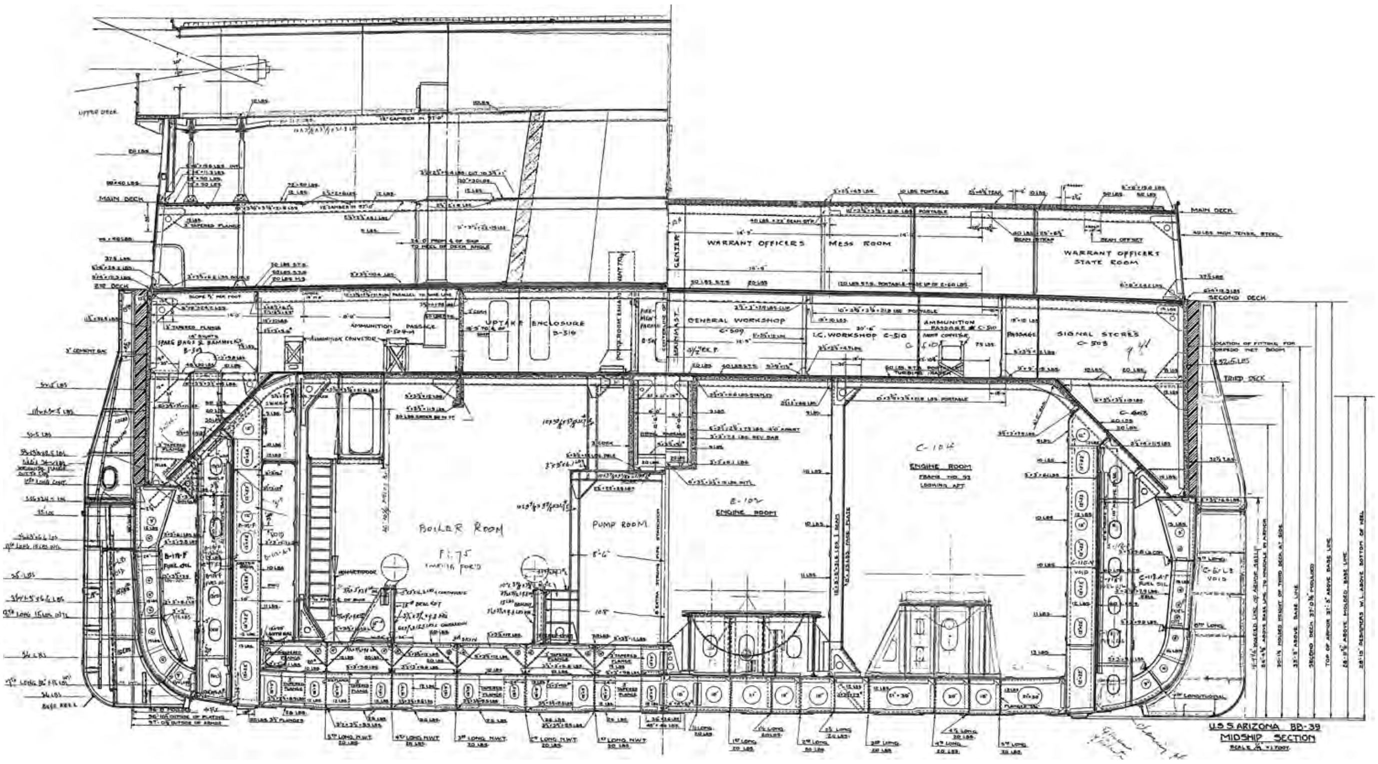

Figure 1. USS *Arizona* vessel plans showing a composite cross-section of frame 75 looking forward (left) and frame 93 looking aft (right) (USS *Arizona* Memorial Archive).

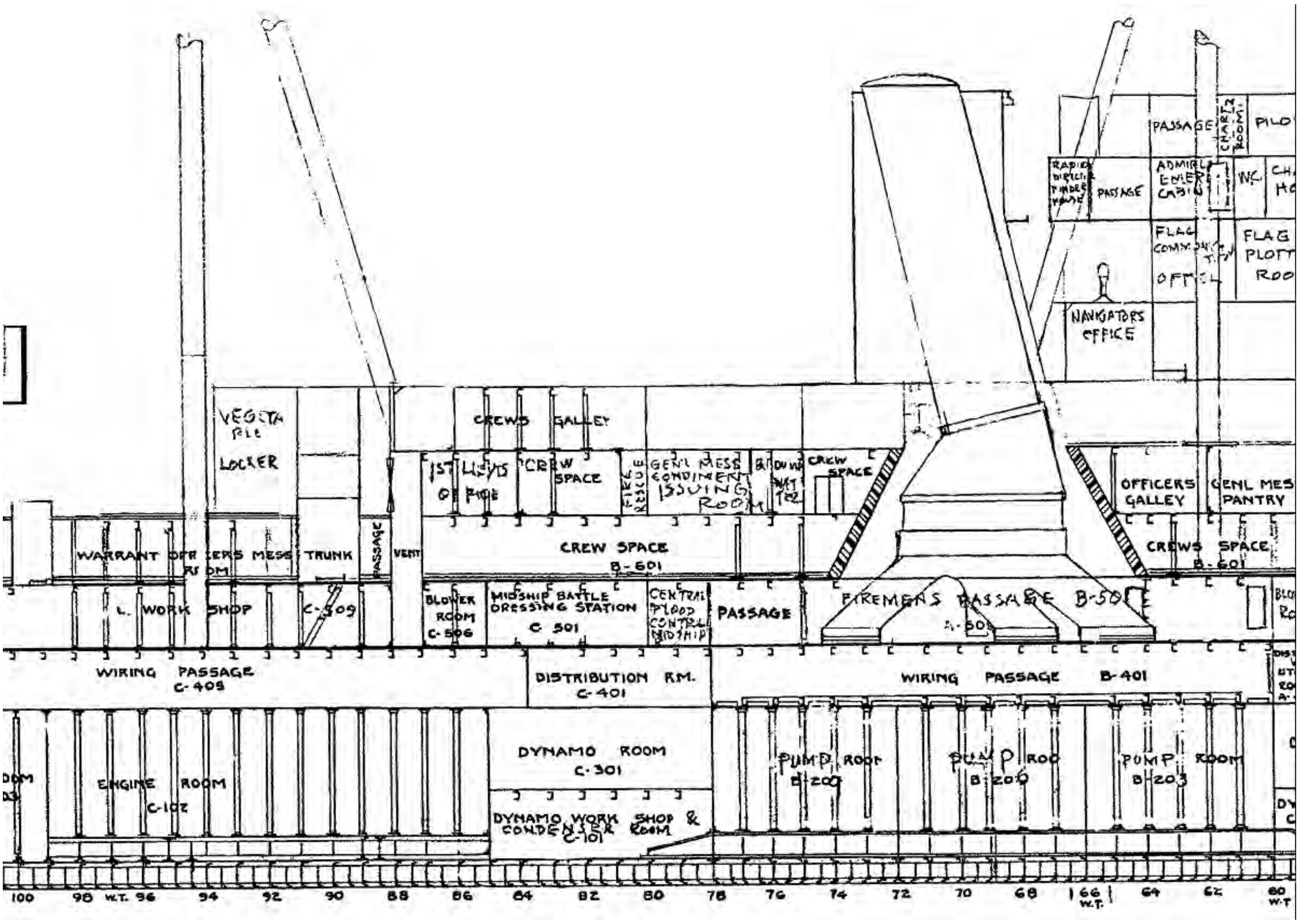

Figure 2. Midsection cutaway of USS *Arizona*'s hull from frame 60 to 100, showing beams and girders (USS *Arizona* Memorial Archive).

Transverse sections of the ship at frames 75 and 93 gave some finer structural details (see Figure 1), and these combined with the individual deck plans and the midships longitudinal section (see Figure 2) allowed reasonable assumptions to be made about the location and dimensions of all load-bearing components.

The steel of the hull and structure was modeled as an isotropic elastic plastic continuum (i.e., a uniform but stretchable and moldable structure), that ranged in physical properties from complete failure to the strength and characteristics of the original battleship steel. The values of specific properties used (density: 7800 kg/m^3, Young's modulus: 200 GPa, Poisson's ratio: 0.3, yield stress: 309 MPa, ultimate stress: 563 MPa) are all standard literature values or measured using tensile tests on coupons of steel taken from *Arizona* for this study.

The final stage of FEM development incorporated data collected during other aspects of the USS *Arizona* Preservation Project to complete the model of *Arizona*'s present condition and to allow the extension of the model into the future. Details from archeological surveys of the wreck that showed broken structural connections, missing deck plates and any other damage to the load bearing structures were added as modifications to the as-built design in the model.

The viscoplastic properties of the sediment upon which the wreck sits have been measured by the United States Geological Survey (USGS). These properties were used in the model as part of the lower boundary condition, where the steel of the outer hull is in contact with the mud, allowing both load transfer and for the mud/steel interface to slip as the ship settles and deforms. The concretion on *Arizona* has been found to have a fairly dramatic impact on the decay and eventual collapse of the wreck. The layer of biomass, shells, mud, sand and corrosion product that is encasing the wreck has been studied. The concretion layer, while stiff and fairly hard, is also quite brittle, with the constituents being poorly bonded to each other and to the surface of the steel. The effect of the encrustation on the FEM is due to the weight, and consequent stress that it puts on the surviving hull. As the wreck's steel components corrode, they lose thickness and weight. But overall the encrustation grows faster than the steel corrodes, and thus over time the wreck actually gains mass. This deadweight must be added to the weight of the steel itself, as both of these factors are driving the collapse of the wreck.

The model contains roughly 57,000 elements and 255,000 degrees of freedom. Once the model is developed in geometry and element placement, a definition of the boundary conditions is imposed. The open ends at frames 70 and 90 were constrained from motion along a line parallel to the long axis of the ship. The steel elements in contact with the first layer of mud were prescribed to remain in contact as both are allowed to deform. The mud bottom supporting the lower hull was proscribed as a large enough entity that any movement and deformation of the lower hull that occurred in the model was still mediated by the supporting mud matrix. Each element was given a weight with a density that can be independently set or changed as part of a zone, and the surfaces of the elements were allowed to bear additional loads from the concretion.

A major limitation of the FEM is due to the fact that the geometry of the body being studied is fixed, while the loads, boundary conditions and material properties are changed, to study how a design performs under different loading conditions. This works very well for design issues, which is where FEA is commonly used. In the present study, the inverse problem is being studied: the loads and material properties are fixed, while the geometry is changing with time due to corrosion of the steel. Under ordinary circumstances, the entire model would need to be re-meshed with the new measurements for every area of the wreck to be studied. In order to be able to run a parameter study, where the variables that can be changed are varied in a systematic way to evaluate the stability of the system, a model was developed where the density of the elements was changed to simulate the loss of section thickness, and allowing the stress to increase toward failure.

The critical parameter in this study is the stress that any given component experiences under the weight of itself, what it is attached to, and the concretion. Stress loads are modified by the cross-sectional area of the element that it is propagated to and from. For example, a small load propagated through a relatively small cross section produces high stresses, while a large load propagated through a large cross section produces relatively low stresses. The stress in any given section increases if the area decreases (due to corrosion — the real physical process) or the load increases (due to, in this case, increasing density — the simulation process). Using this technique, the physical dimensions of the element are kept constant, but the density is increased so that the stress in the component increases as it 'thins' in the model. Many test cases on beams and columns of different dimensions were performed to confirm that increasing the density of a uniform dimension beam gave a stress equivalent to decreasing the thickness of a corroding beam under its own weight. The results of those tests confirmed that this is a valid technique for introducing corrosion into finite element analysis, and this appears to be the first application of this technique to this class of problems.

Results

It is perhaps most illustrative to present the results from the model in chronological order as the wreck decays, describing issues that develop and warrant examination. The rate of steel corrosion is taken directly from data collected on the USS *Arizona* site — corrosion rates of exposed hull fabric above the harbor bottom are approximately three-times faster than those buried below the harbor bottom. Once an element has reached its breaking stress, it is defined as having no strength in the model, and is removed. The results presented are those where the steel exposed above the harbor bottom is allowed to degrade three times faster than the buried steel, which appears from corrosion analysis to be a reasonable scenario. The approximate equivalent dates were determined by assuming a linear corrosion rate from 1941 through the dates of the actual thickness measurements on the wreck (2002), and extrapolating into the future. Since the corrosion rate is most likely non-linear, being affected by many factors such as the presence and thickness of the encrustation, this is only an approximation that will need to be refined in future work. For the purposes of this article, the approximation is useful for fixing the 'age' of the wreck at the present day for planning purposes at 20% of its ultimate degraded state.

The as-built model indicates the computed stresses when dimensions of the ship are taken directly from the design blueprints (See Figure 3). The stresses everywhere are very low, which is to be expected, as this is a warship and it was considerably overbuilt to be able to withstand battle damage. The stresses are higher in the vertical walls in the lower levels, as expected, since these walls are supporting much of the weight of the ship above rather than having the entire turn of the hull supported uniformly by water pressure.

The equivalent of 10% loss of steel from corrosion (which roughly equates to the year 1980 at measured corrosion rates) shows that the stress distribution is very similar to the as-built condition, but with the overall stress levels somewhat higher. It is noteworthy that the deck beams in the upper deck have jumped significantly in stress, and the second, first and main decks remain almost unstressed.

When the hull reaches 20% loss of steel from corrosion (roughly equivalent to the year 2020), the upper deck show sagging beams and deck plates as hull members continue to thin. Stresses at the turn of the bilge of the torpedo blisters are approaching the tensile strength of the steel, while stresses in the vertical members continue to increase (see Figure 4).

At an estimated 30% loss of steel (roughly equivalent to the year 2050), the turn of the bilge area of the torpedo blister, as well as the connections of the lower bulkheads to the hold platform are very close to critical. There is additional sagging in the upper deck, as well as increased stresses in the bulkheads of the lower deck (see Figure 5).

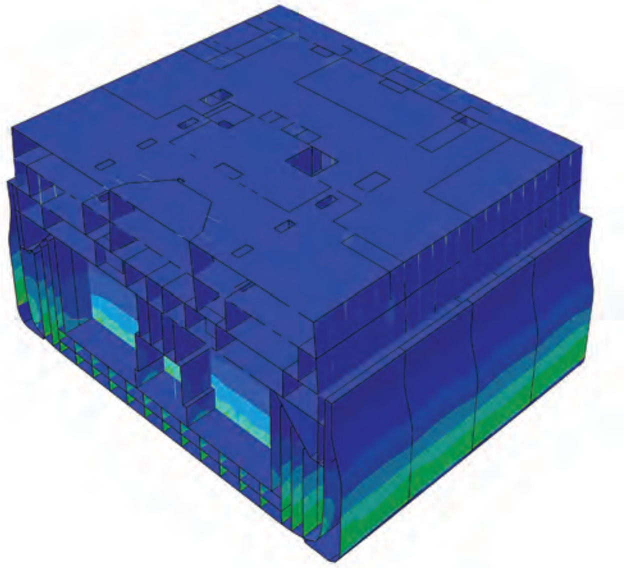

Figure 3. Weight stress in as-built condition.

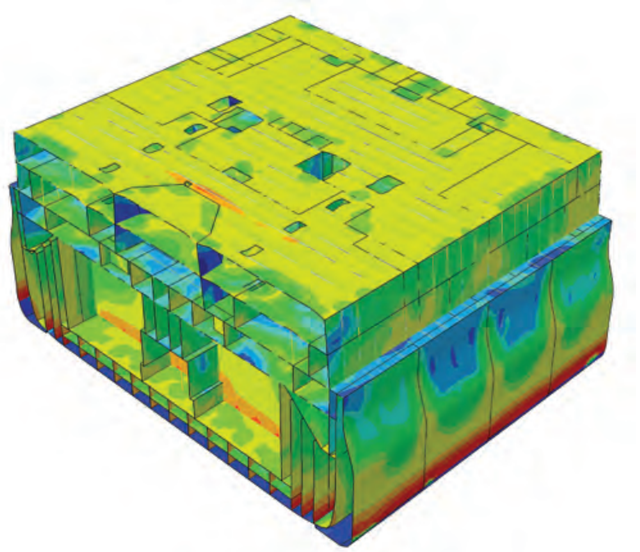

Figure 5. Weight stresses after 30% thickness loss due to corrosion, approximate date = 2050.

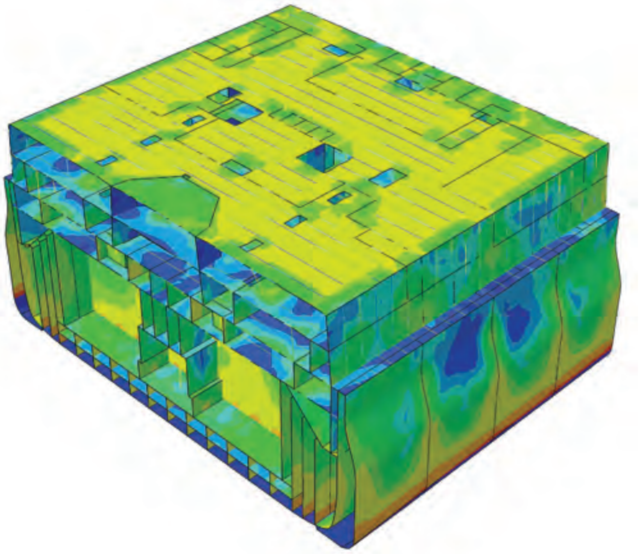

Figure 4. Weight stresses after 20% thickness loss due to corrosion, approximate date = 2020.

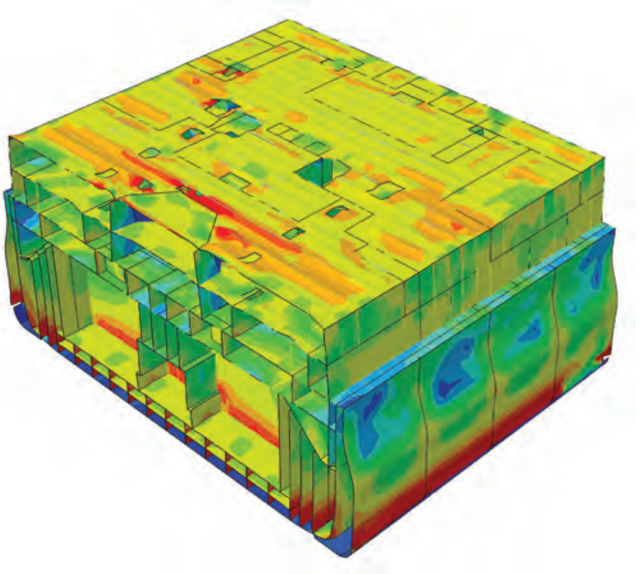

Figure 6. Weight stresses after 50% thickness loss due to corrosion, approximate date = 2120.

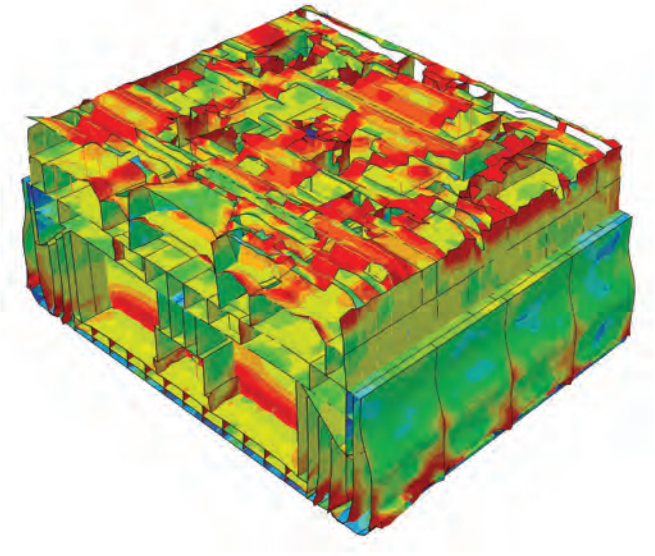

Figure 7. Weight stresses after 70% thickness loss due to corrosion, approximate date = 2180.

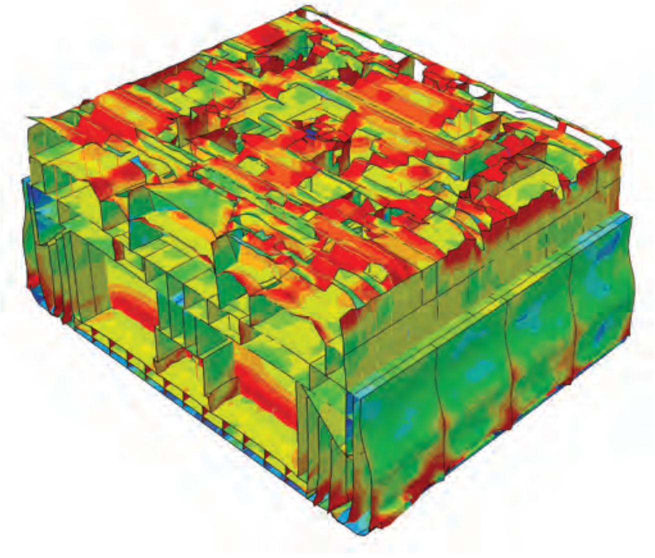

Figure 8. Weight stresses after 90% thickness loss due to corrosion, approximate date = 2240.

When 50% of the steel is lost due to corrosion (roughly equivalent to the year 2120), localized collapse events begin to appear, including portions of the torpedo blisters, double bottom vertical wall segments, upper deck beams and the region around the stack armor, undoubtedly collapsing under the weight of this very thick steel (see Figure 6).

At 60% loss of steel due to corrosion (roughly equivalent to 2150), there is general collapse of the deck plating on the upper and main decks, collapse of the outer hull plating and torpedo blisters, and very high stresses in the bulkheads at the hold platform in the engine spaces. Buckling of the hull shell plating begins.

The upper deck is unrecognizable after a 70% loss of steel (roughly equivalent to the year 2180), and much of the deck plating and deck beams have fallen onto and accelerated the collapse of the main deck and those below. The hull shell and torpedo blister continue to collapse, as well as the double bottom (see Figure 7).

When the hull steel reaches 90% loss due to corrosion (roughly equivalent to the year 2240), the decks of the superstructure (upper, main, and second) are expected to collapse further and pancake onto the third deck. The double bottom will completely collapse. Importantly, however, the core cylinder of the wreck, consisting of the volume bounded by the third deck, the inner bottom and the side oil tanks are still relatively intact — this is where much of the fuel oil aboard *Arizona* is stored (see Figure 8).

Analysis of Results

A number of caveats about and limitations of the results of the above finite element model of the wreck of the USS *Arizona* must be discussed. As mentioned, the usefulness of the results is strongly tied to both the input data and the assumptions built into the model, and in most cases the FEM results represent a bounding set of data describing the stresses in the wreck and not an actual physical state.

In reality, connections such as this are prime locations for complicated degradation mechanisms such as stress corrosion cracking and pitting corrosion, which occur at features that are not smooth, flat metal surfaces. This idealization will add to the conservative nature of the estimation, especially in regard to the details of the progressive collapse of the upper decks.

The model only covers roughly the central 80 feet (24.3 m) of the ship, and the ends of the model are artificially constrained to provide an adequate set of boundary conditions. In reality, the stresses along the central line of the ship will be significant, since the composition and properties of the mud supporting the wreck vary along the length of the ship. If one end of the ship settles faster than the other, which is likely, stresses will develop in the hull and decks in this direction, adding to the collapse forces, and this detail is not presently captured in the model.

Finally, the effect of non-steady state influences, such as wave action, are not included in the model. Pearl Harbor is an active port, and ships entering and leaving the harbor produce wakes that can exert considerable force on the hull of *Arizona*, particularly those coming from ships with large drafts such as aircraft carriers. A planned addition to the model is to subject the current mesh to a wave impact study to determine if this form of shock loading drastically increases the stresses in the structure, and could lead to premature collapse of the wreck.

Conclusion

Results of the FEA for the USS *Arizona* indicate that, after nearly seven decades on the bottom of Pearl Harbor, the wreck is approximately one-fifth to one-fourth of the way towards sufficient loss of hull steel due to corrosion, to induce the collapse of key structural elements. A surprising aspect of the FEA results is that collapse is predicted to initiate in the side and bottom of the hull before any significant collapse occurs in the exposed regions of the upper decks. In addition, an important observation from this analysis is that, while the exposed decks above the harbor bottom become extensively deteriorated, the core cylinder of the wreck, consisting of the volume bounded by the third deck, the inner bottom and the side oil tanks, is still relatively intact even after 95% of steel thickness has corroded. This means that many of the oil containing spaces within the ship may retain integrity until the year 2250 or beyond. Based on the present information and understanding of the wreck and processes affecting it, this is a conservative estimate. As the vessel reaches 20% corrosion thickness loss (estimated at the year 2020), the model predicts that upper deck areas begin to show sagging of the beams and deck plates as they continue to thin. This corresponds well with observations in 2006 of limited upper deck collapse in the galley area, and increased release of secondary oil in the area as more breaches begin to open. To date, therefore, the model seems to be predicting actual behavior reasonably well. Future monitoring is important to validate FEM accuracy.

Acknowledgements

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Q & A SESSION

Paul Mardikian: Did you put in your models somehow the effect of the oxygen inside the boat? It is different from what you have on the exterior, that's pretty obvious. Looking at the thickness of the concretion inside out, you see that the concretion on the interior is thinner than on the exterior. I always found that [the thickness of the concretion] is a reflection of the corrosion rate. Generally speaking that is something that we find. How can you model that big difference in corrosion inside out? And what is the effect of the oil on the oxygen level, and the effect of the oil on the corrosion rate? How do you model that?

Tim Foecke: The inside of the hull, interior surfaces are different corrosion zones from the outside. So we have dialed in a different corrosion rate and we've done parameteric studies on that. What we have it nailed at, at the moment, is about 1/5 of the outside and about ½ of what is going on below the mud line. From the analysis of the oil coming out, it appears that the environment is primarily anoxic and sulfur reducing. So actually the character of the encrustation – yes, it's thinner and it also has different constituents in it and so it does have a significantly different environment inside. The effect of the oil – we do not know. We don't know what the presence or the effect of all those complex hydrocarbons is on the system.

Paul Mardikian: My third question was about the mud line. So you responded to that already.

Chris Watters: You said that the concretion has no strength. Did you test that? Is that insignificant strength compared to the strength of the steel or is that no strength.

Tim Foecke: When I say no strength, I mean insignificant in comparison to the steel. We did 3-point bending on it and on a bar ½ inch square and 6 inches long it broke under 5 pounds, the steel would break under 10 000 pounds.

Ian MacLeod: Tim, I think probably the lack of questions is not due to any lack of erudition on your behalf, but it's just that you have answered essentially every question that could be possibly asked at this stage of the development of the model. So I would like to thank you very much.

Tim Foecke: One thing I did want to add to this is that: this is a living model. Now that we've got the thing meshed out, every advance we make in terms of figuring out a corrosion rate – the corrosion rate is being monitored all over the ship at 60 different sites since 1983 – anything we can do in terms of new information, I can just plug it in and my solution space gets smaller and Nirvana is somewhere in the middle. So we're going to continue to plug away at this thing – it's not just a done and walk away [scenario].

Arlen Heginbotham: Just a quick question, I'm curious how long it has taken you to build this much of the model and how long you expect it to take to complete the model?

Tim Foecke: The first part of the model was about a year and a half, but that was seriously part-time on our part. The rest of the model – Li has actually been shunted off to work on infrastructural liability and structural health monitoring actually. So I'm getting back up to speed on Abaqus myself and I am going to finish the meshing – I would imagine it would take a couple of years. And it is also going to be hobbled by the fact that I don't have a whole lot of structural information outside of frames 40 to 100.

Lyn Wilson: I just wondered if you had thought about incorporating computational equilibrium thermodynamics for future prediction of the corrosion rate when you have so much water chemistry information and information about metallurgy.

Tim Foecke: One thing that we do not have very good information about is how the various constituents permeate through the encrustation. And that seems to be a very seriously rate limiting step and that's going to be a big X-factor going out as the collapse occurs and the stuff starts cracking and the corrosion rate could take off overnight. So I don't think we have enough information on that to get into any kind of sophisticated thermodynamic modeling. We are going to have to pretty much stay with phenomenological stuff for the moment.

Paul Mardikian: I was kind of emotional and moved when I saw those dates – 2050, 2200 - that was amazing to see that. And I guess that is the reality of things. That stuff is going to collapse, like the *Titanic* and like the other ships. But how would these people that are so attached to the *Arizona* cope with the idea? I mean if you show that to them, they are going to start crying!

Tim Foecke: I deliberately don't show some things to some of the survivor groups.

Paul Mardikian: So in your mind with all your knowledge – do you think that there is any technique that you would know that would be safe for this boat? We always get back to an impressed current or some kind of protection. I know that with that amount of oil in the boat that would maybe be completely insane. So what is your opinion about the way to reduce the corrosion besides getting those big boats out of the area?

Tim Foecke: Some things can be done with sacrificial anodes and impressed currents. But in terms of if we ever had to excavate the hull and dry it out the angle of repose for the mud is such that we would have to take back the mud $^1/_8$ of a mile laterally in order to be able to expose the hull! It is similar to the angle of repose for the *Titanic* – it would take that much excavation. I think this is just one you will have to resign yourself to the fact that it is going to be iron ore at some point.

Molly Carlson: Is there a response plan being worked on for the oil that you expect to come out of this?

Tim Foecke: Yes there is boom storage and the guys that run the shuttle boats have been trained to deploy very rapidly. So if there is an oil leak they will string two layers of booms around the wreck. That is another kind of hot spot with some of the survivors in that their 800 colleagues are kind of comingled with the oil now and how do you treat it sufficiently respectfully. They don't want to hear that there are booms ready to soak up their brethren kind of thing – so its all kind of weird things like that. But there are contingency plans to catch the oil if there is a fairly catastrophic release.

Engineering and 3D Technology In Conservation

Chair: Ian MacLeod
Panelists: Tonny Beentjes, Lyn Wilson, Jonathan Tse, Vincent Blouin, Tim Foecke

Aaron Shugar: Thank you all for a very interesting session. This is directed at Tonny probably more than anyone else. As these scanners become cheaper, the one that I use only costs $2500, you could walk into a place and scan a Rodin and print it yourself and cast it, and it could be sold as a fake, a forgery, you could get involved in these issues of forgeries. Peter [Northover] is not here but this is the kind of thing that will keep Peter employed because metallurgists are needed to investigate the metallurgy of sintered granulation as it is basically the only way to tell the difference but I am curious about your feelings about creating forgeries.

Tonny Beentjes: I have thought about that off course, not doing the forgery off course. At the moment as you said with the sintered material that would be quite easy because that's still very porous but you could make a pretty good cast using a 3D model. But that's only one part of it this is just the exterior because if you study bronzes really thoroughly there is much more coming into it: the armatures inside, looking for core pins, tool marks. So I think there is probably a chance you will come across in the future a large quantity of fairly recognizable fakes but maybe you'll get one or two to take a little bit further. I am not sure but I think with the technology we have researching bronzes I don't see real problems for the top end of the market, put it that way.

Eric Nordgren: Hi, I just wanted to ask two quick questions for Tonny about the method again. I am not sure I understood for casting part of the leg, it was scanned and did they make a 3D print which was a positive pattern that was then molded or did they actually make a reverse, essentially almost make a …

Tonny Beentjes: No it was a positive.

Eric Nordgren: OK that's good. Another question that I had was about the modeling and if you knew there were significant cracks present in the material would it be possible to factor that in and get a significantly and more accurate result?

Tonny Beentjes: I think that in theory you could because it all depends on how you position the scanner. If your scanner is accurate enough you could penetrate quite deeply in there. The scan firm told us that scanning the Rodin was rather complicated to get the deep shapes and get into all the areas but it did a wonderful job because there was one area where the leg had sheared off and we did not notice that until the new cast was made. There was damage on there and we thought that's strange, maybe the foundry did that, but it actually turned out that it was in a crevice we could not see before.

Eric Nordgren: Would it be possible to ask an additional question for Vincent Blouin about final element modeling of the *Hunley* and whether when you are evaluating the materials strength if you knew there was significant cracking, would it be possible to use that to alter to model and make it a bit more predictive?

Vincent Blouin: What I tried to explain in the presentation is that there was this multi scale modeling technique which is to model the entire submarine at a global scale. We have to assume that we cannot model the presence of a crack at that scale because the crack would probably be a few millimeters or maybe a few centimeters in length. But we account for it by coupling this global scale model with a small scale model and the small scale model will basically have the model of a crack and then the problem is to coordinate those two models in such a way that they are compatible. The idea is that by calculating the forces that are around that crack on a global scale model and apply those forces on the small model and see what is the corresponding stress around that crack. So if you get 10 mega Pascal on the global scale model that corresponds with the equivalent forces to 100 mega Pascal around the crack. That would be one way of estimating the effect of a crack but this is still being researched and this is the approach we are taking at this point. Maybe Tim [Foecke] may want to comment more on that.

Tim Foecke: One of the things that is definitely a problem with the materials that we are both studying in wrought iron and cast iron is that the length of a crack is a huge x factor and this is not only the physical length of the crack but if the tip of the notch is sitting on the end of a very long flake of graphite that flake of graphite has no strength and this is effectively making the crack longer or if it is coming in coplanar with a large slag inclusion in wrought iron, you might see a one millimeter crack, but it may effectively be a 3 centimeter crack and you have no way of knowing, it so that's where the bounding comes in and the huge safety factors.

Virginie Ternisien: I have a question for Lyn Wilson, it was very interesting the use of the 3D scanning laser. I am concerned about the durability of these kinds of very important documents, because I think that everybody has already been confronted with the use of document and the change of software because the technology goes very fast. So do you have recommendations that conservation laboratories could use to maintain these kinds of documents for the long-term?

Lyn Wilson: File extension names are a very significant issue and we always try to archive our laser scan data in a non-proprietary format so they can be accessed by anyone in the future. We actually have been told that the best way to save this data is print out the xyz coordinates on paper, but you can imagine the size of the files we would generate from that, so we can save it in a very simple format, just in terms of coordinates, and then it can be easily maintained and updated and accessed by anyone.

Tonny Beentjes: We have a similar issue with the Rodin bronze, we are using an epoxy resin, a material that we know has a limited life time, so we have been seriously thinking to use the molds to cast a more stable material such as tin or pewter alloy very detailed, so in 100 years you can redo the infills and just rescan them because, again I am not sure the CD's we use will last and will become completely obsolete.

Tim Foecke: NIST actually has a program with the Library of Congress to recreate some of the old reel-to-reel tape decks and some of the old Daytec reading systems to try to salvage data that people have not been updating on their media, this is an enormous problem, the Library of Congress say they have hundred tons of electronic media they can no longer read because the machines are broken.

Virginie Ternisien: This is a question for Vincent Blouin. How did you evaluate the stresses of the submarine during the rotation?

Vincent Blouin: If we start talking about the rotation itself we could be here all night but I would love to because it's a very interesting problem. Basically for the rotation we don't look at it as a time-dependent problem because it is going to be a very slow process, possibly a few days to rotate it just by 45 degrees so we look at it more as an incremental process from its current 45-degree angle to 90 degrees, it will rotated degree by degree. So it is not really a time issue and to account for the change in stresses during the actual rotation, for each degree basically we have a different position of the submarine and the numerical model accounts for this changing position for each degree. I did not show any of these results but we have a simulation that shows how the stresses evolve during the rotation process for each increment. The main issue is the fact that the submarine is not a cylinder. It is tapered at the bow and stern and to account for this you need a different pull and release on each sling to account for the non-linear behavior due to this tapered shape. So it is a complicated problem and that is why we use computers. I do not think it would be possible to do this intuitively. So the numerical model accounts for all those parameters including the hull shape, the compression of the foam, and the change in tension on each sling during the 45-degree rotation. So we have 45 analysis: one for each degree of the rotation. So it is complicated and this is why the numerical simulation allows you to determine the best tension of each sling to apply the smallest amount of stress to the submarine's hull during the rotation. Does this answer your question?

Virginie Ternisien: Yes thank you.

Vasilike Argyropoulos: For me this session was one of the highlights of the conference and I am really glad I came from Greece to hear the talks today. Thank you very much. As you know Tim [Foecke] this question is directed to you. These ticking time-bombs have made the press in the *New Scientist* where they talk about them. Those two slides that you've showed at the beginning they showed them in that article that Ian MacLeod was also quoted in, and the question I have for you because it is a very big problem around the world and there is a lot of interest about the effects of these shipwrecks or sunken vessels and what effects they will have on the environment in the future and I know also the international atomic energy agency are also interested in this problem and there is concern about the Iraq war with the sunken vessels and what that will do eventually to the underwater environment as well. So the question I ask because you've done incredible work on the USS *Arizona*, will this knowledge be grafted to other areas of the world to help deal with this problem?

Tim Foecke: That is the plan, will it actually happen? The cynic in me says no, and that is simply because new regulations, be they safety regulations, environmental regulations or whatever, are pretty much written in blood and these 1800 tankers are distributed all over the world, they are going to pop one at a time from very large depths and the oil is going to be very distributed and I would bet people are not going to pay a lot of attention because this is not going to be a big splash, very, very unfortunately, but I will do my best shoving from my side.

Vasilike Argyropoulos: Are you involved with anything else around the world or is this just the USS *Arizona*?

Tim Foecke: I am working on the *Arizona* but I am involved with the NOAA group that is having a workshop next week at Newport News and I am going to be active with that group. This is an incredibly complicated problem the ships are all different designs they are in different places they've all blow up in different ways so it's going to be a mess.

Vasilike Argyropoulos: Thank you very much.

PREVENTIVE CONSERVATION

Session Chair: Emma Schmuecker

PRACTICAL APPLICATION OF SORBENTS

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Abstract

Metal artefacts are particularly susceptible to the effects of gaseous pollutants including ethanoic acid, hydrogen and carbonyl sulphide. Sorbents are often used in an attempt to slow corrosion caused by these pollutants. Once a sorbent has been selected, the quantity required and how it will be deployed must be ascertained, and a replacement regime must be considered. There are anecdotal reports of adsorbents off-gassing large concentrations of pollutants. This work presents a series of experiments and case studies using charcoal cloth, Corrosion Intercept and Puraspec 5040 to address these issues for lead and silver objects.

Keywords: sorbents, lead, silver, charcoal cloth, Corrosion Intercept, Puraspec 5040

Introduction

This paper investigates the practical application of sorbents to protect two metals, lead and silver, with very different properties. Reduced sulfur gases react incredibly swiftly with silver surfaces. These gases are generally generated from the outside of showcases, although inappropriate showcase materials can generate high internal concentrations. Relative humidity (RH) appears to have a limited accelerating effect at the concentrations normally encountered in museums. At 100 ppm the tarnish rate increases by a factor of three when RH increases from 15% to 75% (Kim 2003).

Carboxylic acids cause the corrosion of lead. The background concentrations in most rooms are low and the acids generally only cause problems when concentrated inside showcases. Ethanoic acid from wood products is the most commonly encountered. Corrosion of lead often requires a few days, even at high concentrations of this acid. Relative humidity has a very strong effect on the reactions, at 3000μg/m^3 the reaction rate increases by a factor of over 50 between 34% and 75% (Tetrault 1998).

Once a sorbent has been selected, three questions must be addressed to provide suitable environments;

- How much material is required and how will it be deployed?
- How often will the sorbent require replacement?
- Can adsorbed material off-gas under any circumstances and generate a higher concentration?

Two types of sorbent were investigated: adsorbents that bind weakly with the gases (activated charcoal cloth), and absorbents that chemically react with the gases (Puraspec 5040 (zinc and aluminium oxides) and Corrosion Intercept® (finely divided copper in a polymer matrix). Caution should be exercised when using adsorbents in mechanical systems (fans or air conditioning to push air through the adsorbent), as there have been anecdotal reports of spectacular off-gassing.

The following trials have all been undertaken in showcases. There are a number of potential pitfalls with such trials. Many showcases behave differently despite being built to identical specifications and appearances. The air exchange rate can vary widely between identical showcases and this can have a great effect on the ingress of pollutants, the concentration of internally generated pollutants and the efficiency of any sorbents used (Thickett 2008). An alternative approach is to use the same showcase and compare its performance with and without sorbents. The concentration of reduced sulfur gases varies in the ambient air, so it is important to have some form of control or assess a reduction in concentration or tarnish rate in the enclosure as compared to the room. In non-air conditioned buildings variations in temperature and RH occur. The emission of ethanoic acid from wood products is a strong function of temperature and RH and this can effect the concentration in a showcase. Figure 1 shows the concentration of ethanoic acid in a showcase measured every month.

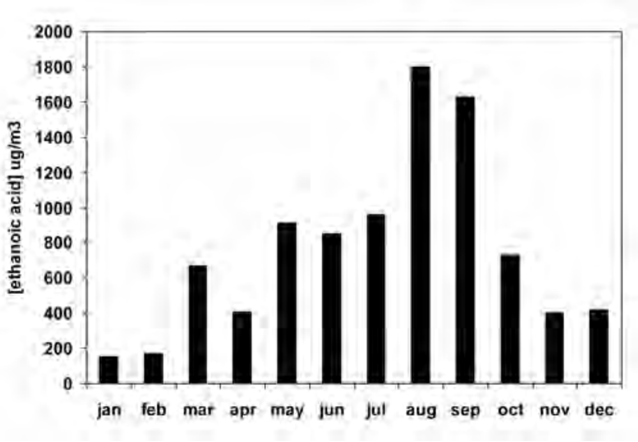

Figure 1. Seasonal ethanoic acid concentration in showcase. Data courtesy of MASTER project.

Methods and Materials

The risk to lead was assessed in two ways: measuring ethanoic and methanoic acid concentrations with diffusion tubes; and measuring the corrosion rates of pieces of lead coupons. The diffusion tubes were provided and analysed by the Norwegian Institute for Air Research (NIKU), and were exposed for 14 days. High purity lead sheet was cleaned by abrading with a glass bristle brush. The composition of the lead is critical for this application as many elements can affect the corrosion rate at low concentrations (Costa 2002). Table 1 shows the analysis of the lead sheet used. The reported concentrations at which the corrosion rate of lead is affected and the limits of solubility of the impurities in the lead are included in Table 1. The lead coupons were accurately weighed before exposure with a six figure balance. After exposure, the corrosion was then removed with 1% ethanoic acid following the method described in ASTM G1 03, and the metal lost to corrosion was determined (ASTM 2003).

Element	Amount (% wt/wt)	Reported Effect Limit (%wt/wt)	Reported Solubility Limit (%wt/wt)
Lead	99.98	-	-
Tin	<0.005		
Antimony	<0.005	0.01	
Arsenic	<0.0004	0.05	
Bismuth	<0.015		
Calcium	<0.002		0.01
Copper	<0.001		0.002
Iron	<0.001		
Nickel	<0.001		
Silver	<0.001		0.02

Table 1. Purity of lead used.

The tarnish rate of silver was assessed with two related methods. High purity silver (99.98%) coupons were cleaned by abrading with a glass bristle brush. The surface reflectance spectra was acquired with a Minolta 2600D spectrometer and converted into CIE Lab coordinates (CIE 2004). A mild steel punch with the same diameter as the spectrometer sampling head was used to produce a feature on the coupon surface to allow repeat measurement of the same area on the coupon. The spectrometer alignment was controlled to further improve repeatability of the measurements (Thickett 2008). Piezo-electric quartz crystal microbalances were also used to follow the silver tarnish rate, using pre-prepared silver coated crystals from Purafil and Onguard 3000 loggers.

CHARCOAL CLOTH

Amount

A new display at the British Museum placed large numbers of leaded bronzes in historic glazed wooden cabinets. The cabinets were made from painted oak, and initial monitoring with diffusion tubes indicated ethanoic acid concentrations at levels high enough to cause concern. Two year's environmental monitoring in the gallery indicated a likely maximum RH of 70%. At that value, lead corrosion has a threshold for ethanoic acid of 430 µg/m^3 (Tetrault 1998, Thickett 1998). The addition of activated charcoal cloth was investigated to determine if the levels could be sufficiently controlled to allow safe display. The amount required was determined in a series of experiments in five, apparently identical, cabinets. As the gallery environment was not controlled, a series of experiments in the same case may have produced different acid concentrations. Therefore, a single case could not be used to compare the effects of different amounts of sorbent. Differing amounts of charcoal cloth were added to the cabinets and the ethanoic and methanoic acid concentrations measured with diffusion tubes. Although the ethanoic acid concentration generally reduced with increasing amounts of cloth, the trend was unclear over three series of experiments and an appropriate amount of the cloth could not be unambiguously assessed. The results from one of these sets of experiments are shown in Figure 2. The air exchange rates of the cabinets were determined using the carbon dioxide tracer gas method (Calver et al. 2005). A very short logging interval (1 minute) had to be used to get enough data to determine the air exchange rates, which were high. The results in Table 2 show that Cabinet 126 has a much higher air exchange rate; reducing the ethanoic acid concentration and giving a misleading result.

Subsequently, the air exchange rates were measured for all cabinets containing bronzes with lead contents above 1%. The recommended ratio of charcoal cloth was adjusted to keep the expected ethanoic acid concentration below 430 µgm^{-3} taking the air exchange rate into account.

Location	Height (cm)	Width (cm)	Depth (cm)	Air Exchange Rate (day^{-1})	Sorbent	Deployed as	Percentage emmisive (wood) area covered
ACTIVATED CHARCOAL CLOTH TRIALS IN HISTORIC OAK CABINETS							
122	25	75	45	67	Charc cloth	Passive	7.8
124	25	75	45	59	Charc cloth	Passive	31.0
126	25	75	45	126	Charc cloth	Passive	15.5
127	25	75	45	83	Charc cloth	Passive	5.2
129	25	75	45	91		Control	
ACTIVATED CHARCOAL CLOTH TRIALS IN WOODEN BOULE DRAWERS							
A	20	60	100	1.5		Control	
B	20	60	100	1.8		Control	
C	20	60	100	2.1		Control	
D	20	60	100	1.8	Charc cloth	Passive	32.7
E	20	60	100	1.4	Charc cloth	Passive	32.7
F	20	60	100	2.0	Charc cloth	Passive	32.7
G	20	60	100	1.7	Charc cloth	Passive	97.0
H	20	60	100	1.9	Charc cloth	Passive	97.0
I	20	60	100	1.1	Charc cloth	Passive	97.0
PURAPSEC 5040 TRIALS							
Trial	100	80	40	0.31*	PS	Pump	
CORROSION INTERCEPT TRIALS							
Batons	100	160	20	2.6			
Orders	132	132	20	3.2			
Snuff boxes	100	160	20	2.1			
Batons	100	160	20	2.6	Corr. Intercept	Passive	10.1
Orders	132	132	20	3.2	Corr. Intercept	Passive	10.1
Snuff boxes	100	160	20	2.1			
Batons	100	160	20	2.6	Charc.cloth	Passive	50.6
Snuff boxes	100	160	20	2.1			
Trial case	100	60	60	8.4			
Trial case	100	60	60	8.4	Corr Intercp	Passive	

Table 2. Showcase characteristics.

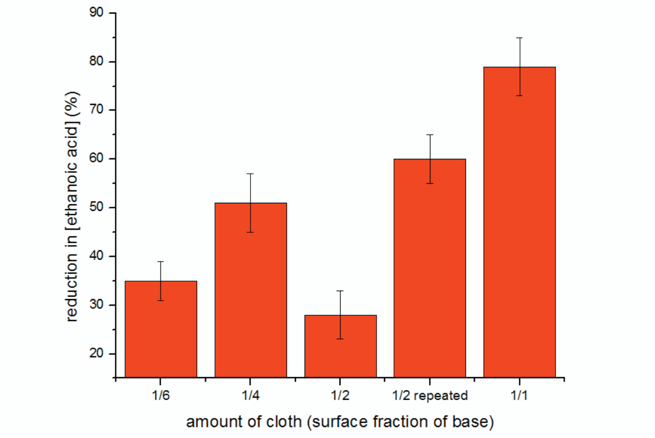

Figure 2. Concentration of ethanoic acid in oak showcases with activated charcoal cloth.

A collection of boule (lead sling shot ammunition) were found to be corroding in wooden storage drawers. Six years prior to the trial, activated charcoal cloth had been added to the base of the drawer covering the entire surface area. This did not arrest the corrosion and a series of trials were carried out to determine how much cloth would be required. Three amounts of cloth were tested in nine different drawers. In three drawers, the present situation was mimicked with new cloth covering the base area only. In three other drawers, cloth was placed on the base and sides of the drawers. In the final three drawers, all of the feasible wooden surfaces were covered with cloth including the underside of the drawer above (the drawer runners themselves could not be covered). The ethanoic concentrations were reduced approximately by 30%, 60% and 90%, see Figure 3. The 30% and 60% reductions did not halt the corrosion process.

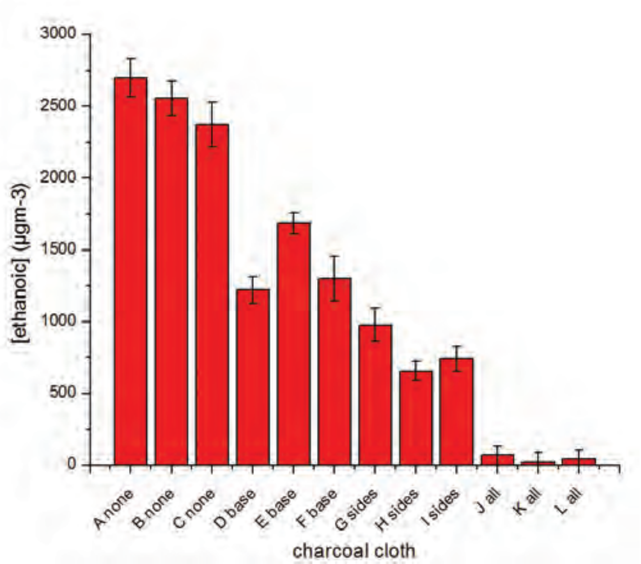

Figure 3. Concentration of ethanoic acid in wooden drawers with activated charcoal cloth.

Lifetime

The remaining adsorption capacity of the charcoal cloth, after six years exposure in the high ethanoic acid drawers, was tested by the manufacturer. The standard test involves equilibrating the cloth to 50% RH and then measuring the mass gain above a pure ethyl ethanoate ($CH_3COOCH_2CH_3$) solution. These tests can readily be undertaken with a balance of sufficient accuracy ($\underline{+}$ 0.0001g). Activated charcoal adsorbs best using London forces to induce a dipole in the target molecule (Druzik 2010). This means molecules with molecular weights below 80 g mol^{-1} are more weakly adsorbed; the molecular weight of ethanoic acid (CH_3COOH) is 60 g mol^{-1} and of ethyl ethanoate is 88 g mol^{-1}. Modified tests were also run using ethanoic acid due to concerns of differential capacity. Results are shown in Table 3.

Charcoal cloth sample number	Remaining ethyl ethanoate adsorption capacity (%)
1	91
2	95
3	92
	Remaining ethanoic acid adsorption capacity (%)
4	87
5	89
6	85

Table 3. Remaining adsorption capacity for activated charcoal cloth for ethyl ethanoate and ethanoic acid.

These tests indicated significant remaining absorption capacity after six years exposure in excess of 5000μgm^{-3}.

This coupled with expectations of lower ethanoic acid concentrations in the historic glazed wooden cabinets suggested a cloth lifetime of 10 years with testing recommended after six, eight and 10 years exposure.

Off-gassing

The potential for off-gassing as a passive adsorbent (not in a mechanical system) was tested in two ways. Method 1 involved placing the cloth samples from the ethanoic acid drawers into a 50ml vessel with diffusion tubes. The vessel was heated to 40ºC for two weeks. The diffusion tubes were then analysed to determine any ethanoic acid released. The cloth was removed from the drawers during a period when the RH averaged 40% and the temperature 16ºC. Method 2 involved placing cloth samples, diffusion tubes and glycerol solutions in 2 closed vessels. One vessel was conditioned to 0% RH with pure glycerol, and the other to 85% with a glycerol water mixture. After two weeks the diffusion tubes were analysed. Samples of the glycerol were also diluted and analysed with ion chromatography to account for any ethanoic acid absorption into the glycerol.

The heated charcoal cloth in method 1 generated an atmosphere of 303µgm^{-3} inside the 50ml vessel. As the loading was quite high (5g of cloth) this concentration is probably higher than would be experienced in many applications. The risk to many object types (and certainly the common metals) is negligible. Method 2 (the low and high RH tests) generated even lower ethanoic acid concentrations.

PURASPEC

The tarnishing of silver has significant resource implications for conservation. On some artefact types, cleaning tarnished silver is extremely difficult, for example silver threads in textiles, silver foils on works of art on paper and silver based photographic images.

A project at the British Museum compared the efficiency of 16 sorbents recommended for use with silver. Previous trials had indicated differences in kinetics between experiments with hydrogen sulphide atmospheres and the complex, mixed atmosphere present in the museum's galleries. Hence, the initial tests involved pulling air from the museum over the materials and silver coupons using a carefully constructed arrangement of inert tubes to keep all the path lengths equal (Lee 1999). The experiment ran for one year, which was calculated to be approximately equivalent to 15 years exposure from the flow rate used and the air exchange rates of silver cases around the museum. The best performing material, Puraspec 5040, was then deployed in showcases in small dishes. Although an effect could be observed, it was quite marginal with a tarnish rate reduction in the order of 10%-20%. This was far less than in the initial trials, at around 80% reduction (Bradley 2005). This poor performance is related to the positioning of the absorbent. Stringent testing of materials in the British Museum has eliminated internal sources of silver tarnishing gases from showcases. The gases originate from the galleries and enter the showcases through small cracks, mainly around the door seals. The doors are full height so the gases have to pass over the silver surfaces to get to the absorbent. The majority react on the silver before they reach the absorbent and have a chance to react with it.

A second test deployed the Puraspec 5040 in a small pump, blowing purified air into the showcase. This had much better results. Measurement of the showcase air exchange rate could allow matching the air flow to the showcase. This would have the potential benefit of optimising the Puraspec 5040 lifetime (which can readily be calculated from the average hydrogen sulphide and carbonyl sulphide concentrations, which were available for that gallery (Bradley 2005). There is also a concern that using a high flow of low pollutant concentration can enhance tarnish rates. Additionally, if very high concentrations of hydrogen sulfide or carbonyl sulfide develop in a gallery, higher air flows through the Puraspec bed may mean that the absorption capacity of the Puraspec bed is overcome and polluted air is emitted into the case. To investigate this approach, trials were undertaken in a showcase. The air exchange rate was measured by the carbon dioxide tracer gas method. Both the average air exchange rate and the instantaneous air exchange rates were calculated and are shown in Figure 4.

The case was fitted with a variable speed pump drawing air through 200g of Puraspec 5040 and into the case. The silver tarnish rate was measured with silver coupons and the Onguard dataloggers, both in the case and in the room. In the first trial the pump was set to just overcome the average air exchange rate of the case. In the second trial it was set to overcome the maximum instantaneous air exchange rate. Results are shown in Table 4. As can be seen (lower increase in b* values), the higher flow rate retarded the silver tarnishing to a greater extent.

	Increase in b*			Tarnish Layer thickness (10^{-10}m)	Pump set to give air exchange rate (day^{-1})
	A	B	C		
First trial room	1.21			26	
First trial case	0.41	0.45	0.42	7	0.35
Second trial room	1.36			34	
Second trial case	0.05	0.05	0.08	1	1.5

Table 4. Puraspec 5040 pump trials.

Activated Charcoal cloth performed second best in the laboratory tests. However, accelerated corrosion tests (60°C, near 100% RH) in direct contact showed extensive pitting of silver and some damage to copper. This is probably due to the approximately 1% of chloride detected in the cloth. The white backing material does not provide protection against this direct contact corrosion (at least in accelerated tests).

CORROSION INTERCEPT®

Recent research has indicated Corrosion Intercept foam can perform well as a passive sorbent (Dufus 2009). Tall, narrow wall mounted showcases have large surface area volume ratios, little room to add the foam and a long vertical distance between the foam and top of the case. This extreme situation was selected to test the foam. Two cases with very similar dimensions were selected. One was of painted wood and contained a series of medals (Orders). The second of wood with a fabric covered backboard (the same wood species) and contained military battens. Ethanoic and methanoic acid measurements were taken in the cases over a two week period. Corrosion Intercept foam was added and the measurements repeated. Silver coupons were also placed in the cases with the corrosion intercept to determine any drop off in effect away from the foam. Three coupons were adhered to the side of each case, just above the foam, at half height and just below the top of the cases. Results for the carboxylic acids are shown in Figure 5 and for silver in Table 5.

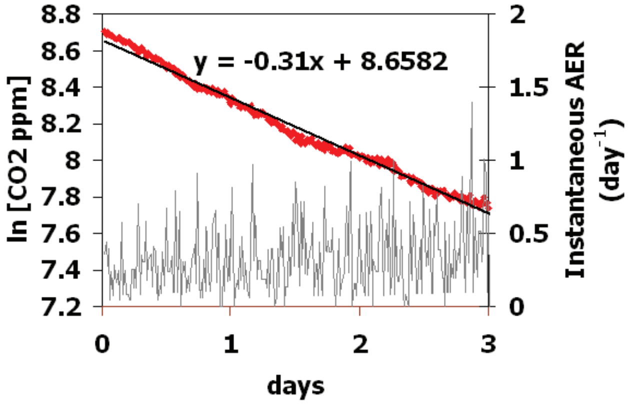

Figure 4. Instananeous air exchange rate of case. Red line is the natural logarithm of the carbon dioxide concentration, corrected for background. Black regression line shows normal method to calculate average air exchange rate (0.31 day^{-1}), the gray line shows the instantaneous air exchange rate calculated reading by reading; this has a maximum value of 1.42 day^{-1}.

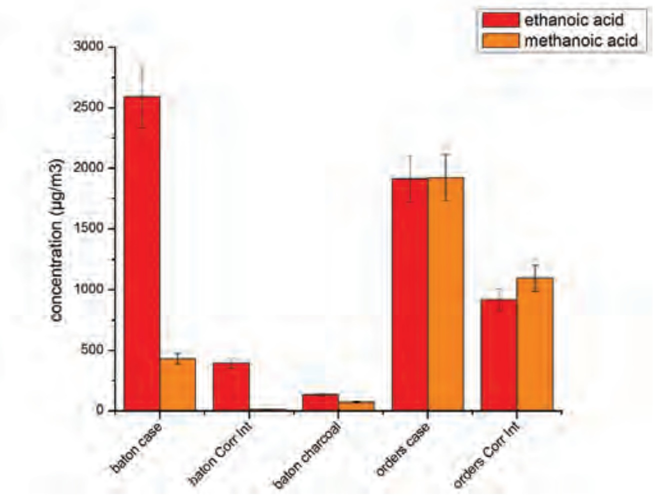

Figure 5. Ethanoic and methanoic acid concentrations in trials with Corrosion Intercept foam and activated charcoal cloth.

The ethanoic acid concentrations in both cases were relatively high and the case containing the Orders also contained high concentrations of methanoic acid. This probably originated from the paint used in the case. The methanoic acid emission from wood and most wood products is under 20% of the ethanoic acid emission. The paint was identified as an oil paint with Fourier transform infrared spectroscopy (FTIR). Oil paints are well known as strong sources of methanoic acid. Addition of the corrosion intercept foam reduced the acid concentration below the threshold of lead corrosion in the Battens case, but not the Orders case. The activated charcoal was applied so the mounting of the silver components on the battens was not in direct contact with the charcoal cloth. Results from the silver coupons and onguard loggers are shown in Table 5.

	Increase in b* on silver coupon			Tarnish layer thickness (10^{-10}m) measured at bottom
	Top	Middle	Bottom	
Orders Case	0.71	0.67	0.57	12
Orders Case CI	0.65	0.44	0.09	2
Battons Case	0.37	0.31	0.43	8
Battons Case CI	0.30	0.32	0.05	1
First Trial room	0.13			10
First trial case	0.07	0.08	0.09	7
Second trial room	0.15			12
Second trial CI case	0.02	0.02	0.01	2

Table 5. Corrosion Intercept trials with silver.

While the corrosion intercept has a dramatic effect on the base of the cases and at half height (50cm and 61cm), its effect is much reduced higher in the case.

The most effective place to locate sorbents for silver is in the showcase seals. Corrosion Intercept foam can be readily cut into narrow strips to achieve this. A showcase with a high air exchange rate (8.41/day) was selected for trials, as this would be a challenging situation. The initial trial was carried out with the case unmodified with its silicone compression seals. Silver coupons were exposed inside the case and in the room and the reduction in tarnish rate measured over a four week period. Corrosion Intercept foam was cut and applied next to the compression seals inside the case, and the trial repeated. This reduced the silver tarnish rate by a factor of six, as shown in Table 5.

Conclusion

Sorbents can perform very well in showcases and reduce corrosion rates in otherwise unacceptable situations. The amount of sorbent needs to be carefully researched and the high variability in showcase air exchange rates, geometries and designs makes generic formulations of limited use. It is essential to know the air exchange rate for passively deployed sorbents and useful to know the air exchange rate to design pump-based systems. Simple standard tests are available for the estimation of remaining capacity of activated charcoal. These tests should be applied periodically for ethanoic acid as the concentration is a strong function of temperature and RH. For silver tarnish prevention using sorbents in pumps, the sorbent lifetime can be calculated with less uncertainty, provided the average hydrogen sulfide and carbonyl sulfide concentrations are known. Placing metal coupons in cases with sorbents to observe the first signs of breakthrough for the sorbent is prudent. No evidence of dangerous off-gassing levels from activated charcoal has been found, at least when deployed passively.

Materials

Onguard 3000 logger/onguard crystals
Purafil UK distributor Prisma Services Limited
Tel: +44 (0)1246 852052
Fax: +44 (0)1246 852085

Activated Charcoal Cloth, Corrosion Intercept foam
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PO Box 100, 2027 KJELLER
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Fax: (+47) 63 89 80 50
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Puraspec 5040
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London, W1U3AN
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Authors

David Thickett graduated in natural sciences in 1988 and worked in the refractories industry before joining the British Museum in 1990, where he specialized in inorganic materials and preventive conservation. He joined the Collections Conservation Team of English Heritage in 2003. Research interests include the tarnishing of silver, light and RH control methods in historic buildings, protection of outdoor metals, reburial of architectural stone, and panel painting microclimate frames. He is a working group co-chair for European Cooperation in the field of Scientific and Technical Research (COST) action D42, Chemical Interactions between Cultural Artefacts and Indoor Environment (EnviArt), an assistant co-ordinator of the International Council of Museums Committee for Conservation Preventive Conservation Working Group, and directory board member of the Infrared and Raman Users Group.

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Q & A SESSION

Helen Ganiaris: Thanks for that Dave. We use quite a bit of charcoal cloth and we asked our manufacturer recently if we could regenerate it. As you know it is very expensive. I think it is £45 per square meter, which is a lot. And they advised washing with soda crystals and then tumble drying. Do you think that is valid and would it be effective?

David Thickett: They've got much more experience with this than me, we've not gone as far as trying to reuse it. Normally with activated charcoal you need to heat at quite high temperatures to get the reactivation. I don't really know Helen. The best way to do it would be to try and run some simple tests to see if it is effective. We've not yet got to the point of having to reactivate it. But I know it is very expensive – well, relatively expensive to buy.

Paul Mardikian: I may have missed one of the comments, but how do you measure the exchange rate of a showcase?

David Thickett: I didn't say. There's a number of ways you can do it. The two main ways are to pressurize it up and measure the pressure difference, but you need to put some holes in your showcase to do that. The other way is to use a tracer gas, carbon dioxide or nitrous oxide are the common ones. You essentially inject maybe 5000 ppm of CO_2 into the case where, you've got a logger and you just watch the decay of the CO_2. And if you plot the natural logarithm against time, the slope of that line is actually the air exchange rate of the showcase. I've spent quite a bit of time trying to get cheaper methods of doing this.

Paul Mardikian: Well, that is not something that one can do on a showcase easily.

David Thickett: We've tested about 400 showcases with this method now, the test takes about 3 days. We normally test every new case that goes in; we specify it, test it, get the manufacturers to tighten it up if it doesn't meet the specification, which is quite common. But the loggers are $400-$500 – it is not beyond the means of many conservation labs. I would say for a lot of preventive conservation, the air exchange rate is absolutely critical for a showcase.

CONSERVATION MAINTENANCE PROGRAMS FOR FUNCTIONAL OBJECTS

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Abstract

Multiple and often mutually exclusive points of view develop around collections and their uses as social resources. In this context, conservators require a decision-making framework for care and maintenance of functional objects. In this article, the authors explain some of the ethical and practical considerations that have led the National Museum of Australia (NMA) to adopt maintenance programs as the best strategy for the conservation of technological heritage collections. The deterioration caused by passive storage is outlined and the lack of deterioration caused by systematic maintenance programs is enunciated. The idea of imbedding a constant monitoring, improvement and feedback plan into the program is explained. An object in the collection of the NMA is examined after a decade on display under this regime. We conclude that ability to function is one of the significant attributes of an object that should be conserved wherever practically possible.

Keywords: Conservation, metals, maintenance, technology, preservation, ethics, restoration, museology, analysis, engineering culture, just noticeable wear

Introduction

Conservators are increasingly challenged by multiple expectations around the care of collection items. Traditional museological ideas about collected objects being captured at a point in time and held in suspended animation are rapidly unravelling as knowledge about chemical deterioration increases, and our society develops new expectations of our historical collections. Multiple and often mutually exclusive points of view develop around collections and their uses as social resources. In this context, conservators require a decision-making framework for care and maintenance of functional objects. Our ethical framework is not only governed by a desire to preserve in perpetuity, but by our technical experience in the practical care of objects that often demonstrate accelerated deterioration, even in the most highly regarded public institutions. Our approach is substantially one that has developed from the question: 'What is our preservation objective?'

In a recent paper, Sloggett discusses disciplinary and cultural intersections in the context of how conservators operate to preserve what is valuable about an object (Sloggett 2009). The author poses the following questions: 'What are the indicators for effective engagement with the cultural and social meanings represented in the preservation of cultural material? Is there a richer, deeper, broader type of practice relevant to cultural preservation that conservators can develop? Who are the partners in the process of cultural preservation?'

It has long been easy for conservators to place institutional barriers in the path of genuine engagement with the communities to whom museum collections matter the most. The open hostility that some individuals demonstrate toward museums about 'letting their collections rot in store' is a genuine reaction by a cultural stakeholder. Scholars and academics who seek preservation without intervention are cultural stakeholders, just as those who seek to restore, use and demonstrate are also cultural stakeholders. Conservators must engage with the expectations of all stakeholders in the communities, for which material is being preserved, or ultimately the material will decline in social significance, and the argument for preservation will also steadily decline.

The National Museum of Australia's (NMA) conservation sections functional object preservation strategy is an attempt to marry and engage with the multiplicity of expectations surrounding its technology collections. Conservators, an interest group with unique views and expectations, have often practiced a policy of minimal engagement with technology collections (Ashton and Hallam 1991). However, for these collections, as for many others, this mantra is challenged by the obvious and steady deterioration of significant material within

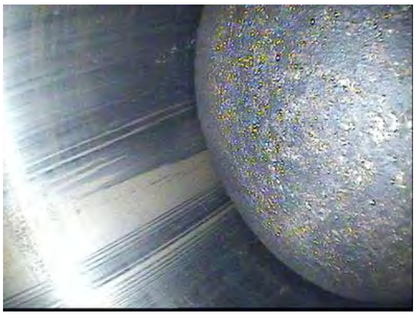
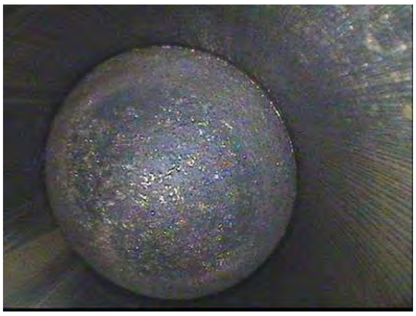
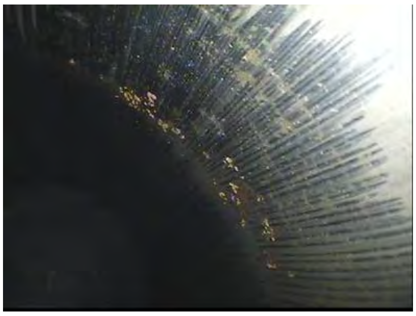
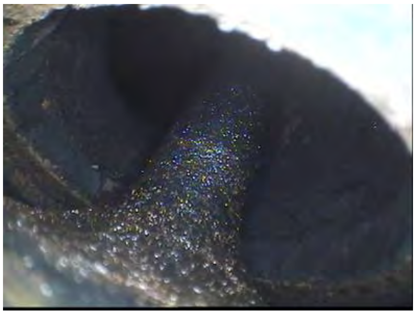
Bentley 1924		
 Cylinder N°1 T.B.C opposite plug Valves closed	 Cylinder N°2 B.D.C piston crown	 Cylinder N°2 scoring on thrust side
 Cylinder No 2Bore & scoring and corrosion	 Corrosion valve N°2 Cylinder	 Exhaust valve open
 Exhaust ports	**Bentley 1924** *Fluid:* Engine oil (probably st/30) *Last driven:* June 1980 Photographs: Michiel Brunott Photographs: copyright Coventry Transport Museum	

Table 1. Boroscope investigation of a Bentley 1924 demonstrating internal deterioration due to extended periods of static preservation.

their custodianship. The following images (see Tables 1 and 2) illustrate the types of deterioration routinely observed in historic engines that have undergone relatively short periods (decades or less) of static preservation in museum storage. It is our belief that this methodology has limited effectiveness and at best provides a 'shotgun preservation strategy' with objects deteriorating at unpredictable rates. Unfortunately, we also often observe a knee-jerk reaction to deterioration that results in 'restoration' and loss of original material and information value. Our approach is a middle way.

Sloggett's engaging questions are an active part of how NMA technology conservators engage with collections and community. In a multidisciplinary approach, significance and community engagement are used to develop an active rather than passive approach to preservation. Bob Barclay's pivotal work on the conservation of musical instruments (Barclay 2005) discusses conservation of function and has had a significant influence on the development of our ideas. We recognize that our decisions around active preservation and intervention include a risk of erroneous and irreversible changes to objects. However, as part of our risk assessment we also recognize that previous passive practices often result in accelerated and avoidable dramatic changes to our collection (Hallam et al. 2004a). We also recognize that currency or continuance[1] as a philosophy provides opportunity for engaging with cultural stakeholders in a far more meaningful way that facilitates preservation of culture rather than only preservation of cultural artefacts. By assisting in preserving the 'culture that cares'[2] we also believe that we will ultimately achieve greater success in the traditional conservation objective of increasing the lifetime and probability of survival of the materials themselves. Museum stores are full of objects that have been disconnected from their communities and cultural traditions. It can be argued that disconnected objects are at greatest risk of survival as their community relevance

Lea Francis West land coupé 1949		
 Into cylinder head cooling space	 Into head cooling jacket via heater pipe	 Crank and rod case area
 Ring marks on bore	 N°2 bore and piston	 Under Rocker cover at shaft
 Under Rocker cover at shaft	**Lea Francis West land Coupe 1949** *Fluid:* Engine oil (probably st/30) I*n the museum since:* 24 March 1973 *Mls of system:* 96552 *Last driven:* June 1972 *Museum running history:* Longest static vehicle in an uncontrolled environment. Photographs: Michiel Brunott Photographs copyright Coventry Transport Museum	

Table 2. Boroscope investigation of a Lea Francis West land Coupe 1949 demonstrating internal deterioration due to extended periods of static preservation.

decreases over time.

The NMA Approach

At the NMA, curators and conservators endeavour to retain, where appropriate, both the form and function of technology objects as the starting point for a preservation strategy. We do not automatically assume that the preservation goals are mutually exclusive of function, or that one objective has automatic precedence over the other. A significance assessment, a document outlining what is important about the object, to whom, and why, in accordance with the methodology outlined in Significance 2[3] (Russell and Winkworth 2009), is the key element of our preservation strategy. The significance assessment outlines what is significant about the object, and what needs to be conserved.

This approach necessarily generates complexity, and at times confusion. The absence of a one size fits all 'policy' for these objects can lead to misunderstandings. At casual observation, it can be difficult to reconcile the reasoning behind a carefully and fastidiously 'conserved', unrestored but stable 1820's horse-drawn vehicle, and the regularly polished and repainted volunteer maintained steam engine that reside at the same storage facility. This practice is recognition that objects have multiple meanings and varying significant elements that the museum seeks to preserve. The horse-drawn vehicle in stable, original, unrestored, used condition would gain no added significance from restoration. Equally, however, a steam engine that has been dismantled, run, restored and adapted by successive generations of steam enthusiasts is not an object that would benefit from a traditional pure materials scientific conservation approach. Any minimal gain in stability and preservation of original materials would be at the expense of the objects significance as a focal point of a community and continuing cultural tradition. In such instances conservation methodology can inform and meaningfully contribute to the culture, but is not a valid substitute.

Opinions are divided (often strongly) in the cultural heritage sector around the preservation of function in technological objects. Kuhn (1989) argues that it is the 'historical integrity' of the object that we are preserving in museums. 'Time leaves marks of a different kind on an artefact ... natural ageing ... signs of past use and abuse ... traces that time has left on an artefact must not be altered – much less removed ... loss of such evidence of past use and age also entails an inevitable loss of historical significance'. This theme is common in the 'scientific conservation' approach (Barclay 2005) where nothing is more important than the historical integrity of an object or its capacity to be an historic document or primary source for analytical study.

Alternatively, many authors in 'Risk and Rewards' (Mapes 1991) argue that use is an appropriate museum activity. The lack of care in storage and notable degradation becomes an argument for use, often incorporating restoration. Much debate has been incorporated into the literature as to whether preservation or restoration is the appropriate path. Much of the literature has developed into pro- and anti-restoration positions. Many supporters of operation do not see any worth in 'original fabric of an object'. Alternatively, Ferrel (1991) in 'Risk and Rewards' argues for preservation and interpretation as opposed to restoration and function; 'Documents be they inscriptions on paper or three dimensional objects like steam locomotives, can be read. Each has a story to tell. And if a document is altered or corrupted its value as a source of information is compromised or destroyed'.

Strong philosophical positions in opposition to intervention rarely also engage with the actual practicalities of managing these types of objects. These frequently are objects designed around presumptions of ongoing maintenance (for example, motor cars, whitegoods), after which (at obsolescence) their accelerated degradation in the absence of maintenance became irrelevant. A position that is not frequently encountered in the literature concerns the maintenance philosophy for these objects. In the museum environment of 'preservation,' these objects deteriorate and shed historic value at an alarming rate if strict minimal intervention philosophies are applied. The internal material structure and composition of the object can deteriorate markedly beneath the shell of exterior aesthetic preservation. This is the problem with the minimalistic preventive conservation approach. The 'pages' of technological objects are as important as the cover. The industrial sculpture approach to preservation, which only conserves what we can see, often comes at a cost. The large amounts of information that an object has to offer are lost.

These factors are well illustrated in the findings of Brunott's (Brunott 2008) recent study at Coventry Transport museum. He stated;

> From this research we concluded the following points:
>
> Vehicles should not be stored with original fluid in situ. The systems should never be left empty without further treatment. All fluids should be replaced with new fluids designed for longer-term storage or at least replaced by fresh fluids of the same specifications.
>
> All fluids should be monitored on a regular basis to trace their degradation.
>
> All vehicles should have a maintenance scheme even if they are to be preserved in a static state.
>
> Further work should be done on the long term storage of static and functional vehicles in Museums.

Maintenance

Functional maintenance of original working objects offers a museologically sound approach to preservation. It is neither strict preservation, nor restoration, and brings with it the preservation of the intangable, including knowledge preservation, opportunities to experience function, reduced costs and ongoing higher levels of preservation of 'original' material. The significance of function to many communities should not be underestimated. Experiencing the operation of a steam engine first hand provides an entirely different experience to witnessing an inoperable preserved 'original'. Both experiences are valuable, and in a majority of instances we have concluded that a limited level of function is beneficial to the preservation of even our most cherished original objects. It also provides a 'relief valve' in the argument for restoration of original objects, for instance the Holden Prototype No.1 (see Figure 1) and the Bean Car (see Figure 6). The highly limited and controlled function of an object, for instance on a five-year basis to changeover corrosion inhibiting fluids, enables us to say that yes, this object functions, and that there is an opportunity for the passionately interested to observe its function.

Functionality does not necessarily mean operation to a point of failure or loss of information value, and can greatly enhance preservation. Preliminary work we have undertaken (Hallam et al. 2004a) towards developing a 'just noticeable wear standard' has suggested that functioning engines operated in this way have a projected lifespan of 10,000 years before wear becomes an observable factor in the objects interpretation (parallel with just noticeable fade standards). The work also suggests significant and accelerated deterioration, with lifetimes measured in decades, for functional objects experiencing corrosion and other deterioration under conventional passive preservation strategies. If identifiable wear and risk of catastrophic failure are greatly reduced by appropriate conservation practices, then strict arguments against use become less sustainable. We currently 'use' watercolour artworks over a projected 500-year fading cycle. Using functional objects, and accepting a degree of risk from this practice is not greatly dissimilar from this practice.

We conclude that ability to function is one of the significant attributes of an object that needs to be conserved wherever practically possible. Even for the most original of objects, the potential to function should be considered, even if the object is not to actually

Figure 1. Prototype Holden No.1 (right) and Citroen 5cv undergoing controlled exercise at Oran Park race track April 2009.

function. Important objects preserved with little regard to their function and how the work will lose significance over time. Shiny on the outside, 'rotten' on the inside technology collections have a greatly reduced potential to speak through time to subsequent generations.

Maintenance Framework

Work conducted at the NMA is resulting in the development of new procedures that assist museum collection managers to adopt scheduled monitored maintenance and preservation of functionality as sound and cost effective approaches to care of technology collections. A key objective of the maintenance framework is to concentrate the museums resources where they do the most good: prioritised protection for the most important, most used and most vulnerable, and a clear projection for the consequences of lesser standards of care.

The approach is to;

- Identify the most sensitive objects using surveys, exhibition requirements and incoming object inspections (conservation and engineers).
- Identify the most important and frequently used (not just displayed) objects using significance test (mainly curatorial).
- Identify the risks of use, storage and exhibition and how to minimise them (mainly conservation and engineers).
- Develop maintenance and monitoring plan for each object in accordance with its significance and use (mainly conservation and engineers).
- Understand the concerns and wishes of stakeholders.
- Understand that all objects require a maintenance program, but that the museum may have to prioritise the application of resources.
- Understand that we can maximise the effectiveness of treatments through research and transfer technologies from the military and engineering to collecting institutions.

Significance/ Risk model

The NMA conservation section uses a significance/ risk-based model for assessing and re-assessing the effectiveness of current maintenance, use and non-use of objects in the collection. With regard to functional engineering and cultural heritage objects, decisions are made by an analysis of the significance of the object and an assessment of relevant risks and probabilities of events that may occur dependent on the type of object and the intended functional event.

Once the risks are determined and accepted, measures can be taken to avoid and reduce the potential occurrence of such risks to a complete minimum. With careful planning and appropriate training a vintage/classic vehicle can be started, run to operating temperature and exercised safely in a controlled manner (see Figure 1).

The NMA Maintenance Framework for Functional Objects (Table 3) has three principle formal steps:

- Planning
- Implementation
- Feedback

We consider the 'feedback' loop the most important element for successful application of the model. Problems are identified, decisions and actions are reviewed as the program develops. Previously published papers on oil films (Hallam et al. 2004b) and brake fluids (Hedditch 2008) are good examples of this process in practice. We use the preservation maintenance process as a tool for documenting and researching our approach in such a way that continuous improvement and generation of new knowledge become standard elements of our conservation practice, and are not separated out as separate 'research' activities.

Planning	
	- Assessment - Curatorial and Conservation assessment - Curatorial Assessment - Conservation Assessment - Engineering Assessment (most important)
Statement of Significance	- Including examination of significance of function - Also including statement re condition object entered collection and wishes-expectations of “donor” Considering wishes of community (e.g. engineers – electricians – clubs)
Risks evaluation	- Static -Used un-maintained- Maintained -Mothballed - Skills audit – history - Mechanical – Materials, parts required - Approach – How, why, how come?
Curatorial Objectives	- Visual - Historical - Functional
Conservation Objectives	- Aims – desired outcomes - Maintenance and monitoring objectives
Treatment Plan	- Funding - Skills audit Options- To meet outcomes - Sustainability – is it?
Maintenance Plan	- What, how, where and why? - Based on what’s possible and integration with monitoring
Implementation	
	- Treatment development - Research and materials selection - Treatment Implementation - Documentation - Training Plan - sustainability - Maintenance Implementation - Monitoring required
Monitoring and feedback	
Monitoring	- pH - Particulates - Engineering - Reporting - Record for risk calculations - Photographic - Technical - Feedback – to implementation
Maintenance	- Reviewing - Advice
Publication	- Web-based - Magazine - Books - Feedback to community – clubs ext.

Table 3. NMA maintenance framework for functional objects.

Figure 3. Francis Birtles leaving London 1926 in the Bean car to embark on transcontinental journey to Australia.

Active monitoring strategies, such as the monitoring of pH of fluids and metal content by XRF (see Figures 2 and 5), work hand in hand with traditional engineering knowledge concerning smell, sound and feel, and become a successful marriage of cultures and techniques for preservation. The dialogue between conservators sharing knowledge about metal concentrations in lubricants with traditional mechanical engineers provides this community with new information. Similarly, engineers showing conservators how a machine should function correctly creates a new body of skill and knowledge and documented understanding that may otherwise be lost to history.

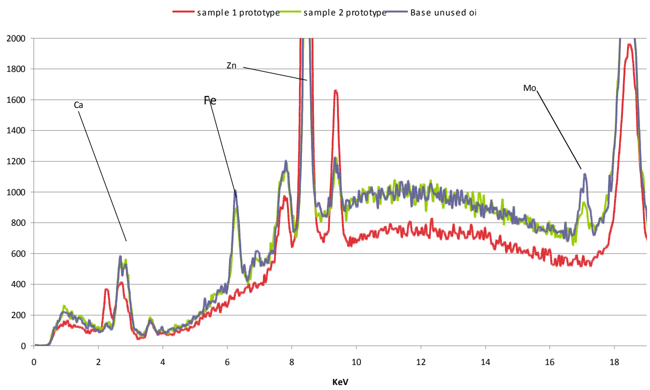


Figure 2. Comparison of Holden Prototype No.1 engine oil vs. standard after controlled maintenance run for 100km at Oran Park racetrack Sydney NSW. Note the Iron (Fe) and Molybdenum (Mo) residues from a previous engine rebuild using Molybdenum DiSulphide grease in the rebuild process.

The first fruits of this kind of collaboration are now coming off display after 10 years as stable maintained objects. Visual and analytical studies of the Bean Car (Table 4, see Figure 5) show that the NMA approach has worked with minimal intervention. In this case we have extended the life of the inhibited oil to cover the full 10 years of display by rotating mechanical parts at least once every six months and adding new oil to the cylinders through the spark plug holes to overcome oil drain-down.

Figure 4. The Bean car in 2000 being driven into the display space during the building of the National Museum of Australia.

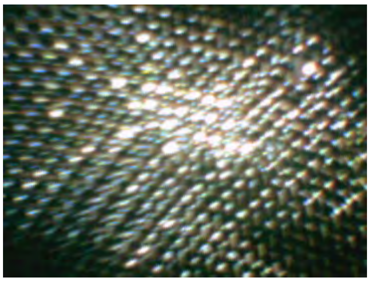
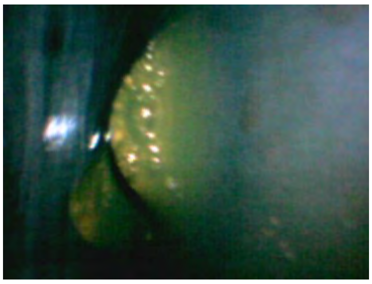
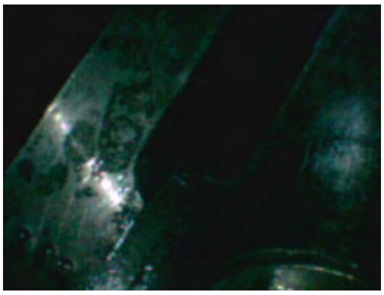
1926 Bean car after 10 years display		
 Oil pump pre Screen Note lack of carbon and corrosion.	 Conrod locknut. Note lack of sludge or carbon build-up.	 Web of crankshaft Note oil film and cleanness of oil
 Cylinder wall through spark plug hole.	 Oil dripping off bottom end. Note cleanness of oil.	 Crankshaft and crank web. Note old stain but no red rust.
 Crown wheel in differential.	 Crankcase Water Jacket Note deposits but no red rust	 Cylinder head Water Jacket Note start of failure. (brown globules present in small numbers)
Bean 1926 *Fluid:* Penrite Shelsley Medium *Last oil change: 2000* *Last driven:*2000 *Museum history:* Longest static vehicle in an museum environment. Photographs copyright National Museum of Australia		

Table 4. Boroscope investigation of the 1926 Bean Car after 10-year display period with basic periodic maintenance.

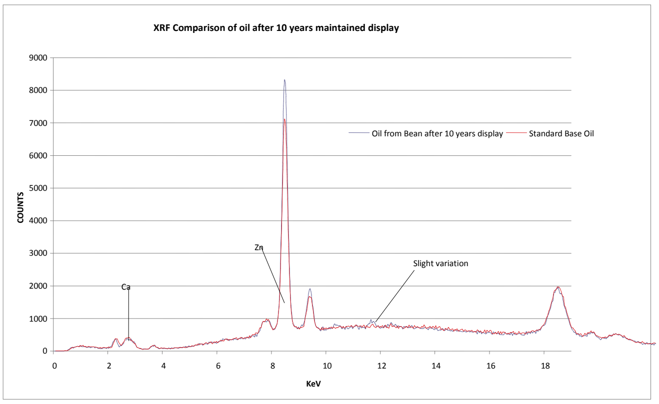


Figure 5. Comparison of the Bean car engine oil after 10 years display and basic periodic maintenance against a current new standard. The "slight variation" is due to bromine that was used as a lead scavenger in the leaded petrol this car ran on in the 1950's.

Conclusions

Ethically, function should be considered as one of the significant material attributes of an object that needs to be conserved. Operation or usage of an object should not be considered as a contribution to deterioration of that object, but as an option available for interpretation of the object through the 'storage and occasional use scenario'. Function should be included in the significance assessment process.

The authors conclude that ability to function is one of the significant attributes of an object that needs to be conserved wherever practically possible. Storage and display of objects without a systematic maintenance program increases the risk of catastrophic deterioration and loss of function.

A maintenance program needs to include a program of skills development and retention of engineering expertise. Continued treatment development, materials selection and monitoring are essential to allow a maintenance program to constantly evolve and improve its effectiveness.

Acknowledgements

Col Ogilvie and Ian Stewart for their unwavering contribution to valuable discussions and engineering guidance. The National Museum of Australia for supporting this work.

Endnotes

[1] The object continues in use, being maintained in working condition using craft skills.

[2] The - Culture that cares - are the people and skills required to maintain and preserve the object in continuance.

[3] Significance defines the meanings and values of a cultural heritage item or collection through research and analysis, and by assessment against a standard set of criteria.

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Q & A SESSION

Vasilike Argyropoulos: David, thank you very much for your talk. I found it to be very interesting and very useful. The question that I have is how frequently are these types of risk and significance assessments being carried out in museums in Australia? Is it just at your museum or is it something that your government requires, for example?

David Hallam: It's something that people are gradually starting to do – it is becoming extremely common. Significance assessments everyone does. If you want a grant, you have to do a significance assessment so it's becoming more and more common. We are working with Joanna Barr, from Artlab in South Australia on this work. She has been pushing with the local historical societies the ideas of risk and significance assessment but the thing I found hard was that no one could really tell me how the risk part worked. Everything else was wonderfully well documented.

Paul Mardikian: I was curious about the fuel lines; about the regimen that you use when you test those cars. Do you flush them afterwards? Do you keep the fuel inside? What is the rule? Because you've got safety rules here and you also have some issues with the gas [petrol] itself.

David Hallam: Yes. You certainly can't leave them with petrol in them. One of the things that Michael [Brunott] did was that he looked at what happens to petrol when it is put into storage. Old-fashioned leaded petrol, the Swedes did a study - and after 8 years you could restart the vehicle with old-fashioned leaded petrol in it. After 8 years with modern unleaded petrol – it turns to a gel and you can't do anything with it. So you have to flush the system out and my advice is to flush it out with a very light oil, and full with Vapor Phase Corrosion Inhibitors. So a 10-weight oil – almost like kerosene.

Emma Schmuecker: David I have one question: I was just wondering how many functional objects you have in your collection? Once you've assessed your risk and your significance and written maintenance plans, do you think this will have a big impact on your resources such as staffing?

David Hallam: Yes I do. We've got 28 vehicles. Now, everyone is saying 'well, you've only got 28' – but it allows us to really minimize the amount of effort we put into them. But just as an aside, this approach is also being applied at the Swiss Army Historical Section by Michael Brunott where he is applying it to a collection of 700 vehicles, and he's doing it with volunteer labor. So he's got all of the old ex-army mechanics and driver-trainers and other things. That's the regimen he has put in place so although we are doing it to a very small collection, other people are trying to apply it to very large collections. In his case, he is really lucky, because they're all functioning. The problem is, if you have 700 vehicles that have been allowed to deteriorate, then you have an immense amount of work to start this kind of program. And that's the hassle.

DOSIMETRY FOR MONITORING IN ORGAN PIPES AND IN MICROCLIMATE FRAMES FOR PAINTINGS

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Abstract

Lead-coated piezoelectric quartz crystals (PQC) were used for the first time to evaluate the quality of microclimates within organ pipes and within microclimate frames (mc–frames) for paintings. A continuous monitoring system was developed for the use within organ pipes, and this system was adapted for measuring within frames. Exposures took place within the organ pipes of St. Botolph Aldgate, London, and in Oergryte New Church, Sweden. It was found that the response of lead-PQC dosimeters within selected pipes was higher in the latter and occurred more rapidly, which correlated with the presence of higher levels of ethanoic (acetic) acid and relative humidity. In the case of mc-frames, it was found that the dosimeter response was higher within the frames than in the rooms, and this was consistent with higher levels of organic acids, which were measured within the frames using passive diffusive samplers.

Keywords: preventive conservation, dosimetry, piezoelectric quartz crystals (quartz crystal microbalance), organ pipes, microclimate frames , wood, organic acids.

Introduction

In the last few years it has become apparent that there is a demand for monitoring in enclosures, in particular where wood is present (Thickett, Stanley and Booth 2008). It is well known that wood emits volatile organic acids, in particular ethanoic acid, which corrodes lead. It has also been demonstrated that these emissions depend on relative humidity (RH) and temperature (T) (Thickett, Bradley and Lee 1998). The advantage of using dosimetry is that it provides information on the synergistic effects of parameters that contribute to the overall damage to materials, and in this case, the combined action of organic acids, RH and temperature, which affect corrosion of lead-based objects. For this reason, lead dosimetry has been used in the form of lead coupons, and recent studies in indoor environments in museums have demonstrated that it is possible to obtain a ranking according to the quality of the indoor environments (Ryhl-Svendsen 2007). In this paper, the use of lead-based PQC dosimeters is proposed. The rationale for using PQC or Quartz Crystal Microbalance technology is that the films are nanometres thick and so the response to reactive environments should occur rapidly and provide an early warning of incipient damage to the coating. The dosimeters can be exposed either as passive samplers or as continuous monitoring devices. Varnish coated PQC dosimeters were tested within the EC-project MIMIC (EVKV-CT-2002-00040) and indoor environments at selected sites were characterised (Odlyha et al. 2007). The basic principles and rationale for the use of piezoelectric quartz crystals is also described in this paper. PQC crystals oscillate when included in a circuit and the frequency of the oscillation is measured. Shifts in frequency occur when a coating is applied, and then with physico-chemical changes in the coating. The frequency shift is directly proportional to the mass of the coating.

The testing of lead-PQC dosimeters and their adaptation for use within organ pipes and frames for paintings was performed within two EC projects. In the SENSORGAN project ‘Sensor System for Detection of Harmful Environments for Pipe Organs’ (contract 022695, http://www.goart.gu.se/sensorgan,accessed 06/02/2010) the aim was to monitor within the lead-based organ pipes, and in PROPAINT ‘Improved Protection of Paintings during Exhibition, Storage and Transit’ (FP6 SSPI no 044254, http://propaint.nilu.no, accessed 06/02/2010) the aim was to monitor organic acids emitted within frames containing paintings. This paper will mainly focus on the testing in SENSORGAN and will make reference to some results from PROPAINT.

The pipe organ is an important part of the cultural heritage of Europe. Over the centuries, the development of the organ has mirrored the technical, social, and economical development in society in different regions in Europe. The organ heritage found in European countries includes more than 10,000 historically valuable organs. A major threat to this heritage is harmful indoor environments. The previous EC project COLLAPSE (EVK4-CT-2002-00088) showed that organic acid emissions from wood in the organ under certain circumstances creates lead-based corrosion inside the pipes leading to cracks and finally holes in the pipe wall (Niklasson et al. 2008). The organic acids, mainly ethanoic acid, are generated in the windchest, which is typically made of oak or pine. They then enter the pipe foot, and the extent of corrosion will depend on the pipe metal alloy, temperature and humidity in the organ. It was found that concentrations of organic acids in the same organ wind system were about five times higher during summer compared to winter. Pure lead pipes are very sensitive to corrosion, but a few percent of tin will have a corrosion protecting effect at lower humidity. However, at higher humidity the protecting effect of tin disappears. Heavily corroded pipes of mainly pure lead were observed in the St Jakobi church in Lübeck, Germany (Chiavari et al. 2008). This prompted, in the follow-up SENSORGAN project, the design of new instrumentation for monitoring and detection of organic acids harmful to organ pipes that was based on the instrumentation developed in the previous MIMIC project (Odlyha et al. 2007). The instrumentation was miniaturised and adapted for use within organ pipes, and a lead coating was applied to the PQC crystals to detect organic acids.

The PROPAINT project was proposed as a result of the growing concern of conservators about the nature of the environment within mc-frames for paintings. The use of such frames is becoming widespread and it is important to know that frames designed to protect paintings do not introduce new risks for the paintings (Grøntoft et al. 2010). In the project, measurements were made for the first time of gaseous air pollutants and climatic conditions at various locations both inside and outside different state-of-the-art mc-frames. Diffusive passive pollution gas samplers were used to measure concentrations of both inorganic and organic pollutants (López-Aparicio.et al. 2010) and different types of dosimeters, including lead coated piezoelectric quartz crystals, were used for damage assessment (Grøntoft et al. 2010). Some of the results obtained using lead coated PQC crystals in selected frames will be described in this paper.

Experimental

PQC crystals (10MHz) were coated using high purity lead that was deposited by thermal evaporation in a custom thermal evaporator designated for the deposition of low vapour pressure metals. The oxide build-up on the lead was removed prior to deposition by immersion in a 1:1 acetic acid:water solution for about one minute. The PQC crystals were located 200mm above the filament side. Crystals were masked using their cans in which 4mm diameter holes were drilled in each side so that only the central gold electrode was coated. The thickness of the deposited film was monitored using an Edwards FTM2 rate monitor connected to a commercial 6MHz quartz crystal. Lead was evaporated onto each side by removing the crystals and turning them over. After deposition, they were canned and stored in a desiccator. Frequencies were monitored during storage and before use.

Typical values for crystal loadings were frequency shifts of 10-12,000Hz and using Sauerbrey’s equation this converts to a loading of 8-9ng and a thickness in the region of 40-50nm. The passivation period showed a further shift in frequency and the change in mass was found to be of the order of 8%. This corresponds with the expected mass gain for formation of lead oxide (PbO). Raman spectroscopy confirmed the presence of lead oxide, and in particular the orthorhombic (massicot) form (de Faria 2007).

Results and Discussion

The responses of lead coated PQC crystals to specific values of ethanoic acid vapour and RH were tested using the same experimental set-up and conditions as in the COLLAPSE project (Niklasson, Johansson, and Svensson 2005). Crystals were supported in a holder and changes were measured before and after exposures. Measurements were performed in the concentration range 425μg/m^3 to 2275μg/m^3 ethanoic acid (170-910 ppb) at RH values from 50% to 90%. Figures 1 and 2 show the change in lead coated crystals exposed to 425μg/m3 and 2275μg/m^3 ethanoic acid at 60%RH respectively.

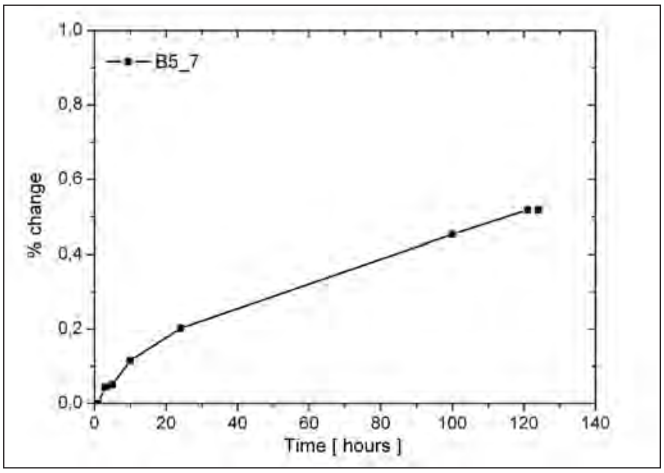

Figure 1. Lead PQC crystal response expressed as change (%) on exposure to ethanoic acid (425μg/m^3, 170ppb) humid air at 60%RH vs. time (hrs).

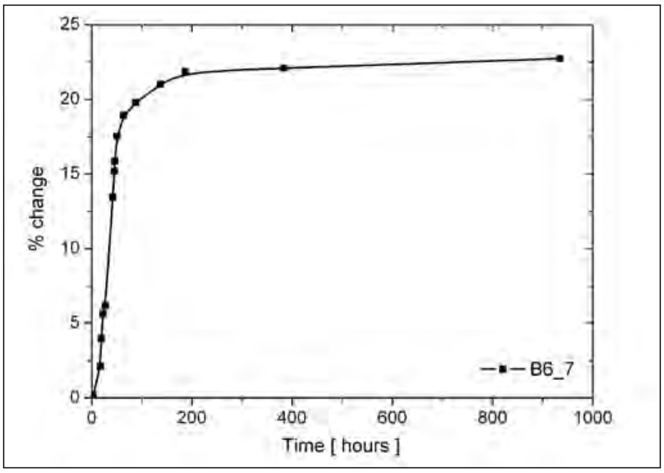

Figure 2. Lead PQC crystal response expressed as change (%) on exposure to ethanoic acid (2,275 µg/m^3, 910ppb) humid air at 60%RH vs. time (hrs).

Higher levels of ethanoic acid caused an increase in the rate of change of crystal response (see Figure 2), as did RH. Measurements were also made using the miniaturised continuous system adapted for the SENSORGAN project.

The development of a continuous monitoring system for the PQC crystals in the SENSORGAN project involved miniaturisation of the electronic components used in the MIMIC project (2007), and the design of a new holder (Delrin) to house the crystal circuit driver boards and the crystals. Figure 3 shows the crystals in the top left hand corner and the arrow designates their location within the holder.

Figure 3. Crystal dosimeter set up in location 1 in St. Botolph Aldgate using a Haut boy pipe in upper swell box (freshly restored pine).

The organ pipe shown was raised from the toe board of the windchest and supported by a small Delrin block. An opening in the side of the Delrin block was machined to allow the insertion of the crystal holder. A vertical hole in the support ensured the pipe could be played during the monitoring and that the crystals were exposed to the organ wind flowing into the pipe foot. For operation, it was necessary to make the system compatible with PC requirements necessitating usb connections. For this purpose, an additional unit, the Handyscope HS4, was used and, with specially designed software, the signals from the three crystal driver circuits could be accessed.

The continuous monitoring system was tested in the laboratory prior to site testing. Simulation experiments were set up using organ pipes and wood in glass vessels.

Figure 4. Laboratory set-up to simulate on site monitoring using an organ pipe. This shows the white (Delrin) support with the crystal holder inserted on the side.

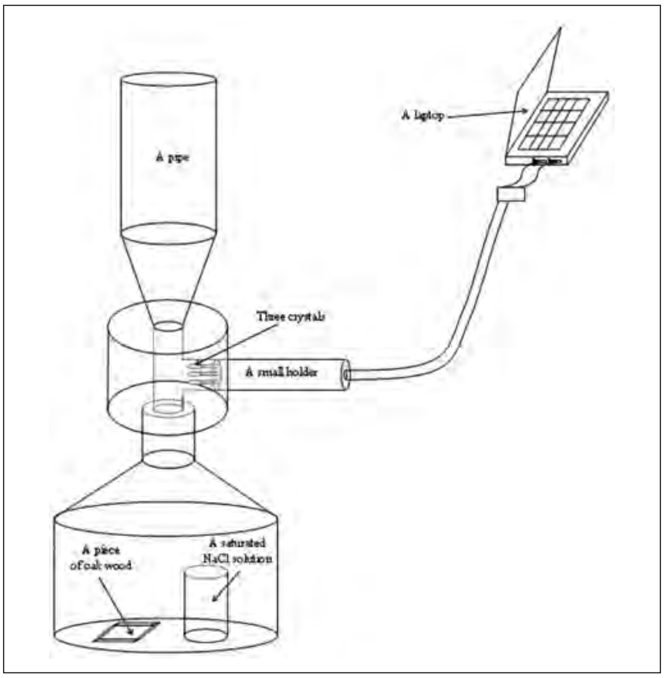

Figure 5. Schematic outline of experimental set-up which shows the position of the crystals in relation to the air stream through the organ pipe.

The crystal readings for this test are shown in Figure 6. Low values were recorded for the first few days at low concentrations of ethanoic acid, indicated by the colour of acid indicator (A-D) paper strips.

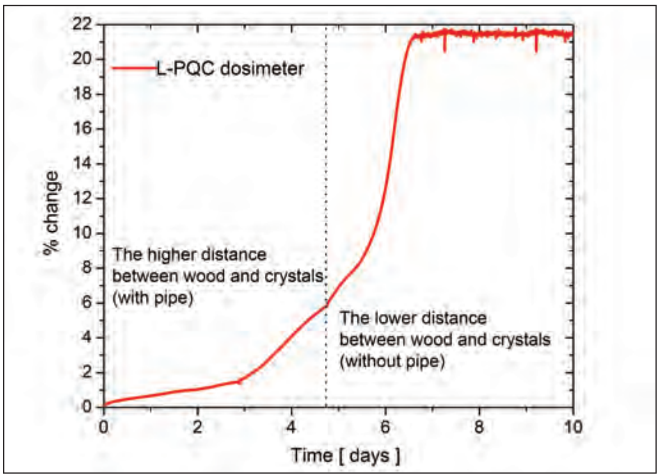

Figure 6. Lead PQC crystal response expressed as change (%) vs. time (days) of exposure to varying conditions caused by differences in distances between crystals and oak wood and then difference in RH values (increases to 60-68%).

After five days, the crystals in the holder were re-positioned closer to the wood (see Figure 7). There was a noticeable change in the colour of the A-D strips (blue-green, ethanoic acid concentration >1250 µg/m^3) and the crystal response increased (see Figure 6). On the sixth day, the RH in the chamber was increased by introducing a saturated salt solution into the chamber. This had a further effect of increasing the change (%) in the crystal coating (see Figure 6) and it reached a maximum value of (21%), which corresponds to the saturation response of the dosimeter for these conditions and period of exposure. The rate of change in the crystal response increased with proximity to an emission source (oak wood), increased concentration of ethanoic acid, and an increase in RH.

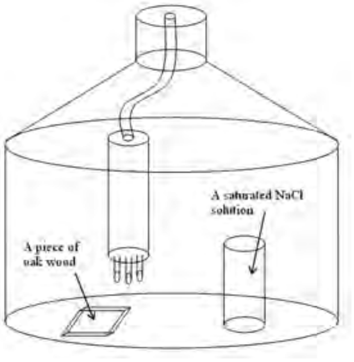

Figure 7. Schematic outline of experimental set-up which shows the closer position of the crystals to the oak wood. After 5 days the holder with crystals was transferred from its position in the organ pipe into the glass vessel.

Exposure of the same prototype took place in St. Botolph Aldgate, London, and in Oergryte New Church, Gothenburg, Sweden. The organ in St. Botolph dates from 1704 and contains a considerable proportion of the original materials. Recent restoration work was performed to recapture its original appearance and sound. In St. Botolph, three different locations were tested; in the windchest using crystals as passive samplers (Bergsten 2010), within a Haut boy pipe standing on the toeboard (pine) in the upper swell box made of pine (recently replaced during restoration) (see Figure 3), and in a Trumpet pipe at the back of the great soundboard. Here, the wooden parts were made of old oak wood. The organ in Oergryte New Church was completed in 2000 in the style of 17th century north German baroque. It was constructed in accordance with historical traditions and materials, and consequently the wooden parts were made of oak. In Oergryte, measurement was made within a Principal pipe standing on the toeboard of the windchest (oak) belonging to the Hauptwerk.

Figures 8 and 9 show the results of monitoring in the first and second locations in St. Botolph. The rate of change in the first 10 days was 4% and 8%, respectively, and the overall change for the period of testing was 35% and 10%, respectively. Location 1, which has the emissions from the recently restored toeboard (pine), showed more damage to the lead coating than location 2 where the pipe was standing on the old oak. Some additional contribution may have also occurred on account of differences in exposure periods. The exposure in location 1 was from February 7, 2008, to April 24, 2008, and for location 2 was from November 4, 2008, to January 8, 2009. The RH and T values shown on the graphs were recorded using Hanwell humbugs and these were placed close to the pipes being monitored. On the whole, values for RH were below 50%, particularly in winter as the church was heated from October to March.

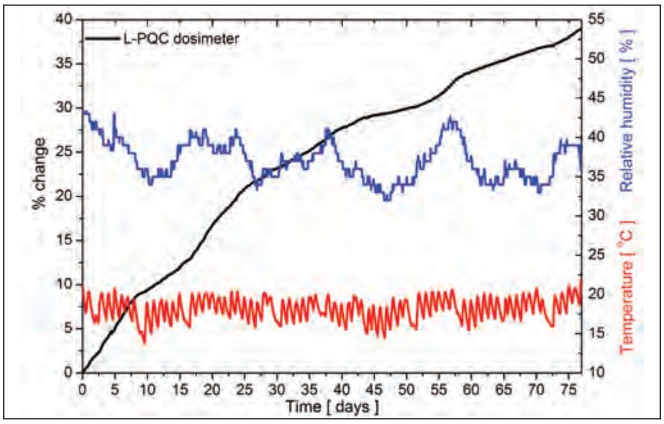

Figure 8. Lead PQC crystal response expressed as change (%) vs. time (days) for exposure in St. Botolph within a Haut boy pipe standing on the toeboard (pine) in the upper swell box made of pine (recently replaced during restoration).

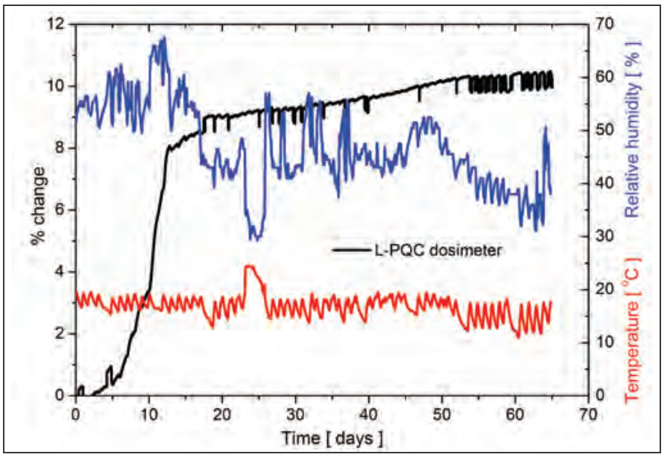

Figure 9. Lead PQC crystal response expressed as change (%) vs. time (days) for exposure in St. Botolph in a Trumpet pipe at the back of the great soundboard. Here the wooden parts were made of old oak wood.

The raised values for RH shown in Figure 9 at the start of the monitoring period were due to the humidifier that was placed in the organ to protect the newly restored wood during the heating periods. The change in location 2 for the first 20 days was about half that observed in location 1, and in the accelerated ageing study (see Figure 2) where the lead coated crystal was exposed to 2,275 µg/m^3 (910ppb) ethanoic acid. Ethanoic acid values measured in location 2 using passive samplers were also lower (511.7 µg/m^3). Changes in the crystals in the windchest were of the order of 20%-30% for exposures of up to 30 days (Bergsten 2010), and comparable to location 1 and the accelerated ageing test (see Figure 2).

Figure 10 shows the response in Oergryte New Church. The overall change differed from that of St. Botolph in location 2 but was comparable to exposure in location 1, and that obtained in the accelerated ageing tests (see Figure 2). Measured levels of ethanoic acid in Oergryte New Church were between 2,000-2,250 µg/m^3 and RH for the period of exposure, December 18, 2008, to January 15, 2009, was in the region of 65%.

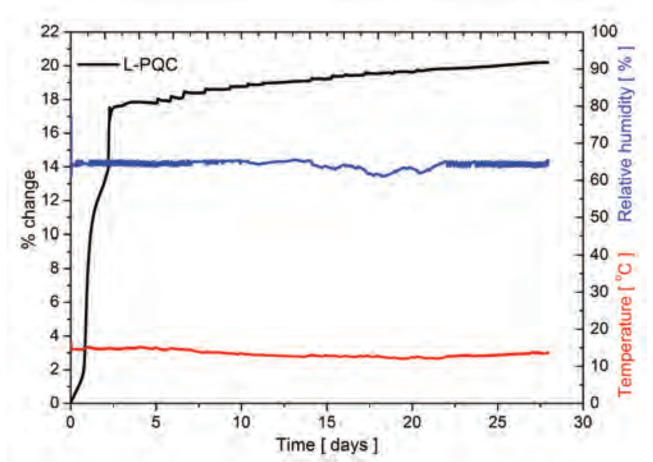

Figure 10. Lead PQC crystal response expressed as change (%) vs. time (days) for exposure in Oergryte New Church.

The rate of change was significantly different from that in location 1 in St. Botolph. The main change in Oergryte (18%) occurred over two days, whereas it took about 20 days to reach a similar value in location 1 at St. Botolph. This could be attributed to the higher levels of ethanoic acid and RH (c.65%) compared to that in St. Botolph (between 35%-40%).

The holders within the organ pipes were still operated using mains power. In PROPAINT, the second stage of the development of the dosimeter electronics occurred with further miniaturisation of the electronic components, and holder and development of a stand-alone battery operated three channel logger with usb connection to a PC. The PC was needed only for downloading the stored measurement values from the logger.

Exposures in PROPAINT were made by clamping lead coated crystals between steel plates as the space was more restricted than in the windchest in St. Botolph. Following this exposure, the continuous system (battery operated) was used within some of the previously tested frames. Values for the lead-PQC dosimeters were found to be higher inside mc-frames than in the rooms for all locations tested, and were consistent with measured levels of organic acids in frames and rooms, in particular ethanoic acid, (Grøntoft et al. 2010). For example, measurements of ethanoic acid were found to exceed 1000µg/m^3 in some frames, and this was significantly higher than in the rooms.

Conclusions

The work in the two projects has demonstrated that lead based dosimetry using PQC crystals has identified locations of different response within St. Botolph where fresh pine wood was present, and also demonstrated that conditions in Oergryte New Church were more corrosive than in St. Botolph as a result of higher ethanoic acid and RH values. The importance of continuous monitoring provides information on the rate of change as well as overall change, and this provides additional information for assessment of overall corrosivity. For the painting frames, the presence of elevated levels of organic acids may be a cause of concern, and further work is in progress to consider methods for reducing these levels and also for testing the effect of such exposure on artists' varnishes.

Acknowledgements

The authors acknowledge the support of two EC grants, SENSORGAN (contract 022695) and PROPAINT (FP6 SSPI no 044254) for development and testing of the dosimeters. Thanks are due to Professor S.Bending and Peter Curran, Department. of Physics, University of Bath, UK, for lead deposition onto the PQC crystals; to Martin Goetze and Dominic Gwynn, restorers of historic organs, for their assistance in setting up dosimeters at St.Botolph (http://www.goetzegwynn.co.uk/); to NILU (Norwegian Institute for Air Research) for measurement of ethanoic acid values in the organ in St.Botolph using diffusive passive samplers; and to the partners and end-users in SENSORGAN and PROPAINT.

Materials

A-D strips acid indicator strips used for atmospheric acidity
(http://www.cwaller.de/ accessed 6/02/2010)

Long Life for Art Christoph Waller
Hauptstrasse 47. D-79356 Eichstetten Germany
http://www.cwaller.de/

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Q & A SESSION

Carla Martini: This is not actually a question, just a comment: thank you David for your interesting presentation. I was very glad to see the results of SENSORGAN because we at the University of Bologna we are one of the partners of COLLAPSE so it was very good to see the follow up. COLLAPSE showed that the higher the tin content the higher the corrosion resistance. So it showed, as you said, that lead is a very good sensor for corrosion of – for sensing the environment inside the pipes. In addition if you consider that COLLAPSE showed that one of the best conservation strategies is to change the environment. In preventive conservation sensors are very important because if you know the microclimate then you can preserve the pipes. So, thank you.

Ian MacLeod: David, I wondered whether or not you had looked at plotting the response of the sensors against the absolute humidity? Because when you use the actual vapor pressure of water, it gets all the variations of temperature and relative humidity back into a constant.

David Thickett: I don't think Marianne [Odlyha] has. There are two parts to this: there is the off-gassing from the wood, which has a function to do with temperature and relative humidity, and then there is the response of the lead. And the response of the lead is predominantly driven by just the relative humidity. But I'll certainly pass it on to Marianne. I don't believe she has, but she has thousands of these charts done in different ways.

Adam Jenkins: I just had a question about the response of the piezoelectric crystals, since you're sputtering lead onto the surface, does that response change with time and if so, what is the expected life of one of these sensors?

David Thickett: That's a good question. It depends how you store the crystal. We normally give them about a week to develop an oxide layer on the surface. And that actual layer will determine how the crystal responds – it's just the same with objects. She's done a lot of work with lead roofing and they found that sometimes you leave the lead out, and it is very resistant because it's got a good thick oxide layer and sometimes you put it on and it corrodes almost straight away in exactly the same conditions. But yes, it depends on how you store the crystals really. Essentially with these crystals, they'll measure up to a certain point. Once you have so much mass on the surface, that you'll not be able to pick them up, but with very careful storage you should be able to get to a point where you can store them for about a year. The commercial ones, provided by Purafer, which is a slightly different crystal – they're silver-based – in their stories, they reckon they'll last for about 3 or 4 years, provided with an absorbent. Naturally how long it lasts in the field depends on how corrosive your environment is.

Emma Schmuecker: It's really interesting research and development of analysis that this project's made, particularly looking at the lead organ pipes. Is there any kind of outreach or education programs you are going to be looking to do?

David Thickett: Yes, they've run several workshops for organ builders particularly, because this is still a living craft. I know they run workshops really all over the world – I think they have about 6, I know one was in the Americas, but they run a number of workshops as part of the outreach. I don't know how much stuff is actually on the website but the web address is there. But all the European projects now have to have a dissemination phase and a plan.

Emma Schmuecker: That's a good start, thank you.

Aaron Shugar: Great presentation. I'm really intrigued by this as a technique to maybe replace Oddy testing. Have you investigated that at all and what are the potential problems you've come across?

David Thickett: We haven't as such. You're right, we've certainly thought about it. The area where we've investigated it has been more to do with organic materials. Because you can put lots of coatings on here, Marianne does one with mastic. We've actually ran Oddy tests with coated crystals with mastic to look at the effect on those things. They certainly would replace it and of course you've got a quantification, which helps us immensely. The problem is – you can buy commercial systems - the sputtering is the difficult bit. The crystals are sort of £15 pounds each before the sputtering – commercial crystals when they're pre-coated, they are £200 each. That's $300 – so it would be quite an expensive thing to do and a lot of materials I suspect would actually saturate the crystal quite quickly.

Karen Stemann Peterson: I was aware that at the Metals conference in 2007, one of the suggestions for the organ pipes was ventilating them – taking in fresh air. That really would help. So it's nice when they also turn up with very easy solutions to get it a tiny bit better. Of course with the lead content, just some percent tin really, the problem is not very large when you get some tin into the pipes.

David Thickett: Yes, absolutely. I showed you that chart of the acetic acid against the air exchange rate. The thing is to get enough ventilation, if you've got a lot of wood in an enclosure. But that's certainly a good thing and of course they get a little bit of ventilation when they are played, but they are often only played once a week or something like that. But ventilation is a good strategy – just ensure that you've got enough. The other thing we did with the tin content is (we quantified it and) I spent a lot of time inside that organ with a portable XRF doing every pipe to get the tin:lead ratios.

PATINAS, POWDERS, AND PRIMERS: SAFETY WITH A MUSEUM COLLECTION OF SMALL ARMS AMMUNITION

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Abstract

Examination of a collection of unfired small arms ammunition from two late 19th century sites in southern Arizona has brought to light safety concerns involved with handling, deactivation, and storing items of this nature. These objects contain black powder (gunpowder) — potassium nitrate, charcoal, and sulfur — with mixed mercury fulminate and potassium chlorate primers. Mercury fulminate is highly explosive, and it poses potential safety concerns when exhibition, research access to collections, preservation treatments, and long-term storage schemes are considered. Non-destructive methods of analysis were used to screen for the presence of mercury and to assign the bullet classifications. Standard thermodynamics calculations, as well as comparison to empirical data reported in explosives and engineering literature, have allowed us to confirm the chemical form and determine the likelihood of stability for all hazardous compounds. This study contributes to the conservation literature by offering a protocol for identifying risk and determining deactivation treatment and storage plans for similar artifacts in museum collections.

Keywords: museum safety, firearms, ammunition, bullets, historic collections, gunpowder, mercury fulminate, military archaeology

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Introduction

The information in this paper is intended to be a reference for understanding the dangers of museum collections of small arms ammunition and for devising treatment plans. The authors hold no responsibility for any mishandling or decisions made based on the information included here, and we urge caution on the part of the handler where unexploded ammunition is involved.

In museum collections around the world, many objects pose human safety hazards. The literature is replete with guidelines for handling poison tipped darts, fluid collections, and pesticide-treated traditional Native American head dresses. However, most of the information regarding historic or retired firearms addresses general care and avoids the topic of unexploded ammunition (White 1995, Storch 1998, Arnold 2006, Gerald R. Ford Conservation Center 2007, American Historical Foundation n.d.). This is a concern for curators and managers of archaeological collections from historic military forts as well as from sites located amidst modern battle fields because, 'for the lay person, it is unclear whether a piece of unexploded ammunition can be made safe, or whether it has to be exploded, and if so, whether it can be moved off location' (Spennemann 1998).

A Safety Protocol

When assessing the hazards of historic military artifacts in particular, it becomes necessary to consider the artifacts' history, the chemical compounds originally present in the objects, and all possible corrosion and decomposition products that may have formed over the years since abandonment. In many historic excavations, like the Steamboat *Bertrand* (North of Omaha, NE), ammunition presents few problems because the flammable and explosive components no longer exist (Petsche 1974). In extreme cases of active or unexploded ammunition, museums may be faced with only two alternatives: deactivate or destroy the ammunition. In this paper we agree with the Society for Historical Archaeology's preservation model that deactivation of historic ammunition is preferred over discarding it (SHA 2007).

The focus of this paper is to assess human risk and weigh the costs of deactivation for a collection of historic small arms ammunition. This collection includes four unfired cartridges excavated in the 1960s from Camp Grant near Phoenix, Arizona, (occupied 1860-1872) and two excavated from the Gila Bend Stage Station (1858-1879) at Gila Bend, Arizona. These artifacts were buried for approximately 80 years with exposure to hot summers, mild winters (without prolonged freezing) and seasonal monsoon rains and flooding. Along with the six cartridges, there are three firearms curated at the Arizona State Museum (ASM), University of Arizona in Tucson. It is possible for historic firearms to contain unfired cartridges in their chambers, but the conservation literature already contains suitable handling protocols for firearms. Therefore, the current paper only addresses safety risks associated with small arms ammunition found separated from firearms.

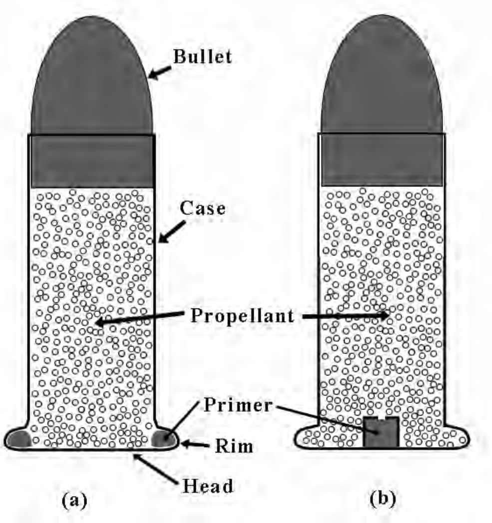

Figure 1. Schematic cross-sections of (a) a rim-fire cartridge and (b) a center-fire cartridge showing the location of the bullet and case. The propellant fills the case, and the primer is pressed into the rim (a) or into the small pocket at the center of the head of the case.

Anatomy of a cartridge

The six cartridges included in this study date to the 1860s and 1870s, and the discussion here is limited to the small arms ammunition of this era. What is often referred to as an unfired bullet is more accurately called a cartridge. The cartridge includes the projectile, propellant, primer, and casing as shown in Figure 1. Since the late 19th century, most projectiles and cartridge casings have been made of metal. The primer and propellant are powdered chemical mixtures, and their potential instability makes these more dangerous components of unfired ammunition. The primer is designed to create a flame or explosion that will ignite the propellant. As the propellant burns it rapidly transforms from a solid to a gas. This reaction results in immediate volume expansion causing enough pressure to force the projectile out of the firearm. The propellant and primer are categorized as explosive — not merely flammable (see OSHA regulations regarding Class A, B, and C explosives). Furthermore, different chemicals have been used over the centuries for the primer and propellant, making it necessary to carefully identify the composition of these substances so that all safety measures can be followed. In every unfired cartridge, the largest safety hazard comes from the primer. The propellant will ignite only if exposed to flame, but depending on the composition, the primer may explode from heat, friction, violent jostling, and even static discharge.

Risk and Cultural Value

Common wisdom regarding live ammunition in museum collections advises that these cartridges be handled with care, not be dropped, and 'if too badly corroded… they should be buried in a safe place or dumped at sea' or 'removed by men experienced in this field' (Burns 1941). Museum practice regarding firearms and ammunition still relies on such vague and out-dated recommendations, which are hardly sufficient when considering the range of storage, handling, treatment, and study environments to which these objects may be exposed. Army manuals and academic journals discussing explosive chemicals offer better ways of handling ammunition, but these are not geared toward antiques, archaeological items, or museum collections. Live cartridges are artifacts with special problems, as they present the museum with significant liability risks in addition to being valuable cultural items. Risk assessments of these potentially explosive objects are often made by law enforcement personnel, and these assessments generally lead to removal and destruction of the objects in question. For example, explosive museum collections are no longer allowed on the University of Arizona campus, and campus police suggested immediate disposal (by exploding all objects) when consulted regarding the collection of the six unfired cartridges discussed in this paper. Basic rules and guidelines for historic firearms and ordinances, such as those developed by the Ohio Historical Society, are particularly useful (Giglierano 1991), but clearly, more in-depth discussion is warranted when considering deactivation and conservation treatment.

In every treatment plan, it is important for the conservator to consider the value of the object in question, and archaeological objects are important for the vast range of information they hold. Stylistic, contextual, chemical, and microstructural analyses can be performed to glean useful information about an object's life history and cultural significance, in addition to assessing stability and informing treatment options. This makes it more difficult to weigh the value of preserving all original components against the value of style, aesthetics, and general stability of the objects. Ethically, it is always important to consider the information that may be lost forever if any particular treatment scheme is selected.

In the case of unfired small arms ammunition, the choice to treat the objects becomes more complicated because the risk of human safety hazards is introduced, and external restrictions and guidelines can be imposed on museum collections by local and state law enforcement. The choice turns out to be between destruction of the object (usually by the local law enforcement) and deactivation of the object. Most museums would choose to deactivate the object in order to keep the historic item in the museum collection.

In some circumstances, a museum may not have to face the 'destroy or deactivate' dilemma, but they must still decide whether to maintain a risk or deactivate the ammunition. Certainly, it is possible to store uncompromised ammunition safely, but with ammunition facing heavy corrosion, cracked cases and possibly unknown environmental exposures — such as that recovered from archaeological excavations — it is important to consider additional risks associated with storing the ammunition. One can argue that the overall value of the compromised ammunition is equal to the uncompromised objects, but the authors of this paper feel that the value of the object cannot be placed above the safety of museum workers and patrons. Safety training for the proper handling of dangerous objects is the best way to mitigate risk associated with collections, but museums are frequented by untrained personnel (or personnel trained outside of the museum's jurisdiction) who interact with objects or their storage containers. Such personnel include interns, student workers, visiting scholars, and janitorial staff. Clearly it is better to minimize a safety hazard rather than rely on safe handling of explosive materials alone. Furthermore, there is not always a safe way to physically identify that a cartridge has been deactivated if it is still intact. If it has been dismantled, it would be clear that it is deactivated, and a deactivated object is better than a destroyed one.

Identifying Risk and Considerations for Deactivation Prior to Conservation Treatment

As with determining treatment schemes, risk assessment for an individual object requires specific knowledge of all chemical compounds and alloys present in the ammunition. For this collection, we have considered the historic context and stylistic typology of the cartridges. The history of ammunition is well documented — allowing us to estimate the compositions of each component of the cartridges (Hamilton 1916, Army 1920, Lewis 1956, Barnes 1965, 2006, Brede et al. 1996). These estimates have been confirmed using non-destructive analyses. Non-destructive methods are preferred so as to not accidentally ignite the primer or propellant by scraping, drilling, or cutting into the samples. Until the threat of explosion is either deactivated or deemed inert, minimal jostling and handling of the objects is recommended.

During the Civil War and post-war years (1860-1880), both rim-fire (see Figure 1a) and center-fire (see Figure 1b) cartridges were common (Driel 2004). As the names suggest, rim-fired cartridges contain a hollow rim filled with the priming compound, and center-fire cartridges hold the primer in the center of the casing head. In both styles, the pocket filled with primer is compressed by the firearms' firing pin, thereby crushing and igniting the priming compound. The six cartridges included in this study are all of the rim-fire and center-fire type, and they have been identified based on their head stamps, caliber of bullet, and general dimensions. The details for each cartridge in this study are reported in Table 1, and the cartridges are shown in Figure 2.

Figure 2. Cartridges included in this study with ASM Catalogue numbers indicated (all images to scale). Arrows on A-31, 558 and A-3, 553 show indentations in the metal caused by tools used to grip the casings as the cartridges were reloaded.

Non-destructive investigation has included low-powered stereo-zoom light microscopy, spot-testing, hand-held X-ray fluorescence (XRF) using a Bruker Tracer III-V, and radiography using a Faxitron X-ray cabinet. The head stamps present on some of the cartridges were examined with light microscopy, which led to manufacturer identification and precise dating. Radiographs obtained with the Faxitron (Figure 3) confirmed the presence and position of propellant and priming compounds. XRF analyses allowed precise identification of the elements

ASM Catalogue No.	Provenience	Bullet diameter (in)	Case length (in)	Cartridge length (in)	Headstamp and notes	Cartridge Identification	Reference	Dates of use
A-31,549-x-1	Camp Grant, AZ Structure B, Rm 2, Floor	0.504	1.223	1.654	F.V.V.&Co. (Fitch van Vechten & Co.)	50 cal (rim-fire) (same as A-31,558)	Barnes 2006:161	During and after Civil War
A-31,553	Camp Grant, AZ	0.506	1.836	2.280	None	50-70 Musket (50 Govt.) (center-fire)	Barnes 2006:161	1866-1873 (US military)
A-31,555	Camp Grant, AZ; Structure A, Floor	0.467	1.108	1.619	none	45 Colt or 45 Colt government (center-fire)	Barnes 2006: 311, 335	Introduced in 1873
A-31,558	Camp Grant, AZ Structure C, Floor	0.510	1.215	1.562	S.A.W. (Sage Ammunition Works)	50 cal (rim-fire)	Barnes 2006:161	During and after Civil War
A-33,189-x-12	Gila Bend Stage Station, AZ; Stratum 2, fill	0.369	0.797	1.392	U.M.F.C. (Union Metallic Cartridge Co.)	38 S&W (center-fire)	Barnes 2006:301	Introduced in 1877
A-33,189-x-7	Gila Bend Stage Station, AZ; Stratum 3, basement	0.377	0.771	1.217	None	38 Short (rim-fire)	Barnes 2006:483	1866 - 1940

Table 1. Cartridges included in this study

present in the cartridges. Because portable XRF is not yet a quantitative method on inhomogeneous materials, these compositions are reported in Table 2 as element lists rather than quantitative results. The results and implications of these investigations are summarized below:

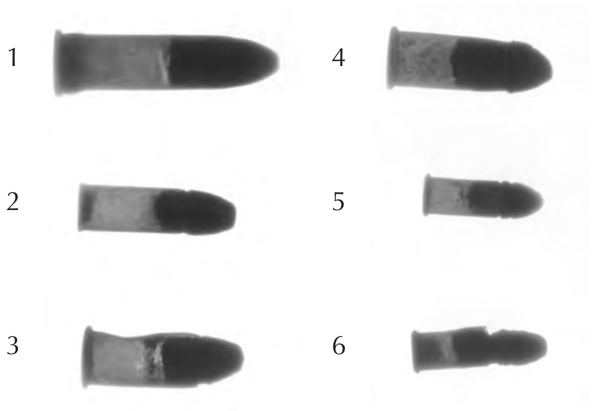

Figure 3. X-ray images of the cartridges in this study. (1) A-31,553, (2) A-31,555, (3) A-31,558, (4) A-31,549-x-1, (5) A-33,189-x-7, (6) A-33,189-x-12. Notice the darkened head for (1), (2), and (6), these are the center-fire cartridges. The rim-fire cartridges do not contain a cup filled with mercury fulminate primer; rather, the primer is spread around the rim. The granules of propellant are also visible for many of the cartridges.

ASM Catalogue No.	Location of analysis	Major (and minor) elements present
A-31,549-x-1	Bullet	Pb, (Sn, Cu, Ni, Fe, Hg)
	Casing (side)	Cu, Zn, Ca, (Pb, Fe)
	Casing (head)	Cu, Zn, Ca, (Fe, Ni, Pb, Sn)
A-31,553	Bullet	Pb, S, (Cu, Ni, Fe, Hg, Sn)
	Casing (side)	Cu, Zn, Ca, (Fe, Pb, Sn)
	Casing (head)	Cu, Zn, (Fe, Pb, Ca)
A-31,555	Bullet	Pb, S (Cu, Ni, Fe, Sn, Hg)
	Casing (side)	Cu, Zn, (Fe, Pb, Ca)
	Casing (head)	Cu, Zn, (Br, Fe, Pb, Ca)
A-31,558	Bullet	Pb, S, (Hg, Sn, Cu, Ni, Fe)
	Casing (side)	Cu, Zn, (Fe, Pb, Ca)
	Casing (head)	Cu, Zn, (Pb, Hg, Fe, Ni, Ca)
A-33,189-x-7	Bullet	Pb, (Sn, Cu, Zn, Ni, Fe, Hg)
	Casing (side)	Cu, Zn, (Fe, Pb)
	Casing (head)	Cu, Zn, (Fe, Pb)
A-33,189-x-12	Bullet	Pb, Sn, (Cu, Ni, Fe)
	Casing (side)	Cu, Zn, (Fe, Pb)
	Casing (head)	Cu, Zn, (Fe, Pb)

Table 2. Alloy compositions determined by XRF analysis

(1) Bullets:

During the 1850s and later, bullets were made of either pure lead or with small additions of antimony and tin to increase hardness (Hamilton 1916). The radiographs (see Figure 3) show that all of the bullets in this study are solid, and Table 2 shows that the bullets consist of a lead-tin alloy. Antimony was not detected in any of the bullets. With these results in mind, one should include corrosion products of both tin and lead when considering chemical and material interactions.

(2) Casing:

In the late 19th century, cartridge casings were made of brass (Cu-30wt%Zn). The casings in this collection all contained primarily copper and zinc, but with different peak ratios and often accompanied by iron and lead. Lead is typically added to brass to increase its machinability and iron additions make brass more wear resistant. It is entirely reasonable that these elements would be added during manufacture.

Although the early 19th century saw production of cartridges in small scale batch operations with little standardization, by 1850 these cartridges were mass-produced in factories using punches and dies (Hamilton 1916). For both rim-fire and center-fire cartridges, the process began with small discs of brass that were forced through a series of dies to gradually shape the casing (see Figure 4). This method of manufacture results in uniform products, but the metal has been heavily worked and is highly stressed. This poses concerns for treatment since embrittlement and stress-corrosion cracking of the cartridge case are both common.

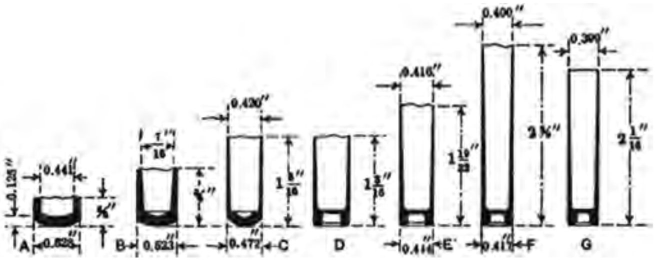

Figure 4. Casing manufacturing method where the brass metal goes through a series of dies to gradually thin the metal and elongate the case (Hamilton 1916).

Cartridges were also commonly reloaded after firing. Tooling marks on some of the cartridges (see arrows on Figure 2) indicate they were reloaded. Because reloading does not always leave visible marks on the casing, it is difficult to determine whether all of the cartridges in this collection were previously fired and how many times each one was reloaded. In any case, the fact that reloading was common means that even these unfired cartridges are potentially subject to the embrittlement and corrosion problems associated with fired cartridge casings as discussed below.

(3) Propellant:

During the 20-year period in question (1860-1880), small arms ammunition used black powder (gunpowder) as the propellant. The composition of this powder changed over time, but during the 19th century the composition followed the formula 75% potassium nitrate, 15% charcoal, and 10% sulfur (Hamilton 1916, Wallace 2008). Each ingredient was carefully prepared and purified before mixing together into a paste that was then pressed into cake form, and ultimately ground into uniform-sized granules (Hamilton 1916). Smokeless powder, or 'nitro powders did not replace black powder until the 1890's' (Barnes 1965).

(4) Primer:

Primers at the second half of the 19th century were mixtures containing mercury fulminate ($Hg(OCN)_2$), potassium chlorate ($KClO_3$), antimony trisulfide (Sb_2S_3), and glass or quartz powder (SiO_2), with shellac or gum Arabic as binders (Hamilton 1916, Barnes 1965, Brede et al. 1996, Drury 1999). The exact ratio of these components is not clear. One source reports a ratio of 3:3:2 of $Hg(OCN)_2$:$KClO_3$:Sb_2S_3 (Hamilton 1916), and another reports 14% $KClO_3$, 21% Sb_2S_3, 28% $Hg(OCN)_2$, 35% SiO_2, 2% shellac (Fedoroff and Sheffeild 1974), presumably by weight. By 1898, the U.S. Ordnance Department switched to pure potassium chlorate primers (Barnes 1965).

Mercury in the fulminate primers can form amalgams with the cartridge casing, and when mercury fulminate primers are fired, free mercury is released to coat the brass case, interior of the gun barrel, and exterior of the fired bullet.

Mercury was detected on many of the bullets, but not at the head of the cartridge casings, where the primers are located (see Table 2). The absence of mercury at the cartridge heads is not surprising since the primer is contained within the casing behind 0.1mm of brass. This thickness is well above the penetration depth of X-rays in the energy range of 40keV (the maximum energy of the incident x-rays used for these analyses). Mercury was detected on many of the bullets in these cartridges and this reinforces the conclusion that mercury fulminate was present. A test for volatile mercury was also performed according to the protocol outlined in Odegaard and Sadongei (2005), and this returned negative results for all cartridges, indicating that the mercury was not actively volatilizing.

Predicting stability through calculations

Most discussions of mercury fulminate primers mention that long-term stability is only possible when stored in distilled water below 50°C, but these discussions provide little information regarding how instability occurs and what the resulting compounds are. Using the compositional information presented above, we have considered a range of intermediate products and dozens of possible chemical reactions that would neutralize the priming compound and gun powder. A summary of the compounds initially present, introduced through burial, and present as corrosion and degradation products are listed in Table 3. For each chemical reaction, the free energy of formation (Gibbs free energy, G) has been calculated to predict the likelihood of the reaction to proceed at room temperature using the following equation:

$$\Delta G^o_{reaction} = \Sigma\Delta G^o_{products} - \Sigma\Delta G^o_{reactants}$$

When ΔG is negative, the reaction is considered to be spontaneous and is favorable; when ΔG is positive, the reaction is unfavorable. Room temperature (25°C) is used as the reference for these reactions primarily due to the availability of thermochemical data. The most probable reactions for this collection of compounds are listed in Table 4 along with the corresponding energy of formation. Sources for standard state thermochemical data for these reactions are reported in Table 4. Helpful thermochemical data is reproduced in Table 5 for future reference.

Initially present	Introduced by the burial environment	Some degradation and corrosion products
$Hg(OCN)_2$	H_2O	PbO
$KClO_3$	O_2 (g)	$CuCl$
KNO_3	NO_3^-	$Cu_2(OH)_3Cl$
Pb-Sn alloy	C	Cu_2Cl_2
Cu-30wt%Zn alloy	SO_4^-	$CuCl_2$
C	Cl^-	$Cu_4SO_4(OH)_6$
S	CO (g)	$Cu_2CO_3(OH)_2$
Si	CO_2 (g)	HCl
Sb_2S_3		CuO
Gum Arabic or		Cu_2O
Shellac		HgCl (g)
Hg		$HgCl_2$
		Hg_2Cl_2
		$HgNO_3$
		$HgSO_4$
		Hg-Cu-Zn amalgam
		HCN (g)
		KCN

Table 3. Compounds present in cartridges.

Reaction	ΔG^o (kJ/mol)
$Hg(OCN)_2 + S + 2H_2O \rightarrow HgSO_4 + 2HCN + H_2$	-588.979
$Hg(OCN)_2 + 2HCl \rightarrow HgCl_2 + H_2O + CO + N_2$	-785.479
$2Hg(OCN)_2 + 4KClO_3 + H_2O \rightarrow Hg_2Cl_2 + 2HCl + 4KNO_3 + 4CO + ½O_2$	-964.684
$2Hg(OCN)_2 + 4KClO_3 + H_2O \rightarrow Hg_2Cl_2 + 2HCl + 4KNO_3 + 3CO + CO_2$	-1221.864
$Hg(OCN)_2 + 2Cu_2(OH)_3Cl + 3/2O_2 \rightarrow HgCl_2 + 2Cu_2CO_3(OH)_2 + N_2 + H_2O$	-1366.626

Table 4. Probable reactions with mercury fulminate.

Compound	ΔG^{o} (kJ/mol)	Reference
CN_2	574.246	Stull and Prophet 1971
CO_2	-394.360	Barin 1995:404
CO	-137.180	Barin 1995:403
$CuCl_2$	-205.853	Scott 2002:136
CuO	-127.194	Scott 2002:136
$Cu_2CO_3(OH)_2$	-902.489	Scott 2002:136
$Cu_2(OH)_3Cl$	-566.095	Scott 2002:136
HCN	124.708	Stull and Prophet 1971
HCl	-22.770	Stull and Prophet 1971
H_2O	-306.675	Chase 1998
$HgCl_2$	-184.022	Chase 1986:803
$HgNO_3$	-122.104	Carson and Wilmshurst 1971:254
$Hg(OCN)_2$	272.637	Akhavan 2004:28
$HgSO_4$	-802.938	Binnewies and Milke 2002:592
Hg_2Cl_2	-210.485	Chase 1986:807
KCN (sol)	-101.960	Stull and Prophet 1971
$KClO_3$	-431.744	Binnewies and Milke 2002:320
KNO_3	-394.705	Barin 1995:906

Table 5. Thermochemical data.

These calculations suggest that much of the mercury fulminate, potassium chlorate, and potassium nitrate could have converted into mercury salts, hydrochloric acid, and copper carbonates. However, we can ensure the decomposition of the flammable and explosive compounds by taking additional measures reported by modern research in the area of explosives and high energy chemistry.

Decomposition of Primers and Propellants

Mercury fulminate primers are likely to behave in the following ways:

(1) Mercury Salts: With the high driving force (very negative ΔG value) calculated for the reactions shown in Table 4, mercury fulminate *in contact* with corrosion products and potassium chlorate will convert into non-explosive mercury salts. Mercury fulminate that is not in contact with these compounds cannot convert into salts.

(2) Amalgams: Mercury fulminate does not react with metals, but most mercury fulminate primers contain as much as 1% free mercury — forming due to exposure to light and heat. Free mercury readily forms amalgams with the brass casings causing embrittlement (Barnard 1973, Ben-Bassat and Azrad 1978, Army 1984, Barnes 1965). This reaction proceeds more rapidly with the presence of moisture (AMCP 1971, Fedoroff and Sheffield 1974), and mercury monolayers are stable on copper surfaces even at room temperature (Rosenborough et al. 2006).

(3) Oxides: Mercury fulminate has been shown to decompose into mercury carbonate oxide ($HgCO_3 \cdot 2HgO$) and CO_2 when exposed to moderate temperatures (over 90^{o}C) for extended periods and when exposed to specific doses of ionizing radiation (^{60}Co γ-radiation, at 1.2MeV and 1.3MeV) (Zhulanova et al. 2001, Akhavan 2004). Neither of these conditions were likely with this collection, and there is no evidence that mercury fulminate is affected by X-ray radiation used in XRF and radiography, which has much lower energy (in the keV range) compared to gamma radiation.

(4) Detonation: Mercury fulminate will detonate when exposed to flame, friction, temperatures above 170^{o}C (Akhavan 2004), and static discharge of 0.025 to 0.07 J (Army 1984).

(5) Desensitization: Mercury fulminate can be desensitized (but not permanently deactivated) by storing in distilled water.

(6) Degradation: Storage of mercury fulminate at 50^{o}C for 11 months or 80^{o}C for 24 hours can cause it to deteriorate to 92% purity (Army 1984). When the purity of mercury fulminate is reduced to 92% or less, 'the initiating efficiency is practically destroyed, although the material will explode when ignited' (Fedoroff and Sheffield 1974). Even though degraded mercury fulminate is not likely to be ignited by friction, exposure to flame or static discharge can still cause small amounts of remaining primer to explode. The primer is not safe just because it is partially degraded.

(7) Deactivation: The only way to completely render mercury fulminate safe is to chemically deactivate it. $Hg(OCN)_2$ will decompose when combined with 'at least 10 times its weight of 20% sodium thiosulfate', which will also cause the evolution of some cyanogen gas (AMCP 1971). When mixed with sodium thiosulfate ($Na_2S_2O_3$) in water, the following two step reaction occurs (Army 1984, Hulst 1969):

$$Hg(ONC)_2 + 2Na_2S_2O_3 + H_2O \rightarrow HgS_4O_6 + 2NaOH + NaCN + NaNCO$$

$$\rightarrow HgSO_4 + Na_2SO_4 + 2NaSCN + H_2O$$

The threat of explosion is low for historic and archaeological ammunition containing mercury fulminate, but a low risk may still be a risk worth neutralizing. This is a decision for the museum and what follows is a protocol for dismantling unfired cartridges should the museum choose to do so.

Conservation treatments

Treatment can be addressed in two parts: deactivation of the human safety hazard, and stabilization of the corrosion and degradation of the cartridge. Only the first part is described here. Handling should include nitrile gloves due the presence of mercury-containing compounds and other irritants.

Mixtures of dry sodium thiosulfate with dry potassium nitrate (as found in gun powder) are explosive. Therefore, as an extra precaution, it is recommended that the first step in conservation treatment is to remove the gunpowder before submerging the cartridge in aqueous sodium thiosulfate. In addition, all sodium thiosulfate solution should be rinsed before allowing the cartridges to dry. For archaeological objects, corrosion of both the bullet and the casing may be such that the bullet has expanded and tightened into the casing making disassembly difficult. The propellant can be removed by dismantling the cartridge or by carefully piercing the cartridge casing to rinse out the gun powder. Dismantling the cartridge and mechanical removal of corrosion (i.e. scraping away) must be performed in a static-free environment using discharge mats, or while the cartridge is submerged in distilled water.

During disassembly it is vital to know whether the cartridge is of the rim-fire or center-fire type. If rim-fire, do not grasp or squeeze the rim of the casing head with tools — this may cause compressive forces on any primer remaining in the rim to result in explosion. The guidelines and methods suggested for dismantling non-archaeological cartridges (Barnes 2006) can cause damage to brittle and corroded cartridges, so it is necessary to avoid traditional aggressive methods.

If gunpowder is rinsed out of the cartridge case, the rinse water should be filtered or evaporated to leave the propellant in a solid form for appropriate disposal. Propellant mixtures varied throughout history, so it may be useful to save the propellant recovered from each cartridge for future investigations. However, state and local laws may require the disposal of this hazardous material.

Once the propellant is removed, the cartridge casing can be soaked in a solution of aqueous 20% sodium thiosulfate in a fume hood to deactivate any remaining mercury fulminate primer. The primer sits along the rim in a rim-fire cartridge and in a center pocket for a center-fire cartridge. In both cases, the primer compound is not completely sealed off from the chamber filled with propellant. The limiting factor is the ability of the solution to diffuse into the priming cup, but once in contact with the primer, the reaction will proceed quickly. Because the reaction produces sulfates it may be possible to monitor the concentration of sulfate in the solution as an indication of the progress of the reaction. However, this has not yet been tested as a reliable indicator. After the casing has been soaked in the sodium thiosulfate solution, rinse with distilled water to remove all traces of the primer. Mercury may still be present as stable solids, and therefore the water should be disposed of as contaminated waste and the cartridge should only be handled with gloves.

Prior to deactivation, the cartridges can be stored in normal conditions for metals (35-60% relative humidity and room temperature). To prevent initiation of the primer, it is important that the cartridges not be heated above 80°C or be exposed to acidic solutions. After deactivation, the cartridges can be handled, treated, and stored according to institutional protocol for handling archaeological metals, keeping in mind the likely presence of Hg-Cu-Zn amalgams.

Conclusions

From our experience and research, we have established a protocol for handling, examination, treatment, and long-term storage of this collection of unfired cartridges. Both radiography and XRF have proven to be useful analytical methods for confirming the presence, position, and composition of the cartridge components. Also, we have determined that treatment with sodium thiosulfate provides the easiest and most effective means for deactivating mercury fulminate. The methods reported here allow the removal of safety hazards while preserving the majority of the cartridge components, and we hope that this research encourages the museum community to continue research in this important area of study.

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Q & A SESSION

Molly Carlson: That was a great paper. I had the misfortune of having to deal with black powder that was from 1710 that had come out of an iron cannon. It was very difficult to find the pathway to get it analyzed and also it's part of the artifact. So how do you go through all that ethically?

Lesley Frame: This was a big discussion for us and yes it is part of the artifact. Unfortunately for us, the University said, you can't keep this. We could have hid it from them I guess but there is a 'no firearms' policy on the campus and even though it was historical, it was an explosive and they said that 'you can keep the object if you make it safe'. So what I would recommend for people who don't have such strict guidelines imposed on them is: it is possible to remove the gunpowder but still keep it and store it properly for future analyses or future study. So you can remove it from the object making the object safe. That is kind of what I was getting at with drying it on the filter paper. If we had not disposed of it and just stored it, after we had recovered it, and kept it in a separate storage facility then that is definitely a possibility. I think that that's a really good point that yes, you're removing part of the artifact, you're removing part of the story that goes along with it.

Wendy Welsh: Molly hit on one of my questions as well. I was wondering if you wanted to identify – but in your time period you may already know – what your gunpowder is actually made of. So what we wanted to do – we have some grenades that are full – and we wanted to analyze some of the gunpowder but we were worried about 'some of the potassium nitrate is going to be dissociated so are we really going to be able to get some readings off of it?' So what I was wanting to ask is how one might go about analyzing – and if anybody here in this room may know – some gunpowder that may have already been waterlogged. What would one do?

Paul Mardikian: I've had the experience of unloading a live shell from a cannon that sank off the coast of France on the CSS *Alabama*. That cannon was a bit of work, because it was a rifle bore cannon and the live shell was stuck something like 1 meter away from the bore so we had to work a number of months to free the shell. It was really scary because when the gun was recovered there was a big crab pushing against the fuse of the live shell and eventually we were able to capture the crab and then ship the cannon 1000 km south of Cherbourg, and start working on that live shell. I'm going to present that work at the next metal conference. But in essence we were able to remove the fuse from the shell and work with the EOD [Explosive Ordinance Disposal] and we were able to remove that fuse and when the fuse was removed it made a hissing noise and it really got scary. But we were able to remove the black powder from the shell. We analyzed the black powder and basically one would think that potassium nitrate would be extremely soluble, right? So we were not expecting to find any traces of it and we actually did not. What we found was just charcoal. I ended up collecting that mass of charcoal and freeze-drying it and we kept it so far so good. But sometimes marine ammunitions are extremely dangerous. So in one case you can be fine and in other cases you can blow up yourself. So that's just my experience here.

Wendy Welsh: And how did you go about analyzing it?

Paul Mardikian: I don't recall. I would have to dig up the information. But the EOD people analyzed it in their laboratory so basically you need to talk to your police department.

John Scott: I'm glad Paul mentioned the danger that happens with shells like cannonballs and stuff like that. You do hear it occasionally in the news – not too long ago there was a major fatality of a guy who was a collector and dealer in cannonballs in the south of the United States. But I wanted to mention about terahertz spectroscopy – it allows not only imaging in a way that is a little bit similar to X-radiography but also simultaneous identification of elements and compounds. I'm not an expert on this at all, but I wanted to mention it because it is the kind of thing that could be used. In the Conservation Science Annual – I think it was last year, we had two sessions on heritage analytical projects using terahertz spectroscopy. The reason I mention that is that the abstracts only are accessible on the Eastern Analytical Symposium's website. So if anyone wants to contact me about that it's possible to go and look – see who is working with what and contact them then independently about that kind of technology. It is used very much in security for going into airports and so forth like that – that they are able to actually very well identify materials that are inside of closed containers and so forth.

Lesley Frame: Thank you that is a very good suggestion, I think.

Molly Carlson: This is a suggestion for the *Queen Anne's Revenge* person [Wendy Welsh] – the sample that I managed to finally get permission to send to Michigan to an ex-ATF [the alcohol, tobacco and firearms division of CIA] – he was a chemist that was specific with explosive material. He analyzed our sample and he said the nitrates were pretty much gone but when he burned it, it did burn in his ignition susceptibility test. This was from black powder 285 years in the sea inside a cannon. So he said the implications were that if we had a mass [of the material] that he couldn't guarantee that it wouldn't do something.

Lesley Frame: Right yes, and I think that brings to light a really good point that it depends on your burial conditions in a lot of cases. These are from Arizona and it is pretty dry. We have seasonal wetness but the places where these were excavated were not in waterlogged environments – they're dry. So the potential for potassium nitrate to still be present is probably a little bit higher. But also the other concern is not just the gunpowder but it is the primer with these which is not necessarily the case with the cannonballs, which are usually just filled with the gunpowder.

Preventive Conservation

Chair: Emma Schmuecker
Panelists: David Thickett, David Hallam, Lesley Frame

Aaron Shugar: David, I was wondering in regards to your talk, first of all, I have seen many museums where people donate their cars, and I am curious to know how you approach that when someone comes to you and says, I want you to have this, how do you deal with that? There is a car museum in Pennsylvania that has to turn people away because they cannot deal with it anymore.

David Hallam: Everything that comes into the National Museum [of Australia] has to go through the collections committee process. Basically that's a significance assessment. The Wolseley motorcar which is one I showed, was one that we actually have accepted into the collection, and that was because it was unique, well provenanced, one owner right from new, the owner was a famous physics professor so we could tell his story as well. A lot of the things that come to the collections committee never make it through, so I mean, that's the control, is the collections committee process.

Katherine Cuffari: A question for David Thickett about the organ pipe analysis. Is there any effect, vibrational effect, of the organs being played on the dosimeters?

David Thickett: I don't know as I have not been involved with that side of Marianne's work, but I do wonder, you saw some of the charts have sharp little spikes down on the dosimeter response, and I do wonder if that would be either due to vibration or possibly with the air flow desorbing out the corrosion products. The dosimeter is just measuring the mass so it would measure absorbed water. Not with these because they are higher frequency but those with a lower frequency, but I do wonder because those spikes are quite discreet at certain times

Maickel van Bellegem: Question to David Hallam - are you being consulted for the significance assessments and whether work is required before accepting an object into the collection?

David Hallam: Yes, it depends on the size of the acquisition but recently we acquired a Royal Tour vehicle from 1954, and we actually flew around Australia looking at 2 or 3 different ones before we made the decision, and it was a joined curatorial conservation decision.

Maickel van Bellegem: Thank you.

Aaron Shugar: This is for Leslie. You have mentioned that these cases or the bullets were sometimes reused or reloaded and if they were fired then the mercury goes everywhere, did you find that on the surface, how did you deal with this? How did you identify that on the surface was it in the corrosion products?

Lesley Frame: So we did a few things to look for mercury. First, XRF analysis and we analyzed many points on the cartridges and the bullets to look for the presence of mercury and we only really saw it on the bullets. But another test that we did was a spot test for volatile mercury to see if we were losing any mercury that may have been going into the storage room and we did not have any volatile mercury from many of our samples.

Paul Mardikian: I have a 37-year old car and I have a daily experience of what it is to have a functional object. Because if it does not start I don't get to go to work or the children cannot go to school so the implications are huge. In addition, I have already assessed the risk and it is pretty high to ride in my car, not only because I am a bad driver but because the car is 37 years old. And you'll get to see my car this afternoon. But my question is that we know that on old cars the first things that break down are the rubber parts. Rubber is prone to disintegration due to the heat and due to the fluids. There is also another element of risk which is fire. Especially on Volkswagens, some of you might have already experienced that, when the rubber starts to break down you may have a pretty nice fire in your engine compartment and destroy your car and kill yourself so the question is: how do you practically deal with these rubber elements on historical cars that have to run? Do you replace them?

David Hallam: That's a very interesting question. In a lot of cases, let's say with the rubber in contact with the coolant system, we would tend to view the rubber as changeable. But the wiring loom from the ABC outside broadcast fan for one of the television channels, it definitely isn't. So eventually that wiring loom will change its characteristics and the outer casing of the wiring loom will go from being an insulator to being a conductor and we would hope that our maintenance procedures will catch it before that actually happens. That's when the risk is too high. This is why your risk will change so if you drive a Volkswagen then obviously the risk is too high and you should never get into it.

Paul Mardikian: I have replaced the fuel lines so I should be OK.

David Hallam: But what you will notice on some of the vehicles I have actually assessed if the wiring loom is a replacement loom then I drop the significance of that system right down because it is not an original part.

Paul Mardikian: Electrical problems can really cause great damages to a car.

David Hallam: Therefore you need to have someone who is capable of assessing that and making sure that it is safe and again that's part of your risk management.

Paul Mardikian: My risk assessment tool is to smell the car and when I drive my car, even if it is a convertible, when there is a weird burning smell I know that there may be something going on and I have to stop.

John Scott: I have to say along with Paul that I always drive older vehicles because I like to spend my money on other things than new ones. And my wife is always sensitive to the smell of something burning. Anyway, I find the ammunition study quite interesting particularly when you are talking about finding mercury on the bullet and I hope you are talking about the corroded lead surface. You mean on the projectile is that what you mean?

Lesley Frame: Yes the bullet refers to the projectile.

John Scott: Why would the mercury be detected on the bullet because of reloading, because in my experience, I am not sure what they were doing at the time in Arizona when these bullets were used, the bullet would not be able to be used again. The cartridge would be reused. The marks that you've showed on the cartridges indicate that they were very likely reloaded but probably not with a reused bullet. So I was wondering if the mercury you are detecting in the bullet might be something to do with the lead that was used to make the bullet because mercury often occurs with lead and it might still be there.

Lesley Frame: Yes that is a possibility. Yes if the bullet is going to be fired it will be smashed and will not be reused you are absolutely correct. But for example, if you have a misfire and the cartridge never really even leaves the gun and it needs to be taken apart and reloaded, then a bullet could be reloaded into a cartridge case. Also being inside the chamber of the gun, because the chamber of the gun is being coated with mercury, that's another way for mercury to end up on any part of the exterior of the entire bullet cartridge. So there are a lot of possibilities in terms of how the mercury shows up on the bullet. That's why I have said it is just a possible indication of reloading but we used the tooling marks as a better indication, you are absolutely right, that's a better indication of reloading.

John Scott: Thanks.

Tom Chase: The idea of being able to do Oddy Tests with piezoelectric crystals is just wonderful. When I was at the Gordon Conference in 1978 I met Beverley Phipps of IBM in San Jose. He had used piezoelectric cartridges to assess the monolayers of water being absorbed on metals at different relative humidities. [(P. B. P. Phipps and D. W. Rice, "The Role of Water in Atmospheric Corrosion," chapter 8, pp. 235-259. in *Corrosion Chemistry*, eds. Grorge R. Brubaker and P. Beverley P. Phipps, American Chemical Society, Washington, D.C., 1979, ACS Monograph Series 89]. It's a very useful paper, with a particularly helpful diagram showing the thickness of adsorbed water molecules on metals as relative humidity increases. At the meeting, Bev suggested that we use piezoelectric crystals to look at water absorption in copper chlorides but I never got around to it so it would be wonderful to see them used. I think we should look at doing Oddy tests with them and I wonder if the actual crystals are going to get cheaper the way everything does in electronics. We can hope.

David Thickett: Absolutely. The expense is to put the coating on the crystal. That's the tricky part; you need quite a thin layer. If you coat it too much you lose the sensitivity. I agree the crystals themselves are about two dollars to buy that's the measuring equipment that is the expensive part. There's been a whole range of things that Oddy test people have used evaporated thin silver films and measured that with image analysis and try to get a quantification. The real neat way is to use electrochemical reduction, the sort of method Virginia Costa developed and you get really accurate measurements on how thick your tarnish layer is on silver, your corrosion layer on copper, your corrosion layer on lead. I agree they've certainly got potential but actually coating the crystal at the moment is quite a tricky thing to do. To buy the commercially coated crystals is about 300 bucks a piece.

Tom Chase: I would think that if you are using them to do Oddy test which is a sort of comparative gas absorption, perhaps you could do something about coating crystals. It would be cheaper because the starting signal and the ending signal…

David Thickett: You do not need the degree of accuracy absolutely. Yes it is a very interesting idea but it would probably take quite a bit of work to get it to a usable state.

INNOVATIVE TECHNIQUES

Session Chair: David Hallam

QUALITATIVE ANALYSIS OF HISTORIC COPPER ALLOY OBJECTS BY MEASURING CORROSION POTENTIAL VERSUS TIME

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Abstract

This paper describes an electrochemical tool developed to measure the corrosion potential of metal surfaces, often expressed as Ecorr, versus time, as a technique used in the qualitative analysis of copper alloys. The instrument is easy to use and transport, and is ideally adapted to the work of conservators during on-site condition survey. Along with the tool, a database was created that contains the electrochemical plots of 66 reference alloys, representative of the materials typically found in collections containing technical and scientific objects, (for example, those found in industrial heritage, technology and army museums). The plots were obtained in three different solutions; mineral water, potassium nitrate and sodium sesquicarbonate. The electrochemical tool was used to study several objects in the collections of the Historical Swiss Army Material Foundation (HSAM Foundation), and, after confirmation of their composition by energy dispersive spectroscopy, has allowed the authors to validate the appropriateness of the tool and the associated database, as well as to determine their limitations.

Keywords: Monitoring, corrosion potential, qualitative analysis, copper alloys, technical and scientific heritage, conservation, diagnosis

Introduction

During a condition survey of a collection containing metal objects, conservators frequently determine the composition of the objects according to their shape, visible technological elements, condition, and the nature and colour of the corrosion products formed. For example, a hollow cast element with a brown-orange patina from a technical or scientific object will probably be designated as bronze (Cu-Sn alloy) and, if it has localized iron oxide stains, it will be assumed that the object contains or contained a ferrous component. A visually similar material that is stamped and has lamination marks may be designated as brass (Cu-Zn alloy).

The corrosion of metal alloys and their long-term conservation depend on their composition. Thus, if the proportion of zinc contained in a brass object is above 15% by weight, the object may be subject to dezincification (Centre d'Information du Cuivre, du Laiton et Alliages 2009); and if it contains lead, localized corrosion may develop if the object is exposed to vapours of corrosive organic compounds, such as acetic acid (Selwyn 2004). Therefore, knowledge of the main alloying elements as well as secondary elements in a particular object may help determine the most suitable conservation and display strategy. In order to obtain this information, conservators often resort to spot tests, which can be corrosive, as the solutions used are acids or chelating agents. Furthermore, these tests are often insufficiently discriminating (Odegaard et al. 2000).

Conservators lack transportable, almost non-invasive, easy to use and inexpensive analytical tools, which could assist them to quickly determine the composition of a metal object. This problem is particularly acute with regard to scientific, technical and horology objects, which often comprise numerous metallic parts of different composition that may require specific individual conservation recommendations. The SPAMT-Test project ("Suivi du Potentiel d'Abandon des Métaux en fonction du Temps" or in English "Monitoring of the corrosion potential of metals versus time") was set up to answer these needs. The project comprised development of a tool, the SPAMT-Test tool, for measuring the corrosion potential (Ecorr) versus (vs) time of a metal surface using a drop of conductive solution, measured with a reference electrode. By comparing the plot obtained with a database of reference metals, plausible compositions of the metal might be proposed.

Background and methodology of the SPAMT-Test project

Initial research for this project took place between 2004 and 2007 (Degrigny et al. 2007). Since this technique requires good surface preparation, it can only be applied to materials that exhibit light oxidation of the surface, such as historic objects made from copper alloys. The technique was initially developed for brass, before being more widely tested on other copper alloys. The results have shown that each of the studied metals exhibited specific electrochemical behaviour in non-aggressive solutions, such as commercial mineral water and sodium sesquicarbonate. Water is often used for the storage of copper-based objects (marine or from waterlogged sites) and sodium sesquicarbonate for their stabilization (Oddy and Hughes 1970).

Although the initial results were promising in terms of specific plots obtained for each family of alloys, good reproducibility of the plots, non-invasiveness of the technique, and simplicity of use, the developed tool still had to be tried on a large number of historic objects, with different compositions, for its validity to be confirmed. Furthermore, it was necessary to refine the measurement protocol and to improve the surface preparation of the material being studied, so as to increase the reproducibility of the plots and to limit interference between materials with similar composition.

The goal of the SPAMT-Test project was not only to optimize the measuring tool described above, but also to establish a database containing electrochemical plots for use as reference material that would be as complete as possible. Conservators equipped with the measuring tool and the database would thus be able to carry out Ecorr versus time plots on an unknown copper alloy and then refer to the reference plots in the database to suggest one or several plausible compositions.

Experimental conditions for plotting Ecorr versus time curves

Potential measurements carried out for the SPAMT-Test project have made it possible to optimize the pre-established protocol (Degrigny et al. 2007).
The measurement principle is simple. It consists of measuring the corrosion potential of a metallic material when a drop of solution is deposited on its surface and to monitor this potential versus time. The surface (a few millimetres might be enough) of the material being tested must be cleaned of any oxide layer. The measurement is made with a reference electrode dipped into a glass tube, called a junction protection tube, (JPT), whose membrane is in contact with the drop of solution. The JPT contains the same solution as that of the drop placed on the metal surface to prevent contamination of the drop by the solution of the reference electrode. The metal and the reference electrode are connected to a high resistance voltmeter, which measures the difference in potential over a short period of time (5 to 15 minutes). The plots obtained (using Microsoft Excel software) make it possible to follow the characteristic evolution of Ecorr over time and to specify the electrochemical behaviour of the material in the solution. Figure 1 shows how the device is set up.

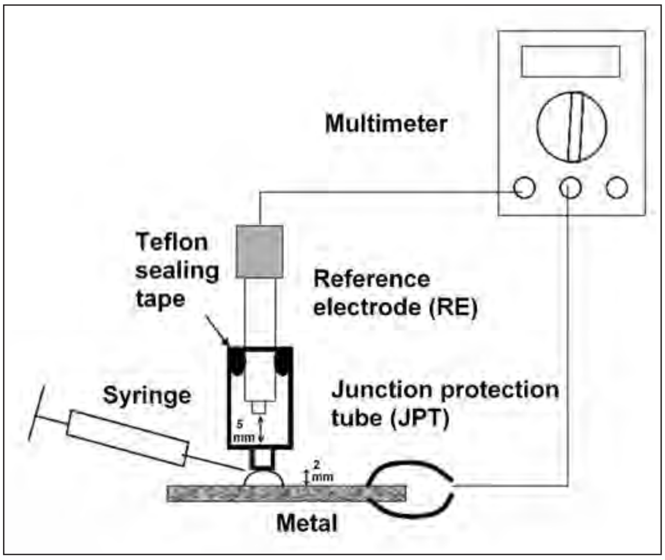


Figure 1. Experimental conditions for Ecorr measurements. The RE / JPT system is placed 2mm from the metal surface and the drop of solution is applied with a syringe. The Ecorr monitoring starts as soon as the drop is in contact with the metal surface.

As the electrochemical behaviour of different materials may be very similar in the same solution, the plots are made in three solutions to further prevent interference problems. Thus, the three solutions used that are non-aggressive for copper alloys were: a neutral solution of potassium nitrate (KNO3) at 1% (w/v) (pH=5.7-6.2, conductivity between 11.7 and 12.4 10^3mS/cm), Henniez mineral water (HW)[1] (pH=7.4-7.8, conductivity between 610 and 670mS/cm) and sodium sequicarbonate (SS)[2] solution at 1% (w/v) (pH=9.5-9.7, conductivity between 7.2 and 7.5 10^3mS/cm). All solutions were used at room temperature.

The measuring protocol was refined throughout this study, and the following steps were established:

- Prior testing of the reference electrode (RE) to compare its potential to that of a new RE, both dipped in tap water, and rinsing out of the membrane with freshly prepared de-ionized water;
- Preparation of the test solution (stirred before use), which is used to rinse out, and then to fill the JPT (except in the case of Henniez water (HW) where KNO3 was used instead as it is more conductive);
- Insertion of the RE into the JPT and over-tightening with Teflon tape so that the membrane of the RE is 5 mm from the membrane of the JPT. This step must be undertaken 30 minutes before measurements begin to ensure the stability of the system;
- Before each plot is made, the surface to be studied is polished with fine silicon carbide paper (Struers 4000). The objects are handled with latex or vinyl gloves during this procedure. The surface of the reference material is held vertically for drying, alcohol is sprayed from top to bottom, beginning with the side tested;
- Place the RE/JPT system at a distance of 2mm from the surface of the polished metal;

- Apply the drop of solution (40µL) between the membrane of the JPT and the metal surface with a syringe, first rinsed out with the test solution;

- Take Ecorr measurement after 5 and/or 15 minutes have elapsed.

In order to prevent contamination of the drop by the solution of the RE, the solution in the JPT is replaced every 3 hours, and the pH and conductivity are checked for any significant difference. Furthermore, the accuracy of the measurements are verified at the beginning and at the end of each series of measurements, by a control plot obtained from a plate of pure copper. Finally, when they are not in use, the three JPTs (one for each of the test solutions), are filled with its test solution, and stored inside test tubes containing the same solution.

Collection and analysis of reference materials

Sixty-six copper alloy reference materials were collected worldwide from colleagues involved in research programs or projects dealing with heritage objects. Archaeological alloys were obtained from the European IMMACO project (Improvement of Means of Measurement on Archaeological Copper-Alloys for Characterization and Conservation) (Ingelbrecht et al. 2001); and cast bronzes from the European project EUROCARE E!2210 BronzArt (EUROCARE 2009). Additional reference alloys were obtained from the collections of the following research centers: Center of Metallurgical Chemistry Studies of the Institute of Chemistry and Materials of East Paris (ICMPE-CECM, France); National Institute of Nuclear Sciences and Techniques (INSTN, France); Research Laboratory of the Victoria and Albert Museum (V&A, London, United Kingdom); Canadian Conservation Institute (CCI, Ottawa, Canada); and the Fraunhofer Institute for Silicate Research (ISC, Bronnbach, Germany). As the study focused on technical objects, the authors also tested modern alloys provided by Swissmetal (Switzerland) and objects from private collections, such as that of the Historical Swiss Army Material Foundation (HSAM Foundation).

Table 1 gives the list of the families of alloys selected, with the various reference materials studied per family. All these materials were analyzed using energy dispersive X-ray spectroscopy fitted to a scanning electron microscope (SEM-EDS) (Degrigny et al. 2010).[3]

Construction of the database

A discussion about the creation of the database has been provided elsewhere (Degrigny et al. 2010). Three plots were made per material tested using the three solutions described above; the first two plots were obtained after 5 minutes, and the third after 15 minutes. During the test, once reproducible plots were obtained (a maximum difference of 5mV was accepted), the authors moved on to the next material in Table 1. When a difference of more then 5mV was found, the measurement was repeated by a different person, and the number of plots was increased so as to confirm or invalidate the lack of reproducibility.

Family	Alloys
Arsenic-copper	CuAs3.3S
Bronze (Cu/Sn)	CuSn7.7, CuSn9.1Ni, CuSn10, CuSn14, CuSn15Pb, CuSn9.4Si3.6, CuSn9Si3.8Bi2.3, CuSn11Ni3.3, CuSn11Zn1.3Ni1.9, CuSn14Zn2.1
Silver bronze (Cu/Sn/Ag)	CuSn5.6Ag12, CuSn5.7Ag5.9, CuSn6.5Ag
Leaded bronze (Cu/Sn/Pb)	CuSn12Pb11NiMn
Brass (Cu/Zn)	CuZn5.3, CuZn5.8, CuZn7.8, CuZn12, CuZn11, CuZn14.84, CuZn24.9, CuZn30, CuZn32, CuZn34, CuZn35, CuZn36, CuZn46.1
Tin brass (Cu/Zn/Sn)	CuZn5.8Sn6PbNi, CuZn14Sn2.7PbFe, CuZn35Sn1, CuZn36Sn1.7
Leaded brass (Cu/Zn/Pb)	CuZn35Pb1.6Si, CuZn35Pb2.1Sn1.2Ni, CuZn35Pb3.1, CuZn36Pb1NiFe, CuZn37Pb1.7, CuZn38Pb0.7, CuZn38Pb3, CuZn39Pb1.6NiFe, CuZn39Pb2NiFe, CuZn39Pb2.6Fe, CuZn39Pb2.1, CuZn40Pb, CuZn40Pb1.3, CuZn40Pb1.8, CuZn42Pb2,3Al, CuZn43Pb
Nickel silver (Cu/Zn/Ni)	CuZn24Ni12PbFe, CuZn26Ni12Fe, CuZn34Ni14Mn4Pb1.2, CuZn34Ni14Mn5.3Pb, CuZn37Ni8.4Mn2.9Pb1.8
Quaternary bronze (Cu/Sn/Zn/Pb)	CuSn3.9Zn4.3Pb3.8, CuSn5.3Zn5.5Pb1.5NiFe, CuSn5.6Zn2.4Pb2.5, CuSn5.8Zn2.4Pb1.6Ni1.1Si, CuSn5.8Zn3.3Pb3.4Si1.3Ni1.1, CuSn9,1Zn7,5Pb5,6NiFeMn, CuSn11Zn1.7Pb2.7SiNi
Beryllium-copper	CuBe2
Nickel-copper	CuNi25Mn
Aluminium-copper	CuAl8.5Ni2, CuAl11Ni1,5Fe1,2, CuAl13Ni5,8Fe3,8Mn

Table 1. List of reference materials (when no number is given after the chemical symbol of an element, the concentration of this element is less than 1% in weight).

Family	General trend of E_{corr} vs time plots	Comments
Cu/As	Depending on the solution	- $E_{KNO3}>E_{EH}>E_{SS}$ - In SS: passivation (E_{corr} increases vs time), - In KNO3 and HW: E_{corr} first decreases and then increases
Bronze (Cu/Sn)	Progressive passivation for all solutions	- $E_{KNO3}>E_{EH}>E_{SS}$ - In HW and SS: 1 or 2 slopes (beyond 7-10 w% Sn, 1st step is quick, 2nd step is slow)
Silver bronze (Cu/Sn/Ag)	Progressive passivation for all solutions	- $E_{KNO3}>E_{EH}>E_{SS}$ Almost no effect of Ag
Brass (Cu/Zn)	Quick passivation (E_{corr} gets stable between 5 and 10 min.)	- $E_{KNO3}>E_{EH}>E_{SS}$ - In KNO3: decrease of E_{corr} after a preliminary increase (10 min.) when cZn < 13w% - In HW and SS: 1 or 2 slopes (beyond 35 w% Zn, 1st step is slow and 2nd step is quick)
Tin brass (Cu/Zn/Sn)	Quick passivation for all solutions	- Quicker if cZn > 35w% - In KNO3 and SS: E_{corr} is similar after 5 min.
Leaded brass (Cu/Zn/Pb)	Passivation for all solutions	- In HW and SS: E_{corr} is more or less constant after 12min. - Poor reproducibility.
Nickel silver (Cu/Zn/Ni)	Passivation	- Slower passivation when cZn is between 24 and 37w% - 1 or 2 slopes
Quaternary alloy (Cu/Sn/Zn/Pb)	Passivation	- In most cases, $E_{HW}>E_{SS}>E_{KNO3}$ - In KNO3: 1st values of E_{corr} are very negative and slow passivation depending on the ratio C_{Pb}/C_{Zn} - Poor reproducibility
Cu/Be	Progressive passivation for all solutions	- $E_{KNO3}>E_{EH}>E_{SS}$
Cu/Ni	Depending on the solution	- $E_{KNO3}>E_{EH}>E_{SS}$ - In HW: corrosion since E_{corr} decreases steadily - In KNO3 and SS: passivation in 1 or 2 slopes
Cu/Ni/Al	Depending on the solution	- $E_{KNO3}>E_{EH}>E_{SS}$ - In HW: the passivation is favoured - In SS: more uncertain behaviour and passivation in KNO3

Table 2. Summary of electrochemical behaviours for the main family of copper alloys in the three solutions described.

Several main trends of electrochemical behaviour were observed with the families of alloys studied, summarized in Table 2. As a rule, once the plot was completed, the authors observed no stain on the surface of any of the unleaded copper alloys, and the results were reproducible. The side effects (staining and lack of reproducibility) observed on leaded brass and quaternary alloys are attributed to the presence of lead nodules in copper alloys that cause localized corrosion.

Validation

Once testing of the SPAMT-Test tool (the measuring tool and the database) was complete, the authors then tested the tool in real conditions on five objects from the collections of the Historical Swiss Army Material Foundation. The copper alloy objects selected for the study were: a cartridge case (HSAM4), a tube (HSAM5), and protection caps (HSAM1-3). Each object was first surveyed to assess its condition and to try to determine the manufacturing techniques used. The data collected for each object is presented in Table 3.

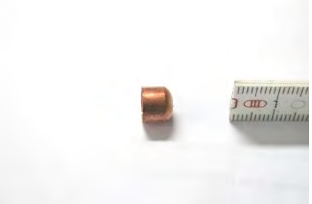
	**HAM1**: cap Cold worked. Bright and yellow tone.
	**HAM2**: small cap Cold worked. Copper-based alloy with a low amount of additional element (red tone).
	**HAM3**: small cap Cold worked. Yellow tone.
	**HAM4**: cartridge case Cold worked. Yellow tone.
	**HAM5**: piece of tube Folded (from a laminated plate around a polished drift), the longitudinal junction between the two edges is legible. Grey tone.

Table 3. General characteristics of the objects tested from the collections of the HSAM Foundation, used to validate the SPAMT-Test tool.

The data gathered from the survey reveal characteristics suggesting that the objects, apart from HSAM5, are manufactured from brass. The condition survey data suggests three types of alloys for these objects: CuZn brass (30-40% by weight) for objects HSAM1, 3 and 4; brass with a low amount of zinc for HSAM2; and probably nickel silver for HSAM5.

The next step involved testing the SPAMT-Test tool on real objects to refine the initial observations made during the survey. As the objects tested belong to a private collection, they were polished as discreetly as possible (often on interior surfaces). The objects were secured in a vice to ensure stability and present as large a testing surface as possible. Figure 2 shows some of the positions chosen (for HSAM1, a piece of aluminium foil was placed between the crocodile clamp and the object to prevent marking of the surface during electric contact).

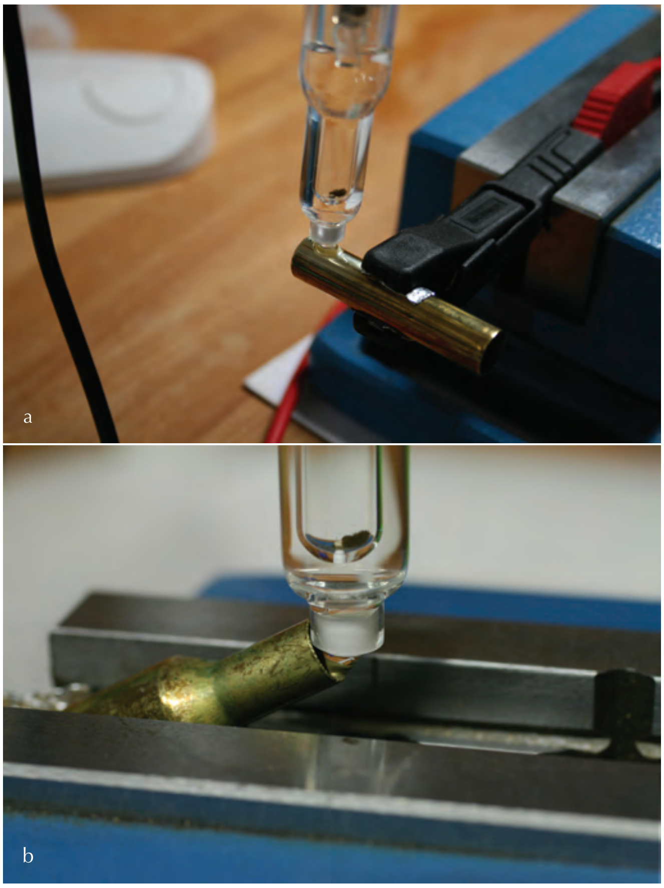


Figure 2. Position of the objects in the vice during the Ecorr vs time monitoring. HSAM1 (a) and HSAM4 (b).

As shown in Figure 3, the electrochemical plots obtained from the five objects reveal four different alloys, not three, as suggested in the condition survey. These are HSAM1, which is almost identical to HSAM3 (not shown), HSAM2, HSAM4 and HSAM5. The reproducibility of the results (tested objects 1, 2 and sometimes 3 for each object) is satisfactory. The plot(s) of the alloy(s) from the database that have the closest behaviour to that of each artefact under study are given.

Use of the SPAMT-Test tool enabled the authors to suggest likely compositions for the five objects from the HSAM Foundation. These results appear in the second column of Table 4 and should be compared to the results in the first column, which were suggested after the condition survey. It should also be noted that the potentials at the start of the plots are often less negative than those of the closest reference metal. This is most likely due to the light surface polishing, which probably leaves a fine layer of oxide on the surface, causing the corrosion potential to be slightly higher (passivation phenomenon). However, this discrepancy is reduced after a few minutes of measurement.

Once the plots were taken, compositional information was obtained using SEM-EDS, on the same area of the metal surface where the electromechanical measurements were taken. The machine set-up was the same as that used previously for EDS in this study[3]. The results are given in the third column of Table 4.

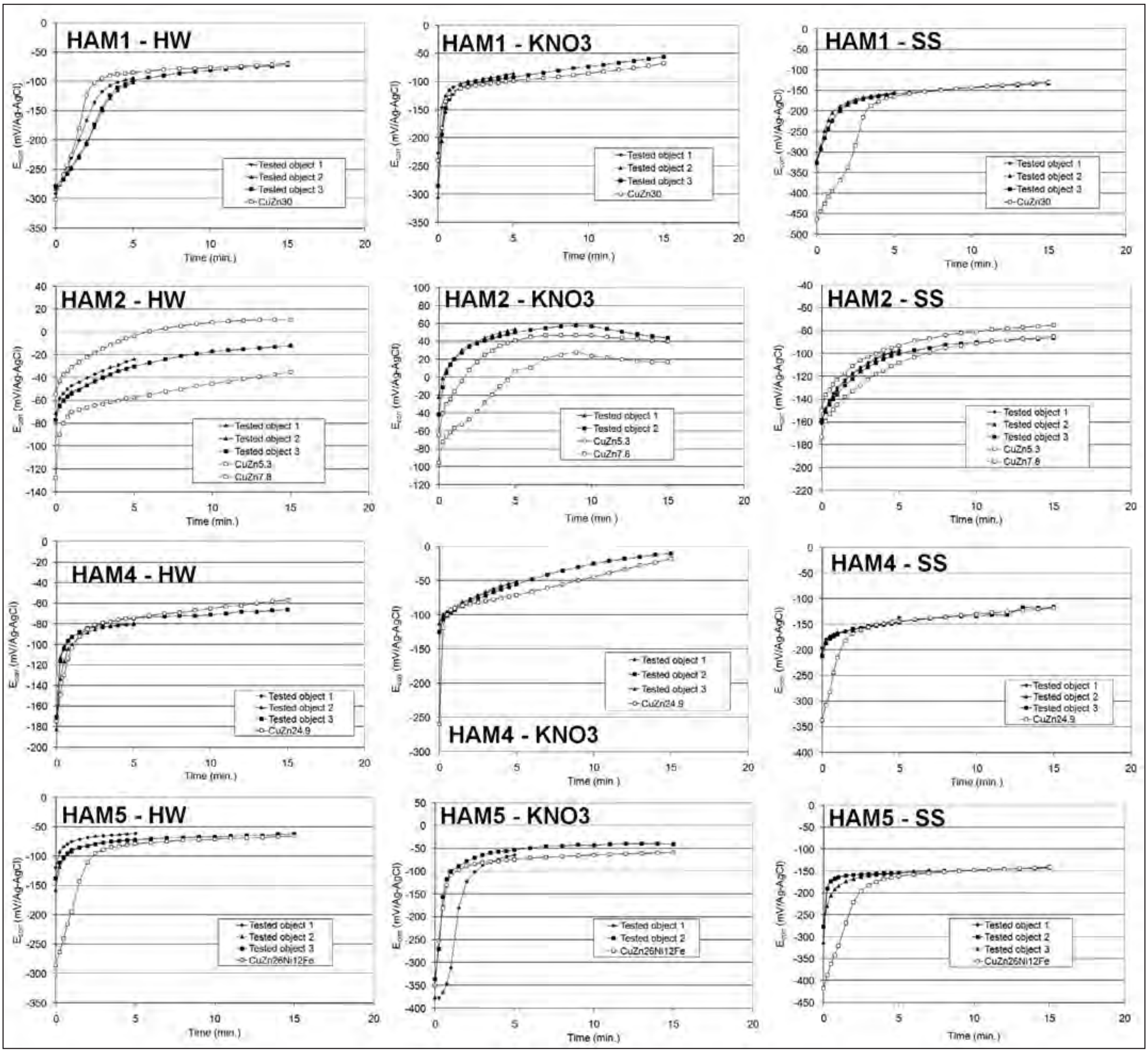


Figure 3. Ecorr vs. time plots in the three solutions described: (top row) HSAM1 with additional plot of CuZn30 monitored during 15 minutes, (second row from top) HSAM2 with additional plots of CuZn5.3 & CuZn7.8 monitored during 15 minutes, (third row from top) HSAM4 with additional plot of CuZn24.9 monitored during 15 minutes, (bottom row) and HSAM5 with additional plot of CuZn26Ni12Fe monitored during 15 minutes.

Objects tested	Compositions suggested from the condition survey	Compositions given by the "SPAMT-Test" tool	Compositions obtained by analysis (EDS – SEM)
HAM1	CuZn[30-40]	Close to CuZn30	CuZn30
HAM2	Cu + Zn ?	Close to CuZn5.3-7.8	CuZn8
HAM3	CuZn[30-40]	Close to CuZn30	CuZn30
HAM4	CuZn[30-40]	Close to CuZn24.9	CuZn28
HAM5	Cu/Zn/Ni	Close to CuZn26Ni12Fe	CuZn27Ni8

Table 4. Composition of the five artefacts selected to validate the SPAMT-Test tool: the 1st column gives the suggested compositions after the condition survey, the 2nd with the SPAMT-Test tool, while the 3rd column gives the actual composition obtained by analysis with EDS.

A comparison of the results presented in columns 2 and 3 of Table 4, confirms that the compositions suggested by the SPAMT-Test tool for the binary alloys, mainly brass, were relatively accurate. The differences are due to the lack of reference materials in the database having exactly the same composition as the tested objects.
In such cases, the closest material(s) available in the database was used as a reference. However, noticeable differences occur when the metal contains more than one additional element. Nevertheless, the developed tool offers satisfactory results given that the electrochemical plots reveal the main elements in a much more accurate manner than can be obtained with a condition survey (for instance zinc (Zn) and Nickel (Ni) for HSAM5).

As a result of the use of the SPAMT-Test tool for study of five objects from a collection of technical objects, composition of three new materials - HSAM2, 4 and 5 -

can now be added to the database. It is envisaged that use of this tool to study an entire collection, or several collections, would greatly improve the performance of the database.

Conclusion

The SPAMT-Test tool is adapted to the requirements of conservation professionals: it is easy to use, relatively non-invasive, easy to transport, and inexpensive. As described in this paper, the tool makes it possible to determine what elements are present in a tested alloy, and in certain cases (binary alloys), to obtain relatively accurate compositions. As good surface preparation is required, the tool is particularly adapted for technical, scientific, and horology objects that are rarely covered with a thick corrosion layer.

Throughout the project, all the measurements were made by conservators who specialize in the conservation of technical, scientific, and horology objects; that is, by potential end-users of the SPAMT-Test tool. The conservators were able to make initial suggestions concerning composition, based on their technological knowledge of the object and its construction. In addition, they have simplified the protocol as much as possible so as to adapt it to on-site use where efficiency is required.

The developed tool is, on the whole, satisfactory; however, a few improvements are necessary before it becomes a staple for use by conservators. In particular, it is essential that appropriate software be developed, which would offer composition suggestions almost instantly based on electrochemical measurements. Indeed, the current database is not particularly user-friendly for anyone unfamiliar with electrochemical plots and their interpretation. The tool, which has been tested mainly in the laboratory, should also be improved to simplify on-site use. For instance, it should be possible to isolate the RE/JPT/drop system to prevent contamination that may influence results.

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Endnotes

[1]. Containing 106ppm Ca; 19ppm Mg; 7ppm Na and 1ppm K. More information is available on the Henniez website (http://www.henniez.ch, accessed 19 January 2010).

[2]. Equimolar mixture of $NaHCO_3$ and Na_2CO_3.

[3]. Beam current: 1nA; acceleration voltage: 25kV; starting angle: 35-40°; tilt angle: 0°; azimuth angle: 45°; surface analysed from 100x200μm to 10x10mm.

Materials

JPT Radiometer AL100
HACH LANGE FRANCE SAS
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Tel: (33) 4 78 03 38 38
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Q & A SESSION

Rozemarijn van der Molen: Thank you for a very nice talk. You might have mentioned it but why is it that leaded alloys are less reproducible in the E_{corr} measurements?

Guillaume Rapp: The exact reason should be investigated further indeed. But I noticed a very typical behavior of lead containing alloys – brass typically, or bronzes sometimes too, which makes in the last part of the curves, which is most of the time quite straight, and slow steep, it makes some fluctuations. It has, how would you say, a kind of wave movement like this, and I believe it that is because there are some spots, some inclusions of lead, that can passivate in a moment and in the next sequence this passive layer is attacked for some reason. Now we can have the potential of the lead then it gets covered again and the potential increases and so on. So it was very difficult to show these variations in our curves because we measured at a given moment – every 10 seconds or every 30 seconds. The fluctuations were not always on the top or on the base of the wave, I would say. But we intended to relate this fluctuation. This is an indicator indeed of the presence of lead in the alloys and this will be integrated in the matching software.

Tom Chase: I saw some CDs of this project out on the table – what is contained in those?

Guillaume Rapp: They contain at the moment the different documents we have made on this project. But I'm not sure they cover all the 600 plots we have! But if anybody wants to know a little more about this project, you can take the CDs - they are for you.

Ian MacLeod: Lead, from the previous papers we have seen during this week, is distributed across the microstructure.

Because you have a clean metal surface, all that is happening is that you are just getting localized corrosion of the lead and as that film is forming and breaking down, that's why you get the erratic responses. So you might like to try looking at an alternative electrolyte that has something like 50 or 100 ppm sulfate in it. Because with just a little "sniffle" of sulfate – that is as much as you need – just a "sniffle" – a little bit of sulfate and then the lead doesn't corrode or at least it corrodes to form a microscopic thin film of lead sulfate, which passivates it and then you get much more reproducible results. Well, that's my experience anyway.

Guillaume Rapp: Thank you. I would say this is interesting for us to have this very typical behavior which at the moment it is useful to have this. I will take note of your comment – thank you very much.

COMPUTED TOMOGRAPHY: A POWERFUL TOOL FOR NON-DESTRUCTIVE MASS DOCUMENTATION OF ARCHAEOLOGICAL METALS

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Abstract

The use of X-ray computed tomography (XCT) as a non-destructive method for mass documentation of archaeological objects encased within lifted blocks of soil was investigated by the Landesamt für Denkmalpflege Baden-Württemberg in southwestern Germany. The main advantages of XCT over two-dimensional (2D) X-ray and conventional excavation techniques, are the three-dimensional (3D) view, the ability to visualise exterior and interior features of objects within the blocks, for example, the damascene structure of a sword blade with polychromatic metal inlays, and the relative speed with which large amounts of material can be processed. The results have confirmed the effectiveness of this method as an additional documentation and virtual excavation tool for use by conservators and archaeologists faced with large volumes of material and fragile finds.

Keywords: Archaeology, mass documentation, block lifts, non-destructive, 3D X-ray computed tomography (XCT), virtual excavation.

Introduction

Each year in the southwestern German state of Baden-Württemberg, thousands of objects are excavated from numerous archaeological sites. As an example, more than 16 tons of metal artifacts are currently kept in a deep-freeze at about -20°C at the Landesamt für Denkmalpflege (LAD) State Institution for Cultural Heritage in Baden-Württemberg, Germany. More than 100,000 finds, many from the early medieval period, are stored in this special storage facility of the LAD. About half of these objects are block-lifted within their surrounding soil and are encased in plaster bandages providing preservation of the finds in their original context.

The documentation and examination of all finds requires excavation of the lifted blocks layer by layer in a manner similar to that of excavating in the field. For complete documentation, the facilities of the lab are superior to the conditions in the field, particularly with regard to the use of instrumentation such as microscopes or two-dimensional-radiography. Two-dimensional (2D) X-ray makes it possible to derive initial information about objects contained in each block lifted unit. Detailed information about the stratigraphy of the objects can only be revealed by careful excavation. With conventional archaeological methods it is estimated that, in order to fully study all the lifted blocks currently in storage, between five and six decades are required. Hence, new approaches must be considered to manage this challenging situation. As a very innovative method, three-dimensional (3D) X-ray computed tomography (XCT) was assessed in the hope that it could provide new insight for conservators and archaeologists when dealing with large numbers of fragile finds lifted in soil blocks. To assist with this goal, a research project was funded by the Deutsche Forschungsgemeinschaft (DFG) that hoped to clarify if the use of XCT is a viable alternative to more conventional approaches of dealing with objects lifted and stored in blocks of soil.

This technique has considerable relevance for conservators and archaeologists and this paper will discuss why the Landesamt für Denkmalpflege (LAD) uses XCT as a standard tool for examination as well as documentation. The LAD is the first institution in the conservation and archaeological field in Germany to pioneer the use of this technique for the systematic study of archaeological finds encased within soil blocks.

Problems of conventional strategy

The main disadvantages of using 2D X-ray, is it's restriction to metal finds, since less-dense materials cannot be successfully X-rayed in blocks. Otherwise, the excavation and documentation of these blocks require time and skilled personnel. Furthermore, the identification of materials within the blocks, and their state of preservation, can be obtained only by thorough examination. Survival of organic material is rare, and often these objects have decayed to such an extent that they leave only an area of discoloration in the soil that is difficult to visualize by conventional X-radiography. However, where organic material survives in contact with metal surfaces, it is often found partially or completely mineralized (Gillard 1994). Previous studies by the authors have shown that some 70 percent of metal finds from early medieval graves preserve fragments of textile, leather, wood, keratinous material or even feathers and plant remnants on their surfaces.

In the case of metal objects that have preserved traces of organic material, the conservator and archaeologist are often faced with a decision as to which material to conserve. Close study of the surface of the metal object may require removal of the organic layers. Both materials may be of great importance, however, an archaeological excavation is by definition a destructive and irreversible process. Subsequent re-examination and reconstruction of an excavated block and its contents can only be done if the excavation of the block has been carefully documented. In addition, excavated objects are often in such a poor state of preservation that they cannot even be analyzed before conservation work has been undertaken.

In order to try and address the time constraints that conventional excavation methods and subsequent conservation processes pose upon such a backlog of unexcavated material, the authors tested the use of XCT on a selection of 9 excavated soil blocks in a pilot project (Peek et al. 2009, Stelzner et al. 2010), since XCT studies have been used only sporadically in archaeological and conservation studies before (Jansen et al. 2006, Kastner et al. 2007, O'Connor et al. 2008). The objective was to investigate whether computed tomography could be of assistance in speeding up the study and documentation of artifacts encased within blocks of soil. For this current project, 45 excavated blocks containing metal and organic objects were selected and measured with an industrial computer tomograph. In the initial stages of the project, a Wälischmiller RayScan 250 E®, cone beam 3D-XCT-system with a 225 kV micro-focus tube was used. Following further tests, a Phoenix X-Ray vtomex 450® industrial tomograph was chosen for the study. The data acquired from the Phoenix tomograph was processed and evaluated with specially designed visualization software from VGStudio MAX 2.0®. The combination of the Phoenix X-Ray vtomex 450® and the software VGStudioMax 2.0® from Volume Graphics gave the best results.

X-ray computed tomography (XCT)

In 3D X-ray computed tomography, the object to be studied is placed on a rotating plate between the X-ray source and a surface detector. During exposure, the object rotates 360°, and the surface detector records data from several hundred different angles. Once the acquisition process is complete, the information captured is reconstructed into a set of 3D digital data, in which different densities of materials are visualized in corresponding grey-values.

The advantages of industrially designed computed tomography over that used in the medical field lies in the much higher radiation intensity, which makes it possible to penetrate materials with a much higher density such as those made from metal. The industrial XCT has a very high resolution down to the micrometer range and information is acquired in a relatively short period of time. Depending on the size of the block of soil, the tomography may require between one to three hours for information capture.

The resolution, or voxel axis size[1], depends on the size of the block and was found to be around 140 µm. In special cases, where a higher resolution was necessary, it was possible to zoom in on one part of the block in detail (Simon et al. 2007). Depending on the degree of detail required, this region of interest (ROI) can be viewed with a resolution down to 30 µm. Figure 1 shows an example of the image quality that can be obtained. Using the visualization software VGStudio MAX 2.0®, the object can be viewed in 'slices' from different points of perspective, both its interior and exterior surfaces can be shown in detail and the different densities of the materials displayed as corresponding grey values (Casali 2006). An extremely useful feature of the software is the 'segmentation' tool, which makes it possible to remove the unwanted structures from the image. For example, an object within the soil block can be viewed without the surrounding soil. Viewing a metal surface in detail depends on the resolution of measurement. The higher the resolution, the more layers can be individually laid bare, i.e. 'segmented'. The next step is to put these single layers together into a 3D reconstruction of the object.

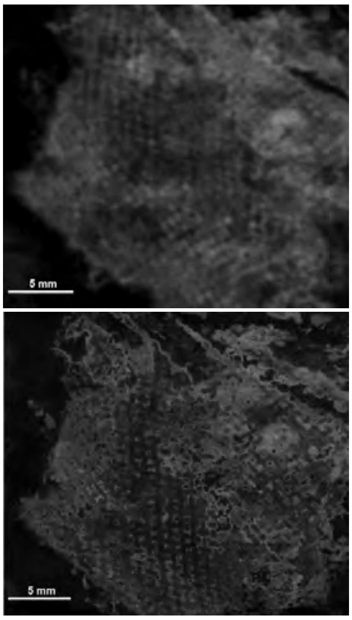

Figure 1. 2D sectional scan of a mineralised textile without ROI, resolution 140 µm (*top*). 2D sectional scan of mineralised textile with ROI, resolution 30 µm (*bottom*).

Case Studies and Results

In this section, a selection of the data gathered from XCT of eight blocks-lifts is given to show the potential of this method. The following three issues are the most relevant from the conservator's point of view. All the block-lifts were excavated at the early medieval cemetery of Lauchheim in the southwestern part of Germany. This site proved to be the largest burial site discovered in central Europe, with 1,308 graves. What is unique about the excavation at Lauchheim is that the remains of the village were discovered beneath this massive graveyard.

Interior and exterior structures and stratigraphy

Block-lifted soil that is suspected of containing weaponry typically involves extensive documentation, particularly where the block-lift may enclose iron weapons, such as swords with surviving scabbards made from various organic materials. The scabbard can survive in multiple layers, which, if in contact with the metal surface, may be partially or completely mineralised. The examination and documentation of composite finds, which may include recording of technical details and manufacturing techniques of the metal and the organic component, is often unsatisfactory due to problems making decisions regarding the significance of the material to be conserved. However, in this study, XCT, in combination with the software program that can segment the image into readable 'slices' or segments, proved a successful combination for the identification of difficult composite materials. The segmentation tool was able to separate exterior and interior structures of all the objects in the block-lift, making it possible to digitally excavate the object and to display its structure. It was possible to non-destructively reconstruct and identify the metal sword, and the organic component that comprised the scabbard.

Figure 2a-f (grave no. 54, block size 969 x 142 x 60 mm; recorded with Phoenix X-Ray vtomex 450®) shows the use of different metals and techniques of production as damascene workmanship (2e) and metal inlays (2d). Although the latter can also be recognized using conventional X-ray radiography, XCT was able to distinguish polychromatic metal inlays (grave no. 15, block size 755 x 113 x 43 mm; recorded with Phoenix X-Ray vtomex 450®; see Figure 3).

Figure 3a-e shows the fine tuned grey scale values obtained played a decisive role in the identification of the different types of metal used in the decoration of the blade. The software allowed precise measurements to be made non-destructively and without extracting the object from its position within the block of soil. In addition, complex stratigraphy can be easily imaged and manipulated. The example shown in Figure 3c shows that various objects can be imaged in their exact position, so that in addition to a precise typological identification, a reconstruction of the original form is possible as shown in figure 3e, even if the organic material, in this case a leather belt strap, did not survive. This kind of detailed information is significant for archaeological research in relation to typology, stylistic classification and stratigraphy.

Manufacturing technique

The high resolution that can be obtained with XCT can provide an extremely accurate record of the original surface of an object. XCT imaging of iron objects in this study found that high-resolution imaging was of such high quality that the 'forging skin', the original surface as made by the blacksmith, was visible on the surface of the object. This is visible in Figure 4 on the left side (grave no. 447, block size 540 x 200 x 86 mm; recorded with Wälischmiller RayScan 250 E®).

Figure 2. (a) 3D CT image of a block of soil. (b) 3D CT image of the heavily corroded iron Spatha. (c) Virtually exposed Spatha. The corrosion layer has been faded out. (d) Detail of stem with inlay work on pommel and crossguard. (e) Sectional scan of the damascene blade. (f) Layers of wood from the sword sheath.

Figure 3. (a) The deposit containing a sword, several pieces of the sword fitting, and parts of a belt. (b) View of the top of the belt buckle and the end of the strap, showing an iron mount with brass and silver inlay. (c) Side view of the belt buckle. (d) View of the reverse side showing the end of the strap with metal inlay. (e) View of the separated components of the belt fitting.

Figure 4. Iron key with the 'forging skin' of the original surface evident (*left*). Bronze mask fibula showing the original surface of a 'casting skin' with tool marks (*right*).

For objects made from copper alloy, high-resolution imaging was also able to reveal detail of the ‘casting skin’, the original surface (grave 44, block size 285 x 280 x 102; recorded with Wälischmiller RayScan 250 E®; see Figure 4 on the right side). Decorative techniques, such as engraving on a copper alloy belt fitting, were also visible using this technique. This level of detail is usually very difficult to see because of surface corrosion, even after the object has been physically excavated and mechanically cleaned (grave no. 54, block size 989 x 142 x 60 mm; recorded with Phoenix X-Ray vtomex 450®; see figure 5).

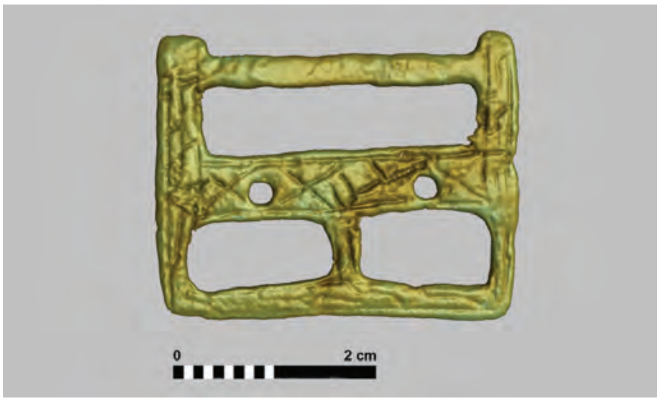

Figure 5. Bronze strap guide with cruciform engravings.

Another example examined with XCT and shown in Figure 6 was a pressed silver sheet strap with an iron core. Images of this object captured in 3D revealed details of surface ornamentation, even though it is completely covered by a mineralised fragment of textile (grave no. 203, single object; recorded with Wälischmiller RayScan 250 E®). The use of a more conventional method, such as manual excavation and examination, would probably have required removal of the textile in order to reveal the decorative surface finish on the silver component of this object.

Figure 6. Decorated pressed silver sheet strap covered with a tabby-weave textile (*left*). Decorated pressed silver sheet strap. Here the textile layer has been virtually faded out (*right*).

Material identification

This study demonstrates that various archaeological materials can be distinguished with XCT via differences in density. The denser the material, the lighter the grey value in the data set. In the end, however, the authors have found that personal experience in the application of X-ray analytical techniques is most useful in identifying the materials being studied. This can be bundled with the investigators knowledge of past manufacturing techniques.

First, an old repair is recognizable on the outer edge of an amulet that was also examined in this study. Examination using 3D-XCT clearly showed the repair, which was attached with the three rivets made of a different copper alloy than the original part of the amulet (grave no. 447, block size 540 x 200 x 86 mm; recorded with Wälischmiller RayScan 250 E®; see Figure 7). Second, the color of a pearl can be determined by its composition: a yellow pearl appears a lighter shade of grey than other pearls. Studies have shown that lead stannate is responsible for this coloration (Heck 2000) (grave no. 343, block size 420 x 270 x 100 mm; recorded with Wälischmiller RayScan 250 E®; see Figure 8)

Figure 7. XCT image of a bronze amulet showing an original repair.

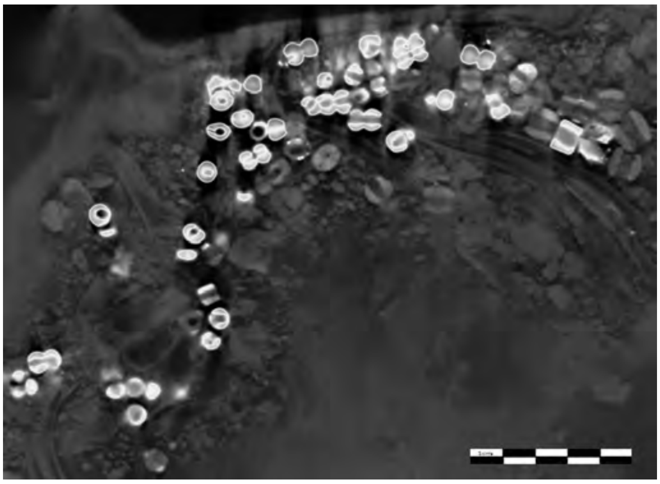

Figure 8. 2D sectional scan of pearls with different chromatic elements, visible as different grey values.

Furthermore, iron can be identified not only on the basis of the density of the metal but also through the characteristic appearance of its corrosion, which shows up clearly in XCT (grave no. 54, block size 989 x 142 x 60 mm recorded with Phoenix X-Ray vtomex 450®; see

Figure 9).

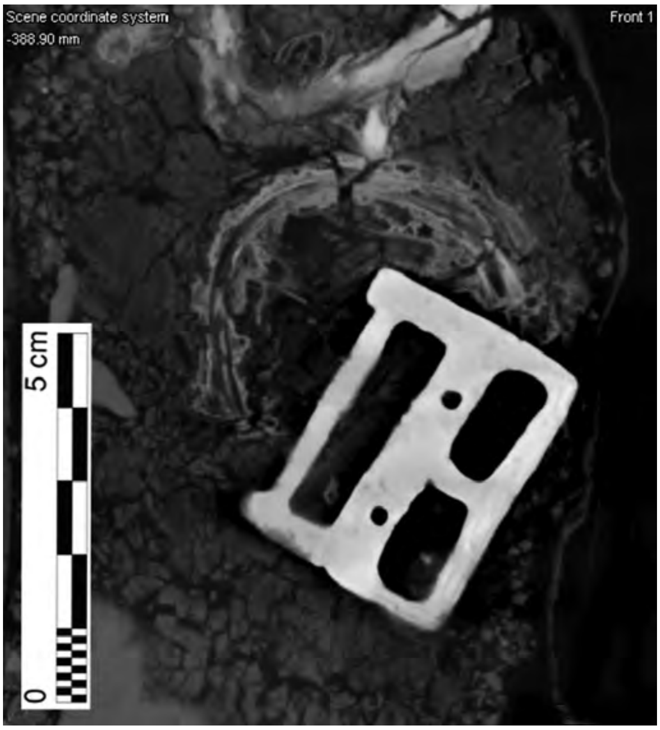

Figure 9. 2D sectional scan of a well-preserved bronze strap guide next to a highly corroded iron ring with characteristic iron corrosion.

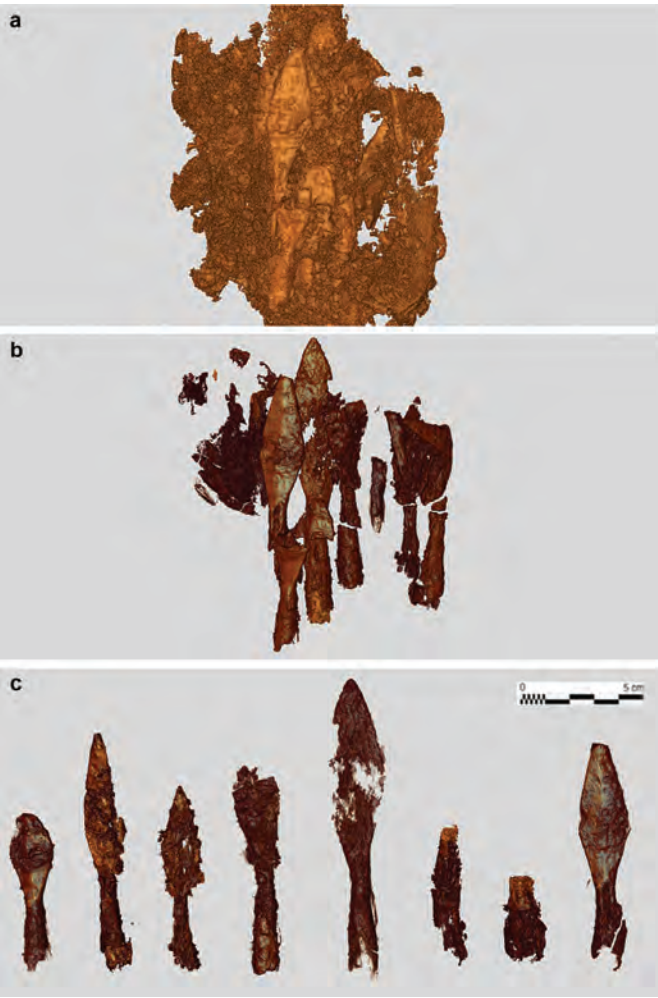

Figure 10. a) Iron concretion b) Detail showing fragmented arrowheads isolated from the concretion c) Reconstructed arrowheads.

Archaeological objects studied with XCT can also reveal areas of damage due to their burial conditions. Even though the objects described in this study were excavated and lifted with their surrounding soil in blocks, they can be very fragile and in a poor state of preservation. In these cases, the software can assist with its virtual reconstruction capabilities. Figure 10 from grave no.1, is an example that further demonstrates the possibilities of the software used in this study, when combined with XCT. This excavated block of soil appeared to contain an amorphous conglomerate of iron upon initial examination with XCT. In this case, the grey values of heavily corroded metal and the surrounding soil appear to be quite similar. However, after using the 'segmentation tool' from the software, it was possible to trace and reconstruct five complete and two fragmented arrowheads. (grave no. 1, block size 182 x 120 x 60 mm; recorded with Phoenix X-Ray vtomex 450®). Manual excavation and restoration would not lead to such a satisfying result, in such a short period of time. Conventional excavation and documentation of a block-lift in poor condition can take weeks or even months, whereas measurement with XCT takes only a few hours and the data received can be analysed in a few days (Ebinger-Rist et al. 2010).

Conclusion

This study has demonstrated how computed tomography can provide extremely accurate information of an objects physical structure and surface characteristics while being completely non-destructive. When combined with appropriate software, accurate 3D image reconstruction is possible. The objects examined were made from organic and inorganic components, and all were encased in discreet block-lifted soil chunks at the time of examination. This technique has proven to be a valuable tool for the conservator or researcher who requires fast, accurate information without compromising the physical integrity of the object.

Surface details and the visualisation of stylistic characteristics also represent a decisive aid for archaeologists in dating such objects. Computed tomography also provides information about the state of preservation of the objects, making it possible to document and virtually reconstruct finds that show significant decay and are otherwise almost impossible to restore. Thus, the 3D results permit documentation and recording of finds that is in no way inferior in quality and information value to that of other approaches used to date. In addition, this technique allows visualisation of interior, material-specific structures, thus in turn providing accurate observations about manufacturing techniques. In this area, the use of computed tomography for recording data on specific finds is superior to that of conventional methods.

A further decisive advantage, in contrast to conventional excavation, is that during study and documentation the objects need not be taken out of the context in which they were found. As a result, the excavation of blocks can be carried out at any time and the dataset can be re-analyzed as technical possibilities progress. Even when the respective find cannot be preserved in its original condition, the XCT image can capture its current condition. The raw data thus acquired can be re-studied at a later date as visualization software continues to progress. On the whole, XCT represents a clear saving in time in the study and documentation of block-lifted finds without any loss of information. Systematic use of this method accelerates the processing of finds by several decades and thus serves as a powerful tool for mass documentation.

This project has shown that research from the field of materials conservation, specifically the conservation of archaeological materials, have had a positive impact on archaeology and the recovery of information from block-lifts containing metal and organic objects. This research has enabled XCT to be adopted as a standard documentation tool at the Landesamt für Denkmalpflege in cooperation with the research institute for precious metals and metals chemistry (Forschungsinstitut für Edelmetalle und Metallchemie, fem, Schwäbisch Gmünd, Germany), which is responsible for the preservation of German cultural heritage.

Endnotes

[1] A voxel is the three dimensional equivalent of a pixel. It is the smallest unit in a volume and is identified by its x,y,z coordinate

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Q & A SESSION

Nestor Gonzalez: Amazing! Really incredible! One question for you - how long did it take to do a study for the sword for example?

Nicole Ebinger-Rist: For a measurement such as the sword we need 3 measurements – it takes around 4 to 6 hours and afterwards we need 2 to 3 days to uncover and to segment the objects out from the block.

Nestor Gonzalez: Remarkable! Thank you.

Wendy Welsh: Again, amazing stuff! Sorry, forgive my ignorance on tomography but is this basically in the detector – the mechanism in the detector – so if you have an x-ray source – is it the detector as to what is creating these images or is it the system in itself which is the source and the detector which make these images?

Nicole Ebinger-Rist: All the data you have, you get it on the detector. It is like in a camera you have the pixels, well here we work with the voxels. And yes we need the x-ray source, it's like if you have a film when you make the conventional x-rays – you have the film, and now it is digital so it is the same.

Wendy Welsh: So it is on the detector.

Nicole Ebinger-Rist: Yes and the resolution of the detector and the size of the detector is very important.

Wendy Welsh: Ok, another question is - what kind of keV are you using with these blocks?

Nicole Ebinger-Rist: It's around 200 to 230 keV.

Wendy Welsh: Because the majority of our objects – everything comes up in a large concretion, with masses of concretion on it, this would just be an amazing tool. Have you ever done anything or know of anything that's been done with marine archaeological concretions or anything like that?

Nicole Ebinger-Rist: Not with marine finds but we have big blocks. Our next project is to measure a whole grave and it is 2 meters high and also about 0.5 meter wide. But we know that we can come close to solving your problem because here we work with 200 to 230 KeV and it is not the limit so we can go up – our x-ray source is to 300 keV .

Wendy Welsh: Still getting it to distinguish between the organics and the metals at that high keV?

Nicole Ebinger-Rist: Yes.

Wendy Welsh: That's amazing.

Valentin Boissonnas: If I am an archaeologist and you show me that - I buy a machine and I fire 3 of the 5 conservators the next day. So I'm really interested: what is the reaction of the archaeologist? Is the archaeologist happy or more than happy he is of course with the result, but are you still doing any treatment? Or does he say 'I get all the information just from the scan, and we put it back in the fridge'? Because then when we have a new problem: we need big freezers and we still have a lot of chlorides in the artifacts and we have a whole new perspective on long-term storage.

Nicole Ebinger-Rist: The archaeologists are also happy because they work very close to us. The next question was: yes this block of soil comes back to our freezer compartment. We are lucky because we have a big freezer compartment. Our experience shows that objects which are in blocks with the surrounding soil are in better condition than single objects in our freezer compartment. So the soil is not too bad around the objects. The finds I showed you in the block of soil – they excavated them in 1986 and the preservation state is very often very good – when we look inside the blocks. In the beginning when we started to open the blocks and look at the conditions from the block – but that now we know we have all the information we can detect every material. We can preserve also the organic materials like the textile and the leather in the surrounding and yes, we store the objects again in our freezer compartment but the archaeologists are very happy because for 300 blocks we need around 30 years and in our project our goal is to make all measurements and to do all examination in around 5 years, so we have lucky archaeologists!

Valentin Boissonnas: I think we still have the problem of the blocks slowly drying out in your freezer. So corrosion probably will continue. Can you actually detect organic material? I can see that you can see wood, you can see leather – can you actually identify different fibers, like wool or hair? Whether it is fox or rabbit? That's what we usually do, when we go and excavate is, we go and put it in the SEM and we get all the real information that is very important for the archaeologist on the clothing and everything. How far can you go with that?

Nicole Ebinger-Rist: With the resolution we have the opportunity and the possibility for textile technology, but we cannot say if it is wool or some other fibre but we have first our researchers that work not with x-ray, we work with neutrons. With the neutrons, the resolution is so great because the samples are smaller so that we can get the technology from the textile but not to say it is wool or... but our textile archaeologists have a lot of experience to work with this material and they know from the technology – maybe you have a tabby weave, and it is not a special material, they are often plant materials.

Valentin Boissonnas: Thank you, wonderful.

Paul Mardikian: I think it is wonderful and seeing those results is just extraordinary. Still, I think it would be great if you could, in a future publication, compare the virtual reality and the real excavation of a block and have conservators and archaeologists assess the results. Because the bottom line is the amount of information you gain and it looks wonderful on those images, but maybe there is much more to learn, or much more to lose. Sometimes I look at one of my objects and x-rays – and I say: 'I doubt that I'll be able to do and produce more than what the x-ray is showing. But sometimes this is not the case. Sometimes you find things that you have no clue about. So it is not black and white – it is just in the grey zone. We are constantly between those two possibilities of losing or gaining. But I was just curious if you had evaluated one object before CT-scan like you have done, and then after full excavation by a conservator?

Nicole Ebinger-Rist: In the beginning we started with a pilot project and also doing a manual excavation where we compared our manual excavation with the measurements. And I must say, I'm sorry, but we had a plus on information after measurement with the computer tomography. So you are right: sometimes we need the original object so, if we find singular objects inside of the blocks we also go and do manual excavation. But we have so many finds that we need a second method, not only to work with conventional methods – with conventional methods we work very well – but we need this. Because we have about 16 tons of archaeological objects, so we have a lot also in original form and also in block form.

David Hallam: It might be an idea if we flick some of the questions we've got over to the panel session afterwards. I think there is lots of interesting ethical – what are we actually doing-type questions. Is it the information we're after or are we after the objects? Thank you very much.

A SCIENTIFIC STUDY AND PRELIMINARY EXPERIMENTS FOR ELECTROLYTIC REDUCTION OF CORRODED LEAD INLAYS ON JAPANESE LACQUER OBJECTS

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Abstract

During assessment of the Japanese lacquer collection in the British Museum, problems with corroded lead inlays were observed. Some of the lead inlays were heavily corroded and have become brittle and friable. The inlays have been analysed by surface X-ray fluorescence spectroscopy and corrosion products identified by X-ray diffraction and Raman spectroscopy as cerussite or hydrocerussite, probably due to complete conversion from lead acetate or formate.
A detailed study of five cross-sections taken from three objects was made using microscopy and scanning electron microscopy with energy dispersive X-ray analysis. The study has revealed that some of the inlays are coated with multiple layers of lacquer dusted with tin, silver or gold particles. Some of the original inlays may have been replaced with modern lead. Preliminary experiments have been undertaken to adapt a consolidative electrolytic reduction treatment to enable the treatment of these friable and highly deformed lead inlays. The application of Paraloid B72® with polyaniline as a conductive consolidant has also been tested.

Keywords: Lead, organic acids, corrosion, electrolytic reduction, Japanese lacquer, Polyaniline®.

Introduction

The collection of Japanese lacquer objects in the British Museum covers the 13th century to the present. The collection is housed in the Department of Asia's Lacquer Store where the environment is controlled at a relative humidity between 50% and 60% by an air-conditioning system.

Materials often used in the construction of Japanese lacquer objects include wood, basketry, paper, textile or leather as a substrate. Ground layers can be mixtures of clay, charcoal and lacquer. The upper layers usually consist of lacquer with possible inlays of metal, wood, mother of pearl, bone or ivory. (Webb 2000).

In 2006, condition assessments of the Japanese lacquer collection identified the problem of corroding lead inlays on 20 Japanese lacquer objects. Details of the problems, such as the loss of the aesthetic qualities of the objects due to colour change and deformation, the fragility and loss of the inlays and the health hazards posed during handling, have been previously described[1]. A few examples of the objects with corroded lead inlays are shown in Figure 1. Following the survey, in early 2009, the boxes were moved from wooden cupboards into drawers padded with Plastazote in a metal cabinet. Lead coupons on aluminium cups were placed in this cabinet as an indicator for the presence of acidic gases that can cause corrosion of the objects. This article describes

a. 1945,1017.394

b. 1952,0211.9

c. 1954,0417.8

d. 1945,1017.399

Figure 1. Japanese lacquer objects with inlay decoration, showing corrosion of lead inlays. a: 1945,1017.394, Writing box, 17th Century (?). W: 18.5 cm L: 26.0 cm H. 6.0 cm; b: 1952,0211.9 Writing box, 19th Century. W: 22.5 cm L: 24.5 cm H. 4.8 cm; c: 1954,0417.8 Lidded container, 19th Century. D: 6.5 cm H: 7.0 cm; d; 1945,1017.399 Lidded box, 13th or 17th Century (?). W: 15.6 cm L: 23.5 cm H: 11.2 cm

the analytical results for the inlay materials and the identification of corrosion products on the lead inlays. Preliminary experiments with a proposed remedial treatment are also described. The principal aim of the experiments is to inform the decision-making process that determines approaches to the preservation and/or conservation treatment of these objects[2]. Treatment would aim to reduce the risk of loss of material during handling and improve the aesthetic appearance of the inlays without compromising the stability of the materials used as a substrate or of the lacquer, which in most cases also covers the lead inlays.

Composition of the metal inlays

The metal inlays were analysed using X-ray fluorescence (XRF) spectroscopy and the results are listed in Table 1. The analysis presents semi-quantitative results for uncorroded metals. For corroded metals, lacquered or painted surfaces, the elements have been expressed as major, minor or trace.

It was found that the corroded inlays on all objects analysed were made of lead with some containing iron, copper and silver as impurities. The uncorroded metal inlays on the writing box 1945,1017.394 (see Figure 1a) and on the inside of box 1952,0211.9 (see Figure 1b) were made of tin-lead alloys. This is consistent with findings by Heath and Martin (1988) that the presence of tin improved corrosion resistance of lead inlays on the lacquer objects in the collection of the Victoria and Albert Museum.

Tin was not detected at all in the corroded metal inlays on the box 1954,0417.8 (see Figure 1c). Lead with small amounts of tin and silver, iron and/or copper was found in uncorroded areas of the inlays. Although iron was also detected in these areas, it was confirmed – by scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) as described below – to be present in the black lacquer covering the metal inlays rather than in the metal alloy of the substrate.

The XRF results showed that most of the uncorroded metal inlays used on the lidded box 1945,1017.399 (see Figure 1d) are silver-copper alloys with impurities of lead and gold, while the corroded inlays were found to contain lead with a small amount of zinc. This box contains a combined inlay of lead and silver where the join does not form part of the design, suggesting that the lead inlays probably are a modern replacement of the original decorations. The presence of zinc may also suggest that the inlay might be a later addition. It has not been confirmed if the zinc is present as metal or oxide. The presence of a zinc oxide could have resulted from the smelting of the lead ores (Craddock and Eckstein 2003). The presence of metallic zinc would be unusual because it was difficult to reduce zinc compounds to metallic zinc during the process of lead extraction in the past (Craddock 2008). Although it has been reported that zinc or its oxides have been deposited on lead during a conservation treatment (Costa 2005), in this case it is unlikely that such a treatment would have been carried out due to the composite nature of the objects. However, at present it remains undetermined if this ‘modern’

Object/Reg. No	Area analysed	Pb	Ag	Cu	Sn	Fe	Au	other elements
1945,1017.394 Writing-box with three monkeys with peach bough.	Corroded monkey	***	nd	trace	nd	nd	nd	
	Uncorroded monkey	35.8	nd	0.4	63.2	0.3	nd	
1952,0211.9 Writing box with chrysanthemums and leaves of mother of pearl and lead.	Corroded leaf on the lid	***	trace	trace	trace	trace	nd	
	Gold vein on a lacquered leaf on the lid	8.3	46.2	0.1	1.9	2.8	40.9	
	Uncorroded foil inside the box	4.9	nd	0.8	94.0	0.1	nd	
1954,0417.8 Small lidded box with poppy flowers and grasses.	Uncorroded lead flower on side of the lid	91.6	3.1	0.2	0.3	4.8	nd	
	Uncorroded lead flower on top of the lid	91.0	2.6	0.3	1.8	4.3	nd	
	Corroded lead flower on side of the lid	***	*	*	nd	*	nd	
	Partly corroded lead on side of the cup	***	nd	**	nd	*	nd	
	Gold lacquer on top of the lid	nd	nd	*	**	*	***	
	Red in the area of gold lacquer on top of the lid	***	nd	*	**	*	***	
1945,1017.399 Lidded box in the style of Kamakura period (13th c.), possibly later (17th c.) or with later repairs.	Deformed wing on the lid	***	nd	trace	nd	trace	nd	Zn
	Corroded area on wing 1 at a side of the box	***	nd	nd	nd	nd	nd	Zn
	Uncorroded area on wing 1 at a side of the box	98.0	nd	trace	0.2	0.1	nd	Zn (1.6)
	Uncorroded wing 2 at a side of the box	0.2	97.0	2.0	nd	trace	0.8	
	Uncorroded wing 3 at a side of the box	0.2	97.0	2.2	nd	trace	0.6	
	Uncorroded wing 4 at a side of the box	0.1	97.3	2.0	nd	trace	0.5	
	Uncorroded wing 5 at a side of the box	0.2	96.3	2.7	nd	trace	0.8	
	Uncorroded wing 6 at a side of the box	0.3	95.1	2.5	nd	trace	2.1	
*** major element, ** minor element, * trace element, nd = not detected								

Table 1. XRF results of metal inlays on Japanese lacquer boxes (wt.%)

replacement is the product of Japanese craftsmanship or from a European conservation procedure.

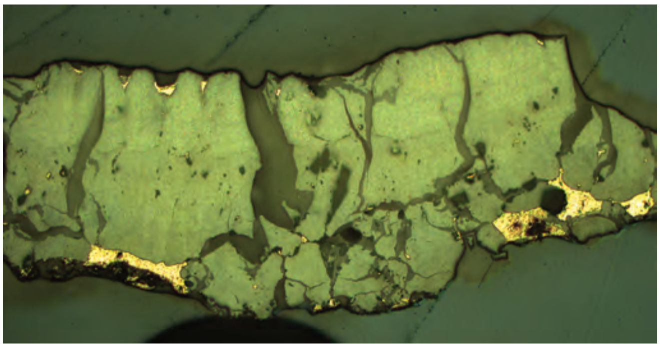


Figure 2. Photomicrograph of a cross-section taken from a lead inlay on Lidded box, 1945,1017.394 (see also Figure 1d). Image width = 1.36 mm.

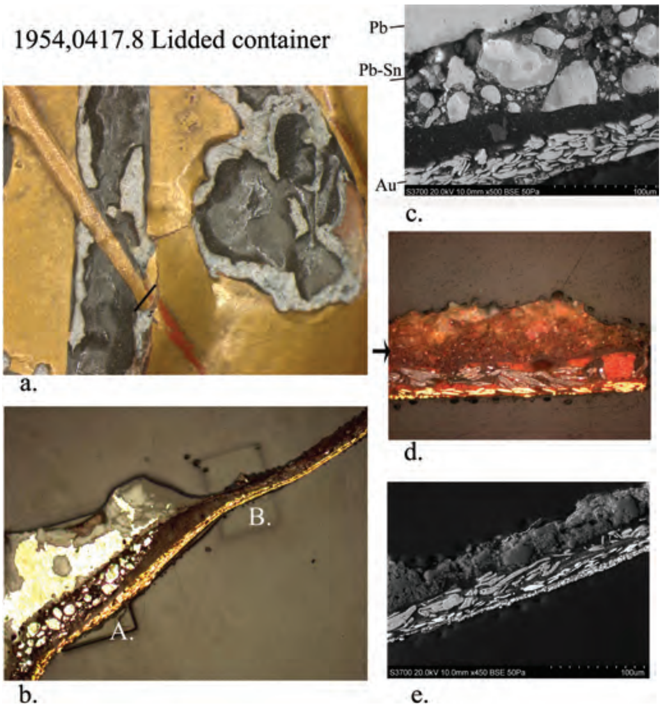


Figure 3. Lidded container 1954,0417.8 (see also Figure 1c). a: Surface detail (marked with arrow in Figure 1c) of corroded lead inlay with overlay coating; b: Photomicrograph of a cross-section taken from the area marked by the black line in 3a. Image width = 1.36 mm; c: SEM-EDX linescan of a cross-section of a lead inlay with gold vein decoration marked as A in 3b, showing the lacquer layers containing different metal particles; d: Photomicrograph of a cross-section from the area marked as B in 3b showing a clay foundation layer (marked with an arrow) and surface layer with metal particles. Image width = 0.27 mm; e: SEM electron image of a cross-section from the area marked as B in 3b, showing the presence of gold particles on the top surface and gold flakes and tin flakes (visible as strips) underneath as identified by EDX analysis.

Cross-section of the lead inlays and their overlay coatings

To investigate the stratigraphy of the metal inlays and the corrosion development, five small cross-sections were taken from three objects for detailed study; these are detailed in Table 2. The polished cross-sections of the metal inlays, some with a coating of lacquer, were investigated by microscopy, Raman spectroscopy, X-ray diffraction (XRD) and SEM-EDX. Examination of the cross-sections revealed that the degree of lead corrosion varied, from substantial metallic lead remaining in some inlays to only small areas of metallic lead remaining in others (see Figure 2 with a cross-section of box 1945,1017.399 from Fig 1d). The lacquer covering the lead inlays was found to consist of three or four layers with metal powders embedded (see Figure 3). There seems to be a ground layer of clay between the lead and lacquer in some of the samples, for example those from 1954,0417.8 and 1952,0211.9 (see Figures 4 and 5).

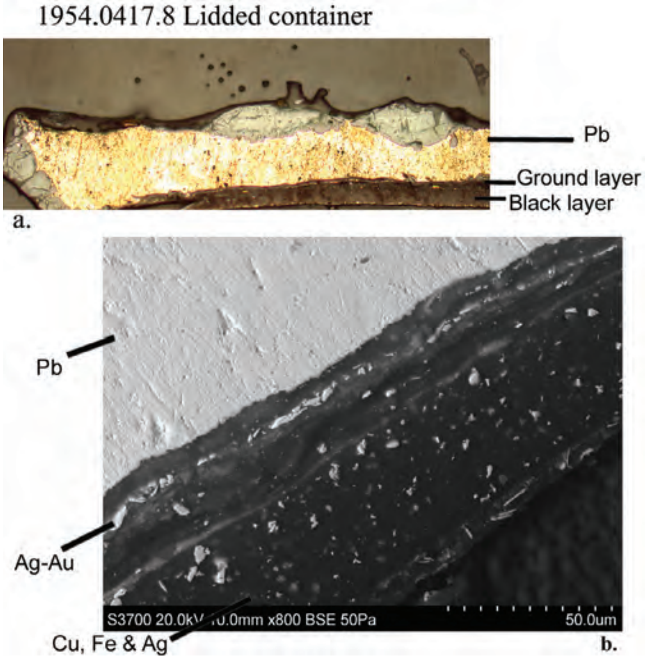


Figure 4. Black lacquer overlaid on the lead inlay on the cylinder box 1954,0417.8 (see also Figure 1c). a: Photomicrograph of the inlay and black lacquer. Image width = 1.36 mm; b: SEM-EDX linescan of the lead inlay and black lacquer, showing the lacquer layers containing different metal particles

SEM-EDX was used for elemental analysis and mapping. It was found that a variety of metal particles were embedded in the lacquer, appearing in the form of flakes (seen as strips of a regular size in the cross-section) and as coarse and fine grains, as shown in Figures 3-5. The lacquer layer for the gold grass decoration on 1954,0417.8 (see Figure 3a) was found to consist of four layers: the layer adjacent to the lead inlay contains lead-tin (Pb-Sn) alloy particles; the next layer iron particles; the third layer has gold flakes; and finally gold particles with a small grain size in the top-most layer (see Figures 3b&c). The grain size of the Pb-Sn alloy particles varies and their two-phase structure is evident (see Figure 3c). A red layer was observed underneath the relief gold layer for most areas but it was exposed in some places or applied over the surrounding areas. It seems also to consist of four layers, including a clay ground layer, then a red layer with tin flakes, a layer with gold flakes, and finally a top-most layer containing gold particles (see Figure 3d and e). The red layer was found to contain iron and oxygen by SEM-EDX, suggesting that it contains hematite. It has been reported that red lacquer used for Japanese lacquer objects was obtained by mixing *urushi* with mercury(II) sulphide (vermilion) or iron oxide (Tafejapan 2007). The clay ground layer was used to make the relief for the gold grass. The size and shape of the metal particles determined the texture or smoothness of the surface.

The black layer on this box (taken from an area indicated by an arrow in Figure 1c) is about 70 μm thick and probably consists of three layers, which were: lacquer mixed with gold-silver (Au-Ag) alloy powder next to the lead inlay, a middle layer containing iron powder and a top-most layer of the coating containing silver powder (see Figure 4). It has been reported that black lacquer used in Japanese lacquer objects was obtained by mixing *urushi* with iron powder and black soot (Tafejapan 2007). On the object studied here the layer with iron powder is in the middle and is the thickest layer.

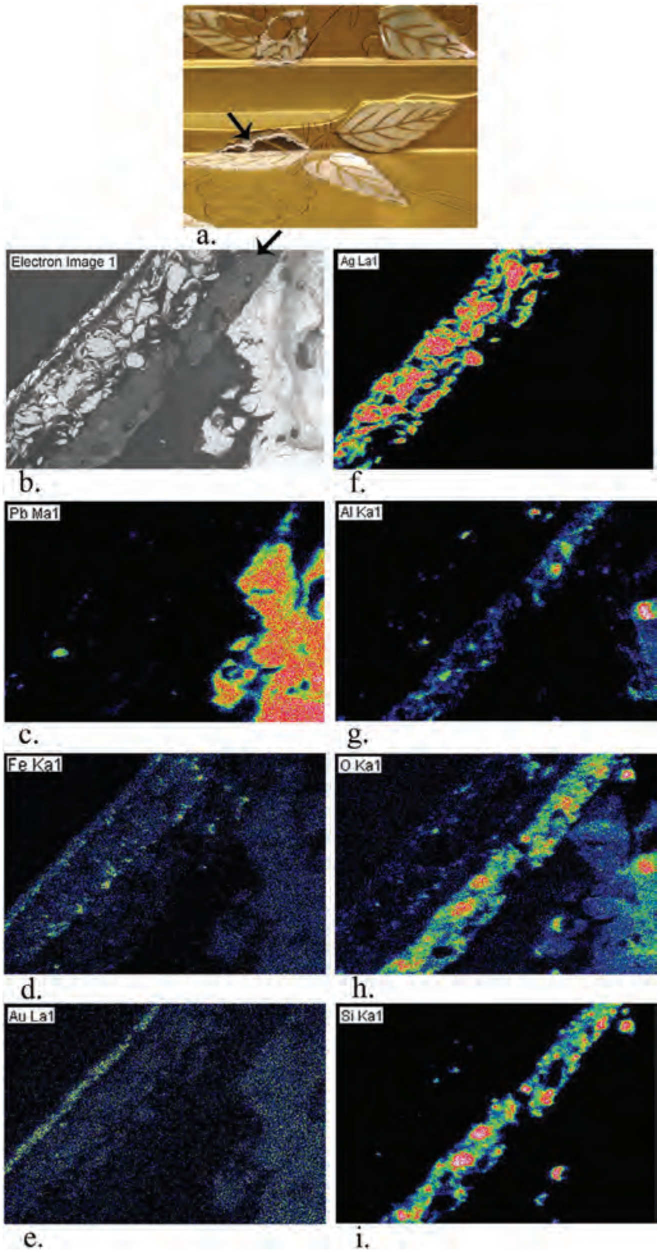


Figure 5. Lidded box 1952, 0211.9 (see also Figure 1b). a: Inside the box, showing corroded lead inlay; b-i: SEM elemental maps of a cross-section taken from the area marked by an arrow on 5a, showing gold particles dusted on the top surface, silver grains underneath and a clay foundation layer (5b marked with an arrow) on the lead inlay.

Some lead leaves on box 1952, 0211.9 (see Figure 1b) were coated with black lacquer, and in places this has been lost. Residual black lacquer was observed adjacent to the gold veins. These gold veins were found to be made of lacquer dusted with gold particles applied on top of the black lacquer, as shown in Figure 5. A sample of the black lacquer taken from the inside of the box (indicated by a white line in Figure 5a) showed that it was made of two layers, a ground clay layer (arrowed in Figure 5b) and a layer including silver particles of variable grain sizes. The presence of aluminium (Al), silicon (Si) and oxygen (O) in the layer confirms the presence of clay.

Corrosion of the lead inlays

It is generally accepted that materials in display cases or storage areas that emit carboxylic acids can cause corrosion of lead artefacts; with lead acetate or formate and lead carbonates (cerussite or hydrocerussite) as the commonly occurring corrosion products (Grzywacz and Tennent 1994, Tétreault, Sirois and Stamatopoulou 1998, Costa 2005). However, only cerussite or hydrocerussite were detected in the corrosion products of the lead studied here. Neither lead formate nor lead acetate were detected by either XRD or Raman spectroscopy (see Table 2). Raman spectroscopy was used for in situ analysis of the corroded lead and as a complementary technique for the identification of lead acetate or lead formate, as XRD is not very sensitive to these compounds.

The absence of lead formate or acetate on the objects studied could either be due to low concentrations of these gaseous acids in the storage environment, or to the transformation of any lead formate or acetate to the carbonates. It has been reported that carbonates alone were found in experiments when the acid concentration was low (Raychaudhuri and Brimblecombe 2000). However, in some areas of this store, the level of the acetic acid (between 88 and 3158 μg m^{-3}) exceeds the suggested acceptable level of 400 μg m^{-3} (Bradley and Thickett 1999). The lack of lead formate or acetate discussed here is more likely to be a result of their complete conversion to lead carbonates. It has been reported that lead acetate compounds tend to convert to lead carbonates with time and the conversion can be rapid in air without acetic acid (Niklasson, Hohansson and Svensson 2008).

Corrosion of the lead could have started at the edge of the inlay, as flaking was observed at these locations, see Figure 5a. Alternatively, deformation could have started in the middle of a leaf and then lead to the rupture at the edge. The deformation of inlays is a result of the combination of volume expansion of the corrosion and the mechanics between the materials used in the construction, that is, the positioning of the lead in or on the lacquer and any wear of lacquer coatings covering the lead inlays, if present. No difference in corrosion products between the internal and external surfaces of the lead inlays could be detected in the results from Raman spectroscopic examination of the polished cross-sections. There is no evidence that the materials used in the production of the objects were the source of the corrosive gases thought to be responsible for the deterioration.

Experiments for the treatment of corroded lead inlays

In the British Museum, consolidative electrolytic reduction (CER)[3] is an established method for the treatment of corroded lead (Watkins and Dove 2002, Berridge and Baldwin 2008). While the potentiostatic method[4] is currently being evaluated, the CER method

Object Reg. No	**1945,1017.394**	**1952,0211.9**	**1954,0417.8**	**1945,1017.399**
Sample descriptions	NA	Sample 1: lacquered corroded leaf with gold vein inside the box Sample 2: corroded leaf without lacquer	Sample 1: lacquered corroded leaf with gold vein and red painting on the lid Sample 2: corroded leaf covered with black lacquer on the lid	A small fragment from a corroded wing on the lid
XRD				hydrocerussite
Raman	cerussite	cerussite	cerussite	hydrocerussite

Table 2. Descriptions of polished cross-sections and identification of the lead corrosion products by XRD and Raman spectroscopy.

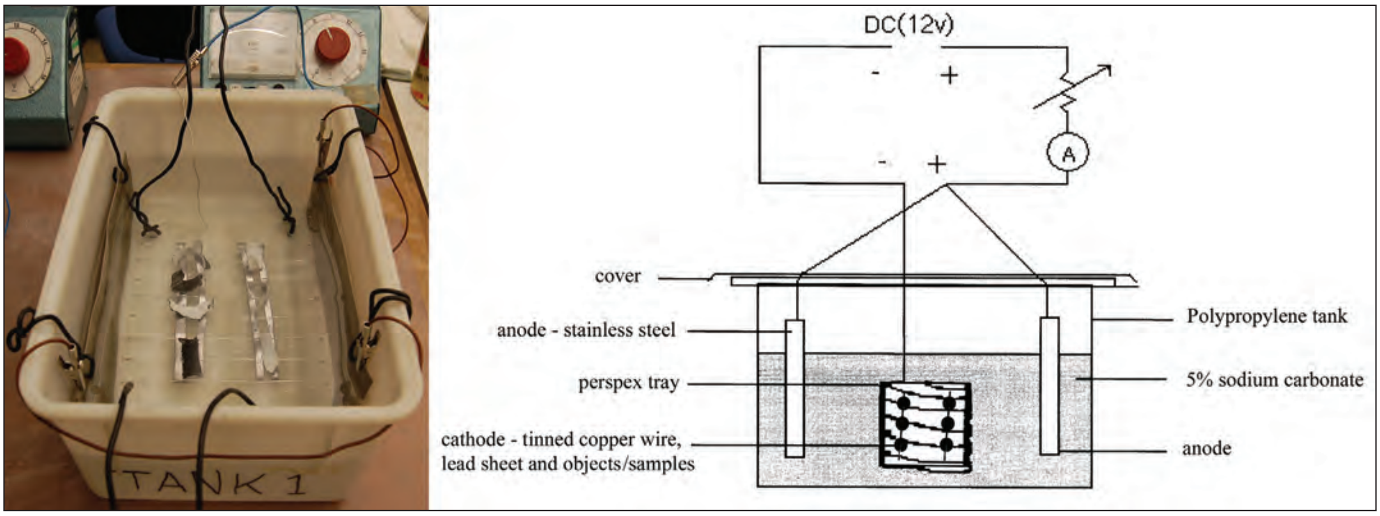


Figure 6. Photograph of samples undergoing CER and a schematic drawing of this set up.

was used in the experiments described here but it is expected that the materials and outcomes of these experiments are transferable to a potentiostatic setup. Neither method is readily applicable to these corroded lead inlays because of the composite nature of the objects with the metal in close proximity to organic material (both the substrate materials and remains of lacquer coatings in engraved or other surface details on top of the lead) and because of the fragile nature of the corroded inlays. To explore the possibility of electrolytically treating completely corroded lead, and to strengthen the lead inlays so that they could be lifted and separated from the boxes, the use of a conducting consolidant was proposed. Based on recommendations from Wolbers (2007) and their availability in the UK, two types of water soluble polyaniline, a conductive polymer, were selected. In this article we will use the following terminology: polyaniline I, an emeraldine salt from hydrochloric acid, and polyaniline II, an emeraldine salt from p-toluenesulphonic acid. Both types of polyaniline (1 wt%) were added to Paraloid B72 ® (35% in 50/50 industrial methylated spirit and acetone) to make it conductive and this was applied to artificially corroded lead samples. Nylon gossamer was embedded to provide additional strength. The samples were then treated using CER. In Fig 6, the set up can be seen in a photograph and a schematic drawing.

Artificially corroded lead and reduction experiments

For experimental work with reduction treatments, modern lead sheets of various thicknesses, decorated

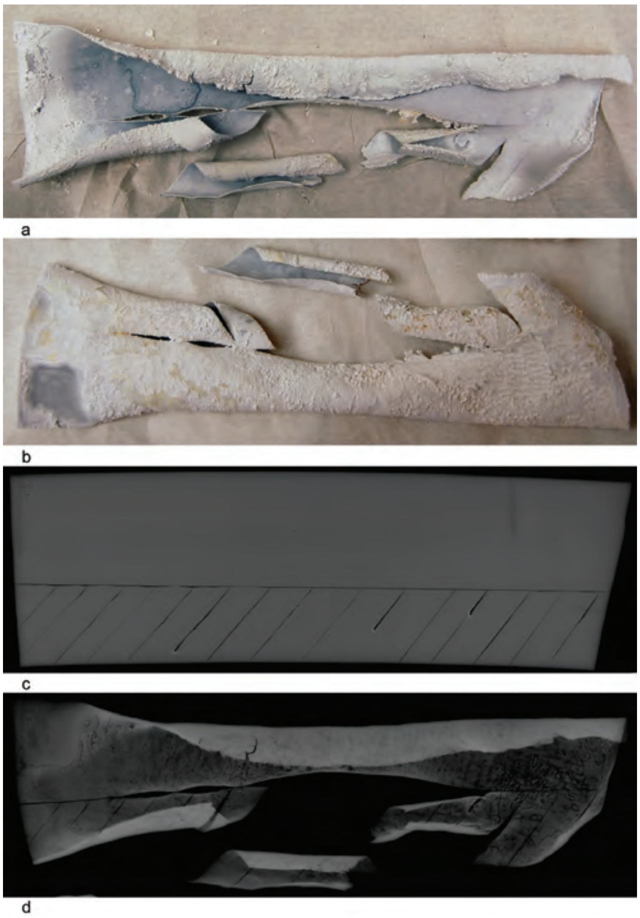

a
b
c
d

Figure 7. Photographs (front and back) and X-radiographs (exposures at 110 kV for 10 minutes) of the lead sheets before and after artificial corrosion.

with engraving, were placed in an enclosed environment for 18 months with a saturated solution of zinc acetate (Niklasson 2007). The development of the corrosion was monitored by X-radiography (exposures at 110 kV for 10 minutes) and analysis of the corrosion products using XRD, see Figure 7. X-radiography was chosen as a method to monitor the changes in readability of surface details and decorations such as engraving similar to that found on the objects[4]. The corrosion products formed on the lead sheets were identified with XRD as hydrocerussite, in accordance with the corrosion products found on the objects. To simulate completely corroded material without a metal core, pellets were produced using loose corrosion products from the artificial corroded lead sheets in a press using pressure up to 1 MPa. A series of CER treatments were conducted on the pellets and sections of the artificially corroded lead sheet (with a metal core). Pre-treatment of the samples was varied to include the application of Paraloid, Paraloid with polyaniline I, and Paraloid with polyaniline II either on the front or back, and also on both sides for the sheets.

Results and discussion

The results of the reduction of the series of pellets can be seen in Figure 8. The corrosion products in all the pellets appears to have been reduced to metallic lead, with the exception of a yellow powdery deposit still visible in some areas. The shape of these areas corresponds to the shape of the lead strips forming part of the grid of the cathode. This yellow deposit was analysed by XRD and found to be litharge, tetragonal lead(II) oxide. Similar deposits have been found previously on objects undergoing CER and a continued treatment normally reduces the litharge to elemental lead (Thickett 2003).

Surprisingly there was no apparent difference in the reduction when Paraloid, Paraloid with polyaniline I or Paraloid with polyaniline II was applied. It must be assumed that the corrosion products are semi-conductive and the reduction process is not obstructed by an isolating layer of Paraloid. There is a difference, however, between the blank pellet and the pellets with any of the consolidants (see Figure 8; compare sample 5 with samples 7-10). The reduced lead from the blank pellet was less coherent and broke up in sections during subsequent handling, whereas the other pellets retained their shape (albeit their surface was prone to minor loss of particles).

The results of the reduction of the series of corroded lead sheet samples can be seen in Figure 9. The corrosion products on these were found not to have been reduced in every case. In particular, sheets with a coating on both sides (see Figure 9 samples 3, 5 and 7) only showed reduction in areas where the consolidant appeared to be thinner, such as along edges. The sheets with a coating on one side (see Figure 9: samples 2, 4 and 6) showed complete reduction resulting in a more coherent layer of reduced lead. The blank sheet of corroded lead (see Figure 9: sample 1) showed a more-or-less complete reduction and also some loss of corrosion products. During the CER treatment on this sheet, the slightest development of hydrogen bubbles (usually an indicator of too high an applied current) appeared to cause the mechanical removal of the corrosion products from the surface, which is undesirable. It is particularly in this respect that the behaviour of the artificially corroded lead sheets seems to differ from that of corroded lead objects undergoing CER.

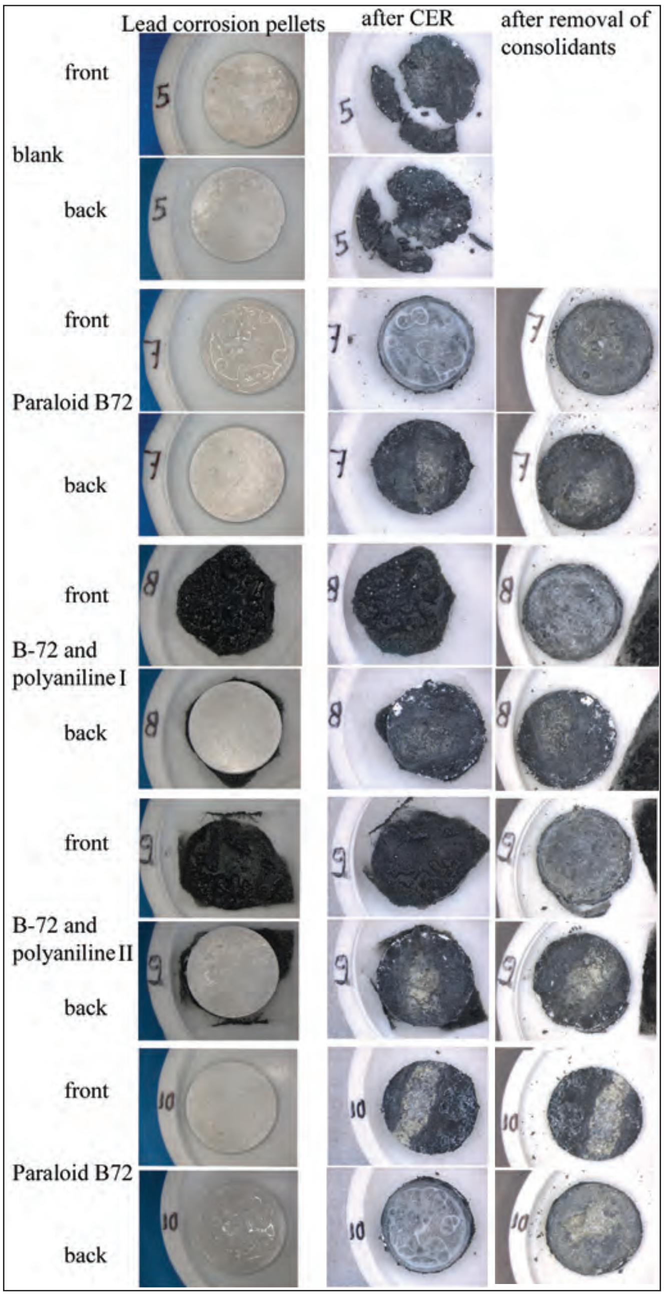


Figure 8. Photographs of the lead corrosion pellets before and after CER. The front was the side facing up during CER.

Conclusion

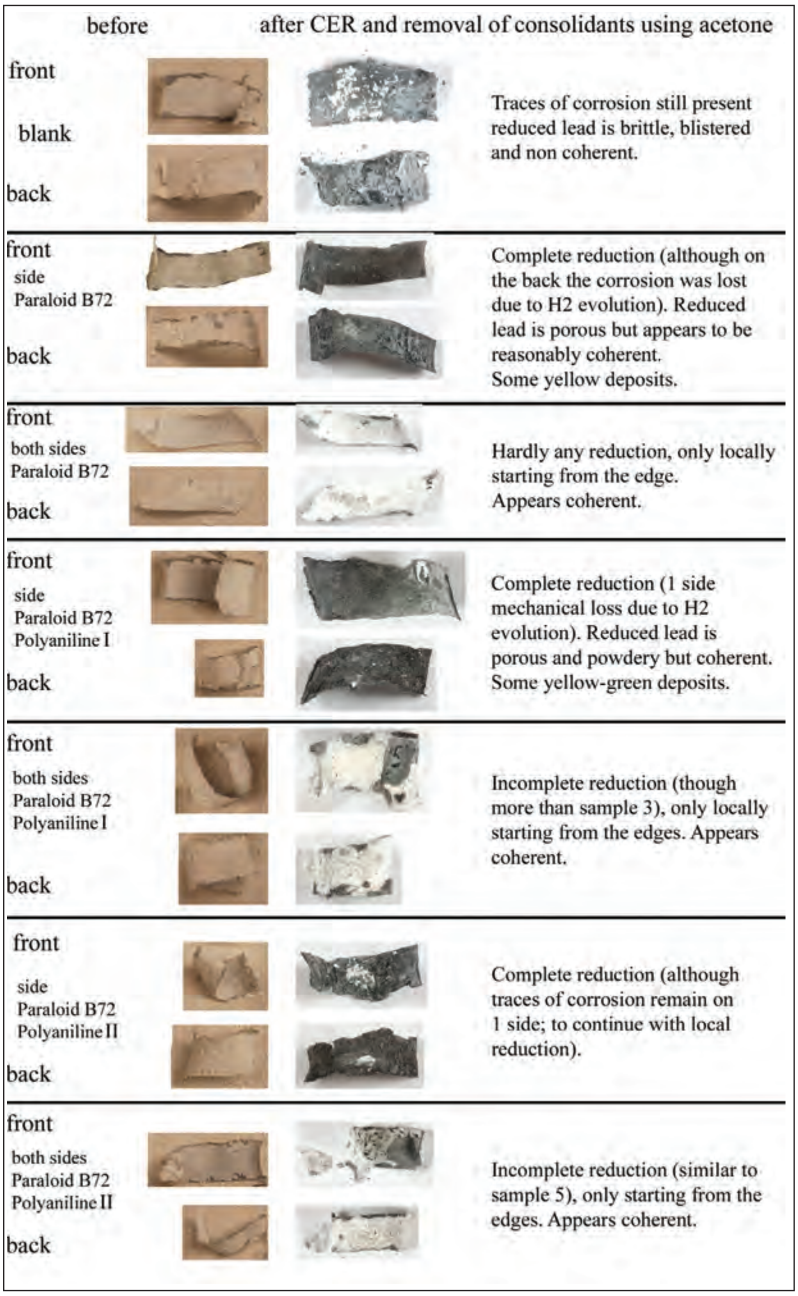
The metals used for inlay decoration on Japanese lacquer include alloys of silver and copper, alloys of tin and lead, and metallic lead. This study revealed that some of the inlays were coated with multiple layers of lacquer dusted with metal particles. The metal powders used included tin, silver, gold, iron and alloys of lead and tin. The study also suggested that replacement of some of the original inlays with modern lead may have been carried out. This study also confirms that lead is more prone to corrosion by organic acids than lead-tin alloys.

All corrosion products on the lead inlays were identified as cerussite or hydrocerussite; neither lead formate nor lead acetate were detected in the lead corrosion studied here. This result suggests that the conversion of lead acetate or formate to lead carbonates was probably complete.

The experiments with CER of artificially corroded lead in combination with a consolidant suggest that such a treatment is feasible as long as the corroded lead is not encapsulated entirely by the consolidant. The application of a consolidant during CER produces a more coherent layer of reduced lead, although this layer is porous and remains prone to some loss of small particles. There appears no obvious advantage to the addition of a conducting polymer to Paraloid. It should be noted, however, that these experiments were conducted on artificially corroded lead, and some difference in behaviour has been observed in comparison with naturally corroded lead objects undergoing CER. The corrosion layers on the artificially corroded lead are less coherent and more prone to loss due to hydrogen evolution compared to naturally corroded objects undergoing CER.

Additionally, for those inlays that retain an upper layer of lacquer that cannot be separated, further adjustment of the electrolyte will be needed to obtain a buffered solution that does not pose a risk of changing the appearance of the lacquer.

The analytical results for the materials used in the construction of these objects, and the results from preliminary experimental work, will inform further testing and the ongoing decision-making process that determines approaches to the preservation and/or conservation of these objects. Discussions have been initiated with the curator for the collection and a range of experts in the field of Japanese lacquer conservation. These discussions will include ethical considerations relating to conservation treatments for these Japanese lacquer objects in a Western collection. The authenticity of the lead inlays on the lidded box (1945, 1017.399) and the possibility of removing these inlays also will be addressed. If removed, these inlays could be used for further testing of the proposed use of a consolidant during electrolytic treatment.



Traces of corrosion still present reduced lead is brittle, blistered and non coherent.

Complete reduction (although on the back the corrosion was lost due to H2 evolution). Reduced lead is porous but appears to be reasonably coherent. Some yellow deposits.

Hardly any reduction, only locally starting from the edge. Appears coherent.

Complete reduction (1 side mechanical loss due to H2 evolution). Reduced lead is porous and powdery but coherent. Some yellow-green deposits.

Incomplete reduction (though more than sample 3), only locally starting from the edges. Appears coherent.

Complete reduction (although traces of corrosion remain on 1 side; to continue with local reduction).

Incomplete reduction (similar to sample 5), only starting from the edges. Appears coherent.

Figure 9. Photographs of the artificial corroded lead sheets before and after CER. The front was the side facing up during CER.

Acknowledgements

The authors would like to thank Timothy Clark, curator in the Department of Asia, for permission to take the cross–section samples. Thanks also go to Richard Wolbers (University of Delaware), Annika Niklasson (Chalmers University) and Nicola Newman (British Museum) for suggestions and useful discussion, and Ingrid Gerritsen, Julie Percheron and Jasmin Abfalter for assisting with some of the experiments.

Endnotes

[1] For details of the condition survey see Bellegem 2006. The problems associated with the corroded lead inlays were presented in a poster presentation (Bellegem 2007) and an oral presentation at the *Crossing borders* conference at the Victoria and Albert Museum London 30-31 October 2009.

[2] See Appendix C in Bellegem 2006 for a range of options or possible strategies.

[3] CER as a galvanostatic reduction process was developed in the British Museum in the 1960s. At present, a direct current power supply is used in combination with stainless steel anodes, a cathode formed by tinned copper wire and lead sheet onto which the objects are placed with a 5% sodium carbonate solution as an electrolyte. The constant current from the supply is set at 0.8 A dm^{-2} (of cathode surface area) at the start of the process and decreased as the reduction progresses. There is no specific control of the potential other than visual observation

relating to formation of hydrogen bubbles, in which case the current needs to be decreased before the loss of corrosion products occurs from the surface.

[4] Potentiostatic reduction came into use in the 1990s (Carradice and Campbell 1994, Degrigny and Le Gall 1999) and uses a constant potential. An advantage of potentiostatic reduction is that the voltage can be set to reduce specific corrosion products but without a risk of hydrogen evolution. Also, the use of 0.5 M sodium sulphate as an electrolyte would reduce the risk of damage in the event of power loss.

[5] X-radiographs of lead inlays on some of the objects showed the presence of such surface details more clearly than could be discerned by visual observation (Bellegem 2007).

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Materials

Acetone, Industrial Methylated Spirit, Sodium carbonate, Zinc acetate, Polyaniline – emeraldine salt from hydrochloric acid (Alfa Aesar), Polyaniline – emeraldine salt from p-toluenesulfonic acid (Alfa Aesar).
All from VWR International Ltd, Magna Park, Hunter Boulevard, Lutterworth, Leicestershire LE17 4XN

Nylon Gossamer Fabric
From Falkiner Fine papers
76 Southampton Row
London WC1B 4AR
Tel: +442078311151

Paraloid B72® (Rohm and Haas Ltd)
From Stuart R. Stevenson
68 Clerkenwell Road
London EC1M 5QA
Tel: +442072531693

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Maickel van Bellegem trained as a goldsmith and a metals conservator at the Netherlands Institute for Cultural Heritage in Amsterdam. After graduation in 2003, Maickel worked for Het Rijksmuseum, Amsterdam and also as a freelance conservator for other museums before starting at the British Museum in November 2005. He has a special interest in silverware and jewellery, Japanese metalwork, underwater archaeology, scientific analysis of materials and historical manufacture techniques.

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Q & A SESSION

David Hallam: Maybe I can slip in with one quickly - what is the lacquer and how susceptible is it to aqueous solutions and pH?

Maickel van Bellegem: What I understood from research that was done by Annelka Shelmann is that the photodegradation of the lacquer creates cracks and, depending on the solution, that partially lifts or penetrates into the lacquer and it causes blanching of the lacquer.

Valentin Boissonnas: Thank you Maickel very much. It is a problem we've been looking into recently as well. We also observed that some of these inlay are actually are covered by the last layers of this *urushi* layer during the making of these boxes, which actually is not necessarily making reduction easier – that is one thing. And it is sometimes impossible to take them away so we were looking into reduction techniques in situ and all the electrolytes that we used they all stained the degraded lacquer surface so we have to look into sealing agents for the lacquer in order to proceed with the reduction in situ and use gels also to contain the electrolyte.

Maickel van Bellegem: It is something that I considered as well and I think definitely also the lifting of the inlays, it is not possible on all of them. I think there's only a few – for example the one with the monkeys, because they are already lifting, bubbling and delaminating. I think if you are able to strengthen them and keep them together during the lifting process, I think it is a possibility. With regards to treatment in situ, with Ingrid Gerritsen I did some tests to make a gel and we managed to get some reduction going but it was still a problem to remove the gel. So I think that is also something worthwhile looking into, but it needs more work.

Karl Knauer: Thanks for taking this on Maickel, that's really scary looking stuff and I'd love to know what you find out. But I was wondering if you had any idea what the original color would have been and if you found any traces of a deliberately applied patina anywhere like a sulfide layer? But that's probably all gone – right?

Maickel van Bellegem: I think on the corroded lead inlay I don't think it is possible to see or measure much of that. I think it is probably the top layers would have been lacquer. I think definitely also from some objects, because of the corrosion, I think that top layer of lacquer is either nearly completely or partially lost. So I think on many pieces the actual original surface, which would have been the lacquer, is gone or in some cases there are still traces of lacquer.

Stéphane Lemoine: We observed that freshly reduced lead – kind of genuine metal is very reactive to pollutants – to components in the atmosphere. How do you plan to protect them against this aggressive context? Secondly, if acetates are coming from the box itself, what could you do?

Maickel van Bellegem: It was a big discussion whether or not the acetates were coming from the materials in the box themselves or from the environment. We did do measurements with diffusion tubes and we placed some of them inside objects expecting to see a build-up inside the object if they would be coming from the materials themselves. We did not find that. It was also only in one of the cupboards at a level which was above recommended levels of acetates, which are supposedly acceptable. We actually did not really identify what the source was but I felt that rather than to spend lots of time on really trying to identify it, I thought it was just much better to get them transferred into metal cabinets. I think that is just the safest. I think that is what for me is the strongest indication that it is not the objects themselves – is the fact that the Victoria and Albert Museum have discovered the same problem on their objects in, I think it was 1987 or '89 – Diana Heath did some work on all this issue and treated a box, which we were able to revisit, and that had not re-corroded.

Paul Mardikian: I've got really strictly no authority on this topic so I'm just asking the question that I have in mind and making comments: I would feel like wetting that artifact or if you are working in situ with any kind of gel or any kind of substance might interfere – like we had – one of the conservators made a comment about that. Is there a method to just clean them? I mean get back to what would be an aesthetically acceptable way, using maybe laser? Have you tried? I don't know if that would work. Would that be something that has been tested?

Maickel van Bellegem: Not that I know of.

Paul Mardikian: I don't know if that would be applicable on a white surface. Usually that is the other way around.

Maickel van Bellegem: But that would be removing the corrosion products.

Paul Mardikian: And that would destroy what you want to keep, right? Ok, so that would not work.

Maickel van Bellegem: That is definitely one thing that we showed with the radiography is that within the bulk of the corrosion products, details of the decoration are still there. And by using a reduction technique, you are able to increase the readability of those decorations.

Paul Mardikian: So you're stuck.

John Scott: A couple of things to wonder - One is I suppose there is some relationship between this and what Tom [Chase] and other people were doing as early as the '70s with restitution of lead in coins and so forth that were published I think in '74, in that one publication. There was something to do with the iron resins, something like that. The other thing I just wandered – was, have you seen any material of the same type that was not corroded, that was still in good condition, that would help you evaluate what you were looking for in terms of results?

Maickel van Bellegem: I think that is a very good point. The problem is that, I think visually it is not possible to distinguish between a nearly pure lead inlay or a lead-tin alloy. We found on the collection at the British Museum that all the corroded ones are nearly pure lead whereas the non-corroded ones are a lead-tin alloy. I think if that is related to the box, which has the silver and the lead inlays – we think that the lead inlays are possibly later repairs. I think there is no clear overview of the development of how lead inlays were used, whether location-wise or time-period. I think that is an interesting thing.

Tom Chase: The box you showed with the three monkeys had two inlays in a lead-tin alloy and one inlay in pure lead. This means to me that there was some visual difference when that thing was made, otherwise they wouldn't have gone to this extent- I don't know what it would be. I have seen boxes with what look like lead inlays that look intact. They may have a very thin layer of lacquer over them, which is preventing corrosion. It is a very interesting general question. I think you've really got to collaborate with the Japanese and talk to them seriously about this kind of thing. There are active lacquerers in Japan working in traditional techniques as well as conservators, so that would be a good excuse for a trip to Japan!

Maickel van Bellegem: I'll try to sell it to the museum to get some money for it!

Innovative Techniques

Chair: David Hallam
Panelists: Guillaume Rapp, Nicole Ebinger-Rist, Maickel van Bellegem

Jon Leader: Great papers, very interesting including all of them outside of my area such as the lacquer. Very, very interesting and quite innovative. I figured that pretty much paid for coming to the conference right there not to say the other papers were not excellent as well but there you go. On the computer tomography, very interesting. A couple of different things come to mind. One is the additional applications beyond what you are actually looking at. The ability to prioritize is extraordinary important both for the archaeologist in terms of cost and for the conservator and off course in terms of the collection. So being able to get a heads up, or prequel if you will, of what is actually in the block is very important and off course the ethics of the situation are still tantamount, they do not disappear regardless. Getting that point across as Paul pointed out as many people pointed out will be very important for us who are stuck in an administrative role specially to our funding agencies. They will say well you have it you're done and off course the reality is that you are not done. You have the beginning not the end point - not your problem. Very pleased you came up with what you did. In terms of forensics a whole other area, and I thought it was quite nice you showed a burial. In Europe burials are burials, in the United States because of some of the issues of indigenous ethics, burials are not simply burials and therefore the ability to actually go through the levels and taking a look at the organics, taking a look at the additional materials in a non-destructive format. In other words you can take it out, hold it in place, go through it and move on is extraordinary important. This is the type of things that is probably negotiable whereas scalpel work and taking it down to the bone is often not so that's very, very important. You can actually do sexing, age related all the usual forensic statements off of that material as well so that all very, very good and I would really see that advance. I was also very pleased by your statement that the kVp you had not maxed it out that's also extraordinarily important. I think we are going to standing on tender hooks until you are totally done and I am very exited to see what the final results are done and I just wanted to command you for the great job that was thank you.

Claudia Chemello: Nicole this is for you and thank you for such a wonderful visual paper that was really interesting. I think we might not have a job anymore but my question is really about objects with inscriptions. Have you done anything like that like that yet like coins, something with an inscription? Would you be able to read that with this technique?

Nicole Ebinger-Rist: You saw this cruciform engravings and at the early Medieval [period] they also have sometimes letters on the back of the object and we can see these inscriptions, and this example from the engravings with the cruciform is an example that if on the object we have inscriptions we can see these. We are sure about this.

Claudia Chemello: Ok, I treat a lot of coins on site and they take forever to clean manually so that would be so fast to be able to get the date, and this is what they [the archaeologists] want.

Nicole Ebinger-Rist: We have examples of coins and we see the letters on the coins and also when the coins are badly preserved we have also the possibility to see the surface.

Claudia Chemello: Wow, thank you so much.

Virginie Ternisien: Is there any plan to present this information to the public?

Nicole Ebinger-Rist: The problem is that the objects are still in blocks so we have no way to present them to the public. In April next year we will have an exhibition to show our virtual results. Please keep in mind we have such a number of finds, we have 1300 graves so we have from this gravesite 32 000 single objects, so if we want to show these objects to the public we have this possibility, but we have such a lot of findings that we need to use this method to investigate inside the blocks for the archaeologists. I want to say that we are the operators of the software so we, as conservators, are able to interpret what we see and our knowledge of the materials is also very important to identify these materials. If we do not have the knowledge and if we are not conservators it is almost impossible to interpret the discoloration of the soil for instance. For the exhibition I think it is very interesting to show the public the many possibilities we have with this technique. I know that excavating these blocks manually is very important but it is also important to find new solutions to work and also to present our work because this technology is very important for funding for projects. As archaeologists and conservators we work together and it is a team project and I have no fear that we will lose our work. For exhibition, we have the real objects as well as the virtual information that we can present to the public.

James Crawford: Again this is for you Nicole. Brilliant, it was amazing. It is a bit of a repetition on some of the remarks. I believe it will add another complementary technique. I do not think it will put conservators out of employment it might actually put them onto other tasks which otherwise might not have been focused on. From exhibition I think it will also involve a bit of public education as you now don't have an artifact in front of you to look at but yes we are getting much more information during the presentation, purely because it is visually striking similar to the 3D laser scanning such as Tonny's work on the Rodin, and it just conveys so much information so much more quickly. Also on a more global perspective I think this really pays dividends particularly to the approach to archaeological iron for people not to excavate and go down to the actual artifacts and there are certain school of thoughts whereby you impregnate, for example, with epoxies. There are other school of thoughts and countries where you leave that and then investigate later when technology has developed and this is that point in time and I think it is fantastic.

Nicole Ebinger-Rist: Thank you.

David Watkinson: Nicole, an interesting talk well presented thank you. Just a quick question is there any indication at this time how this might influence the way archaeologists publish the information about sites? They've got standardized formats they've been using for many years but clearly there is a lot of information in the moving image so they are looking towards web publications or is it still hard copy? I don't know if you reached that far yet.

Nicole Ebinger-Rist: Yes thank you for this question because now we plan and we develop our own online publications. Now we have this 3D information about the objects and also it is not good to print it on paper, so our goal is to present all these results in on online publication and after five years we have one more year to publish this e-book, this is our goal.

David Watkinson: Thank you.

Molly Carlson: Nicole, do you think that there is a possibility for the information you are collecting to transfer to the type of machine that takes like a laser scan and then can make a physical reproduction of an artifact, can they talk together?

Nicole Ebinger-Rist: I hope I understand the question the right way. The information we have from the computer tomography we have the inside and outside structure and we have a special format from the computer tomography but we can change it to a CAD data set, and we can make the same things that our colleagues presented yesterday that we can make ready prototyping. We have a project where we make reproductions of objects, its a very old wooden wheel, and we cannot put it in an exhibition and therefore we have a double information with its outside and inside structures.

Molly Carlson: Thank you.

David Hallam: OK we might try to move to the other speakers.

David Hallam: Michael have you though of using non-aqueous solutions in your reduction?

Maickel van Bellegem: No, good point. I think the vulnerability of the lacquer depends on its condition and which solution you can or cannot use. Yes it is still something we still need to look into.

Ian MacLeod: Maickel, I was wondering whether you looked at very fine sponge or just high humidity [as a source of moisture], obviously not high enough to upset the lacquer, but just relying on microscopic amounts of moisture condensing on the reactive metal surface to provide you with electrical connection so that it's not a wet reduction, but a moist reduction, given that you can get corrosion happening with dew formation whether or not you've tried, reduction at relative humidities lower than you need for dew, i.e. water, formation ?

Maickel van Bellegem: I have not tried it, it might be possible with a sponge. I think one on my concerns with it is that if you just start from the surface, how will you be able to tell how far the reduction has gone through and will it really reduce into the depth of the material.

Lisa Young: I just had a question about the CT scanning because I had access to a CT scanner and was able to scan some objects. When I got the data back it was very hard to interpret the data and I did not have the software to manipulate the data that had already been collected so maybe you can address some questions and what we could ask people that are willing to do the CT scaning for us, like medical organizations and museums who have CT scans, if we were just to give them an object and do the scans. What kind of questions would be good to ask them to get the data back that we need as a conservator?

Nicole Ebinger-Rist: The key is to be able to work by yourself with the software and get these measurements back to our lab and interpret the results. We know how to use the software [conservators and archaeologists] which is critical. Hopefully I have responded to your question I am not sure.

Lesley Frame: Actually there is a free program you can download called Image J and you can take scans, like if you are given individual slices, this program allows you to stich them back together and scan through them so you can download this program for free. It might even be a NIST program.

David Hallam: What I think is happening here is that we are redefining what a conservator does and I don't think we should think that conservators only work in the physical they can also work in the digital.

Johanna Wolfram: A question for Michael. Was the lacquer fine in the metals store, or was it too dry for the lacquer?

Maickel van Bellegem: The metal cabinet is in an annex of the same store, so the relative humidity is the same [the RH is between 50 and 60%].

POSTER SESSION ABSTRACTS

NON TOXIC CORROSION INHIBITORS FOR THE CONSERVATION OF BRONZES AND GILDED BRONZES EXPOSED TO THE ATMOSPHERE

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Abstract

Corrosion inhibitors, associated or not with protective coatings, may be a good solution for planned conservation activities in the case of bronze and gilded bronze works of art. Studies in the cultural heritage area have been mainly focused on the use of Benzotriazole and its derivatives, but they are toxic for people and the environment. In this work, non-toxic corrosion inhibitors for bronzes and gilded bronze are investigated. The inhibitors have been tested both on non-patinated and patinated bronzes, reproducing Renaissance leaded bronzes. The experimentation includes electrochemical measurements in artificial rain and 3.5% NaCl solution, as well as short-circuit tests performed on gold/bronze couples. Materials and surfaces have been characterized with and without inhibitive treatments.

NON-INVASIVE INVESTIGATION OF POLIGEN®ES91009, A WATER-DISPERSIBLE ORGANIC COATING ON METALS WITH REFLECTANCE-ABSORPTION INFRA RED SPECTROMETRY

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Abstract

Poligen® ES 91009 (BASF) is a material which has recently been tested as coating in the field of conservation of metals. Ethylene-methacrylic acid copolymers can be partly neutralized and are commercially available as their sodium, potassium, ammonium or *alkyl-ammonium* salts (which is the particular case of the material under study). Films of the coating material applied with the usual practices (brushing, immersion, spraying) on rough metal surfaces contain geometric irregularities responsible for certain distortions on reflectance FTIR spectra; this makes both qualitative and quantitative measurements from such samples difficult.

DRY ICE DUSTING CLEANING TRIALS OF MUNTZ METAL SHEATHING FROM THE CLIPPER SHIP SNOW SQUALL

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Abstract

The American Clipper Ship *Snow Squall*'s (1851-1864) bow section retains 'Muntz's 24 Patent' brass and other brass alloy sheathing that varies in condition from good to very poor. The surfaces are heavily stained with copper alloy and iron corrosion products. Sheathing and wood samples were evaluated before and after systematic cleaning with the Dry Ice Dusting technique. Temperature, dwell time, nozzle shape, distance from surface and pre/post metallographic observations and application cautions are reported.

COLORANDO AURO: EXPERIMENTS AND ANALYTICAL INVESTIGATION OF A MEDIEVAL COLOURING RECIPE ON GILDED PLATES

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Abstract

The issue of colouration of metals in medieval art objects has often been ignored, leading to inadequate, often unjustified and irreversible restoration treatments. The situation is the same for gilded silver objects. In conservation, a gilded artefact is considered a silver alloy covered with a gold layer. It is generally considered unlikely that gold would have been given a chemical surface treatment in order to change its colour or tone. At the Royal Institute for Cultural Heritage (KIK-IRPA), a study was undertaken of the Our Holy Lady Shrine of Huy (Belgium), a prestigious 13th century masterpiece of Mosan art and one of the four major shrines of the Colligiate of Huy. The study included establishing an appropriate method of conserving the gilding without altering the original colouration. It was discovered that by means of a special recipe, reported in Theophilus' (12th century) and Cellini's (15th century) writings, the colour of a gilded silver surface could indeed be changed into a warmer tone of gold. Based on these results, an extended project was set up with three aims: to rediscover all the details pertaining to these ancient colouring techniques; to investigate to what extent environmental parameters, such as relative humidity, temperature, ultra violet light and the presence of Chlorine and Sulphur influence the coloured surface; as well as to establish the most appropriate conservation approach for these materials.

THE TREATMENT AND DISPLAY OF A 16TH-17TH CENTURY WROUGHT IRON SWIVEL GUN RECOVERED FROM A MARINE ENVIRONMENT

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Abstract

Marine artefacts are often excavated to prevent looting. Therefore conservation procedures must be appropriately planned & budgets adequate for the labour & resource intensive processes required to keep marine artefacts stable in their post-excavation environment. This poster describes a low-budget re-treatment of a 16th-17th century iron swivel gun recovered from the Mediterranean off the coast of Malta. The practical steps of alkali washing, rinsing, accelerated drying, surface cleaning, surface consolidation, as well as environmental control & monitoring of the gun are outlined. Monitoring was carried out over a 21-month period at RH below 30%, & results suggest that preventive conservation measures, with a desiccated environment using silica gel, may provide sufficient stability for the artefact during display. A passive exhibition case with a pressure differential compensation device (PDCD) will provide a low air exchange rate, prolong desiccant life span, reduce intake of aerosol pollutants & minimize maintenance.

IRON FROM LONDON'S WATERLOGGED SITES: THIRTY YEARS ON

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Abstract

Museum of London conservators have worked on iron objects from excavations of waterlogged sites over the last 30 years. In the 1980s, treatments such as electrolytic reduction and alkaline washing were used for selected material. Suzanne Keene and others were instrumental in encouraging the treatment of iron from these sites which produced objects in excellent condition. Current practice in the UK is less interventive – most iron is not treated and dry storage is used to slow down corrosion. This poster outlines conservation policies and treatments of iron at the Museum of London since the 1980s, reflecting practice in the UK as a whole. There has also been an active programme at the Museum of surveying iron objects in our archaeological archive. Preliminary results suggest that a large proportion of untreated finds from waterfront sites are in good condition. Full results of the surveys will be published in due course.

NEW MATERIALS FOR TREATING FERROUS METAL OBJECTS: A CASE STUDY OF A 19TH CENTURY PAINTED, TINNED-IRON SPICE BOX FROM THE WINTERTHUR MUSEUM

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Abstract

This study focuses on the treatment of a spice box from the collection at the Winterthur Museum. Spice boxes, used to hold spices as well as trinkets, were once a common household item in America. The painted surfaces of the Winterthur spice box presented challenges for consolidation and cleaning. Flaking paint on the exterior was stabilized with an acrylic consolidant containing a corrosion inhibitor. The exterior surfaces were cleaned using a solvent based cleaning system constructed from a silicone crosspolymer that contained a small water phase. Corrosion on the interior was reduced using a combination of mechanical and chemical methods including a solvent-based gel containing a strong chelator for ferric ions. This treatment demonstrates the engineering of cleaning and corrosion reduction systems through the application of scientific analysis and materials science. It contributes to the field through the introduction of novel approaches for conservation treatment of degraded paint and corroded metal.

CONSERVATION AND RESTORATION OF A WWII CB-20 SUBMARINE

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Abstract

The CB-20 Submarine belongs to the class of pocket/midget submarines built for the Italian Navy in World War II. The submarine is designated CB-20 meaning ‘corsiero tip B, number 20’. Manufactured in 1943, the submarine was seized and turned over to the Yugoslav Navy after the Second World War, after which it became a P-901 submarine. The CB-20 is the last surviving, complete submarine out of a series of 26 of this type ever produced. Other submarines of this class exist but are incomplete, and usually only the hull survives. In 1959, the CB-20 was donated to the Technical Museum in Zagreb, Croatia, and is the largest object on display in the museum’s Transportation Gallery. This project describes the conservation and display of the CB-20 submarine.

TETRA ALKYL AMMONIUM HYDROXIDE SOLUTIONS – A BETTER WAY TO DESALINATE IRON FINDS?

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Abstract

Post excavation corrosion of terrestrial archaeological iron artifacts is a well-known problem in conservation [1]. Experience shows that the corrosion stability of iron finds can be significantly improved by the extraction of chloride ions from the corrosion layers [2]. To effectively improve long-term corrosion stability all chloride-containing phases, even the insoluble but metastable *akaganéite*, β-FeO(OH), have to be removed. Currently, immersion treatments in aqueous, alkaline solutions are commonly used to achieve this goal. However, particularly long treatment times require further refinements of established methods. The desalination in aqueous and/or methanolic tetra methyl ammonium hydroxide (TMAH) solutions was tested on synthetic *akaganéite* as well as on Roman iron finds and compared to the common desalination treatments using aqueous sodium hydroxide solution with or without the addition of sodium sulphite. Results indicate that alcoholic TMAH solutions neither accelerate desalination nor improve overall chloride extraction efficiency. However, aqueous TMAH solutions promise higher extraction efficiency due to an accelerated decomposition of *akaganéite*. Nevertheless, the possible damage to treated artifacts by partial dissolution of the metal and corrosion layers requires further research.

CONSERVATION OF LT. DIXON'S POCKET WATCH RECOVERED FROM THE H.L. HUNLEY SUBMARINE (1864)

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Abstract

The confederate submarine *H.L Hunley* made history on the night of February 17, 1864 when it became the first submarine to sink an enemy ship in combat. After its successful mission, the *Hunley* mysteriously vanished with its crew of eight. The hand-cranked iron vessel was located in 1995, off the South Carolina coast, but was not raised from the ocean until the summer of 2000. In 2001, a multi-disciplinary team composed of archaeologists, conservators, and anthropologists excavated the crew compartment and uncovered the remains of the doomed crew along with numerous artifacts and personal belongings. Among those artifacts was an ornate gold pocket watch that belonged to the commander of the vessel, Lt. George Dixon. The conservation of Lt. Dixon's pocket watch represented a complex and challenging conservation task. Due to the presence of composite materials a very careful x-ray analysis was conducted prior to opening the watch. A plan to open the watch was devised in collaboration with Daniel Nied from the York Time Institute. Once the watch case was opened, it revealed that the hour, minute, and second hands were still in their original positions. Further disassembly of the watch's inner movement was initiated to provide archaeologists access to data that may reveal when the watch stopped, and allow treatment of its most fragile components. Thanks to an exemplary collaboration between archaeologists, clock specialists, and conservators it is now possible to exhibit this incredible artifact and allow it to be studied and interpreted.

EVALUATION OF SODIUM NITRITE AS A CORROSION INHIBITOR FOR USS MONITOR ARTIFACTS

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Abstract

The treatment of 210 tons of material from the Civil War ironclad USS *Monitor* at The Mariners' Museum (TMM, Newport News, VA) presents conservators with many challenges related to conserving industrial waterlogged composite materials. Sodium nitrite ($NaNO_2$) was suggested and evaluated for TMM by CCTechnologies /DNV Columbus (CCT), a corrosion engineering firm, as a replacement for highly alkaline sodium hydroxide storage and desalination solutions used for large artifacts. The advantages offered by sodium nitrite treatment as presented by CCT are:

- neutral pH (less aggressive to organics);
- low concentration of solution used (100ppm, i.e. 100mg/l or $1,45.10^{-3}$M), reducing cost and disposal factors;
- effective on multiple metals (iron, copper and lead).

Conservators at TMM in conjunction with the Department of Biology, Chemistry and Environmental Sciences (BCES) of Christopher Newport University tested $NaNO_2$ to answer the following questions:

- Is $NaNO_2$ an efficient corrosion inhibitor in the presence of chlorides and corrosion products, i.e. on real artifacts?
- Will O_2 oxidize NO_2 into NO_3 and lead to less efficiency?
- Does $NaNO_2$ help in extracting chlorides from the metal?

HISTORIC IRON STABILISATION TREATMENTS: A PUBLIC SURVEY

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Abstract

This research project explores the influence conservation treatments can have on the appearance, perception, and interpretation of historic iron. There are a variety of materials available to conservators and according to the survey undertaken for this project the most common are:

- Paraloid B72
- Microcrystalline wax
- Tannic acid
- Phosphoric acid Part of the project included testing the materials to evaluate their effectiveness at preventing iron from re-corroding in poor environments. The most effective materials were microcrystalline wax that had been applied hot and Paraloid B72.

In conjunction with the testing of conservation techniques a public survey was undertaken in a social history museum, the Museum of London, to learn about how treatments affect the public's perception of objects. The stabilisation treatments were used as examples and the public's reaction illustrated that their perceptions were influenced by conservation treatments.

TESTING FOR LOCALIZED ELECTROCHEMICAL CLEANING OF TWO 17TH-CENTURY GILT SILVER DECORATIVE OBJECTS

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Abstract

A pair of amalgam gilt sterling silver *Stags* (Augsburg, circa 1680-1700) by Johann Ludwig Biller the Elder from the collection of the J. Paul Getty Museum have been susceptible to active tarnishing and have been cleaned three times at the Museum since 1986. Treatment reports describe that acidic thiourea was applied locally by swabbing and water rinsing. After each treatment, the *Stags* re-tarnished rapidly on display, and for the past eight years they have been stored in a sealed Corrosion Intercept® zip-lock bag with dry silica gel and activated charcoal (10% RH, 21ºC), yet they continue to re-tarnish. The thiourea treatments are suspected to increase their susceptibility to rapid tarnish. As an alternative treatment, electrochemical reduction is being considered. Electrolytic techniques have been developed for tarnish removal of silver sulfide and the reduction potential has been previously studied. Described here is a study to test electrolytic cleaning of gilt metal coupons made out of the sterling alloy. Preliminary results from localized testing on the *Stags* have also been presented.

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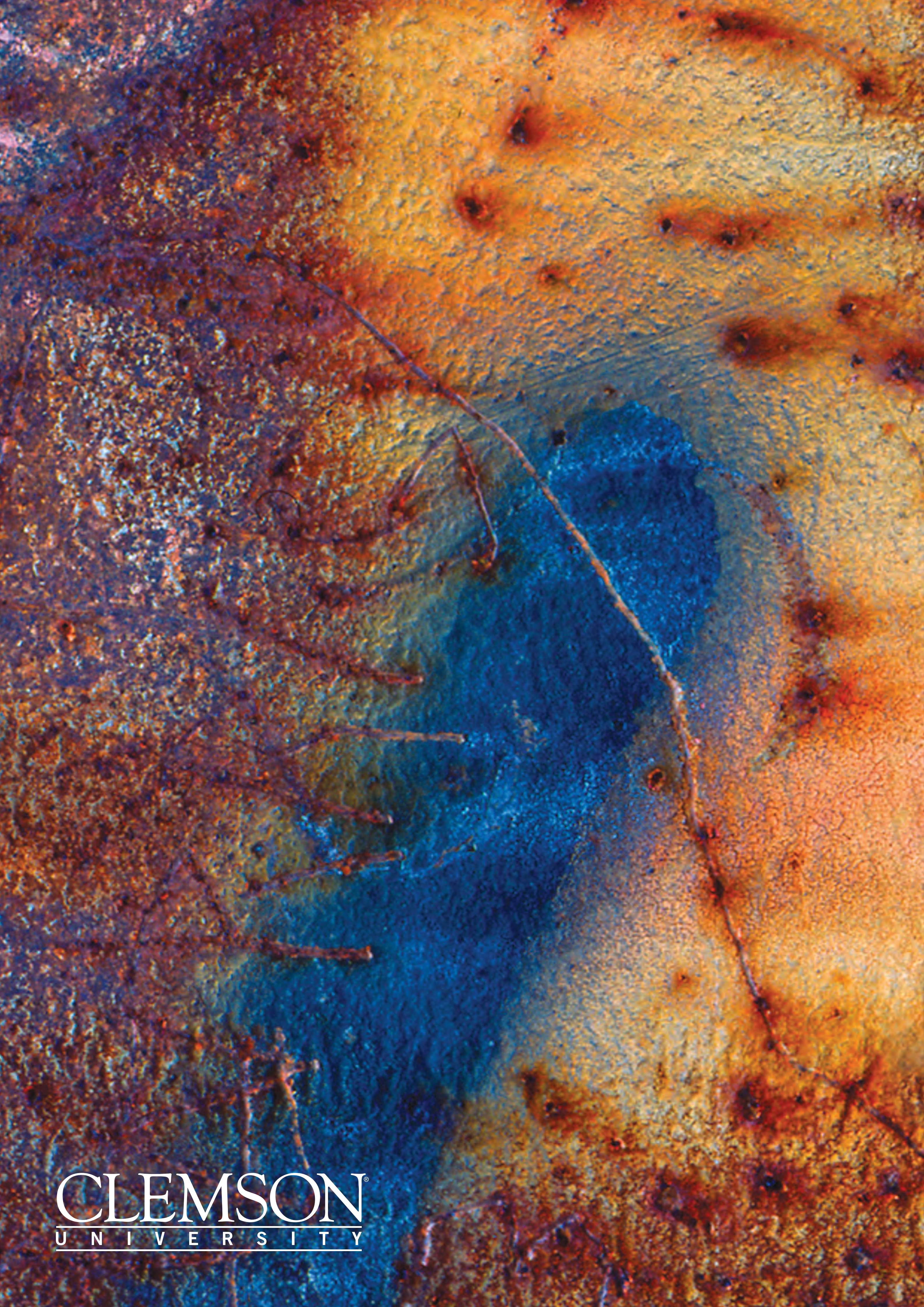

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