



UNIVERSITY OF ROME "LA SAPIENZA"
NANOTECHNOLOGIES ENGINEERING

CHEMICAL PRECIPITATION REACOTRS

PRECIPITATION PROCESS APPLICATIONS

Applications

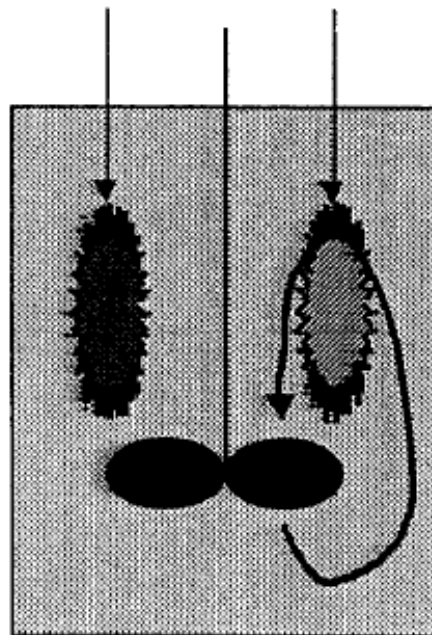
1. Production of solids with specified particulate properties (high yield)
 - inorganic pigments
 - fillers: CaCO_3 in paper, BaSO_4 in powder coatings
 - bulk chemicals: $\text{Al}(\text{OH})_3$
 - silver halides in photography
 - pharmaceutical products
 - polymers
2. Removal of compounds from waste streams (low yield)
 - drink and process water softening
 - phosphate removal from waste water in sewage treatment plant
 - selective removal of heavy metals ions

FACTORS AFFECTING THE REACTOR DESIGN

Mixing and kinetics

Kinetics

Reaction
Nucleation
Growth
Agglomeration



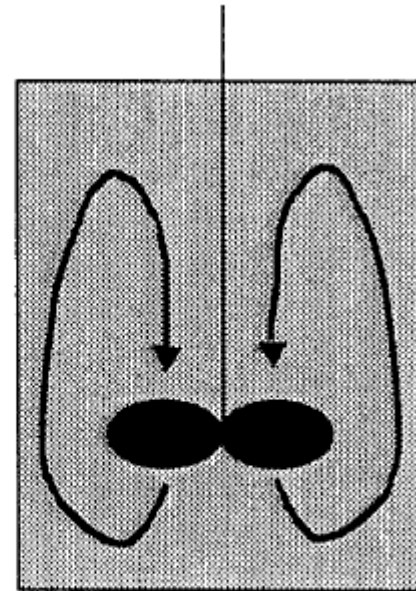
Mixing

Macromixing
Mesomixing
Micromixing

MACROMIXING

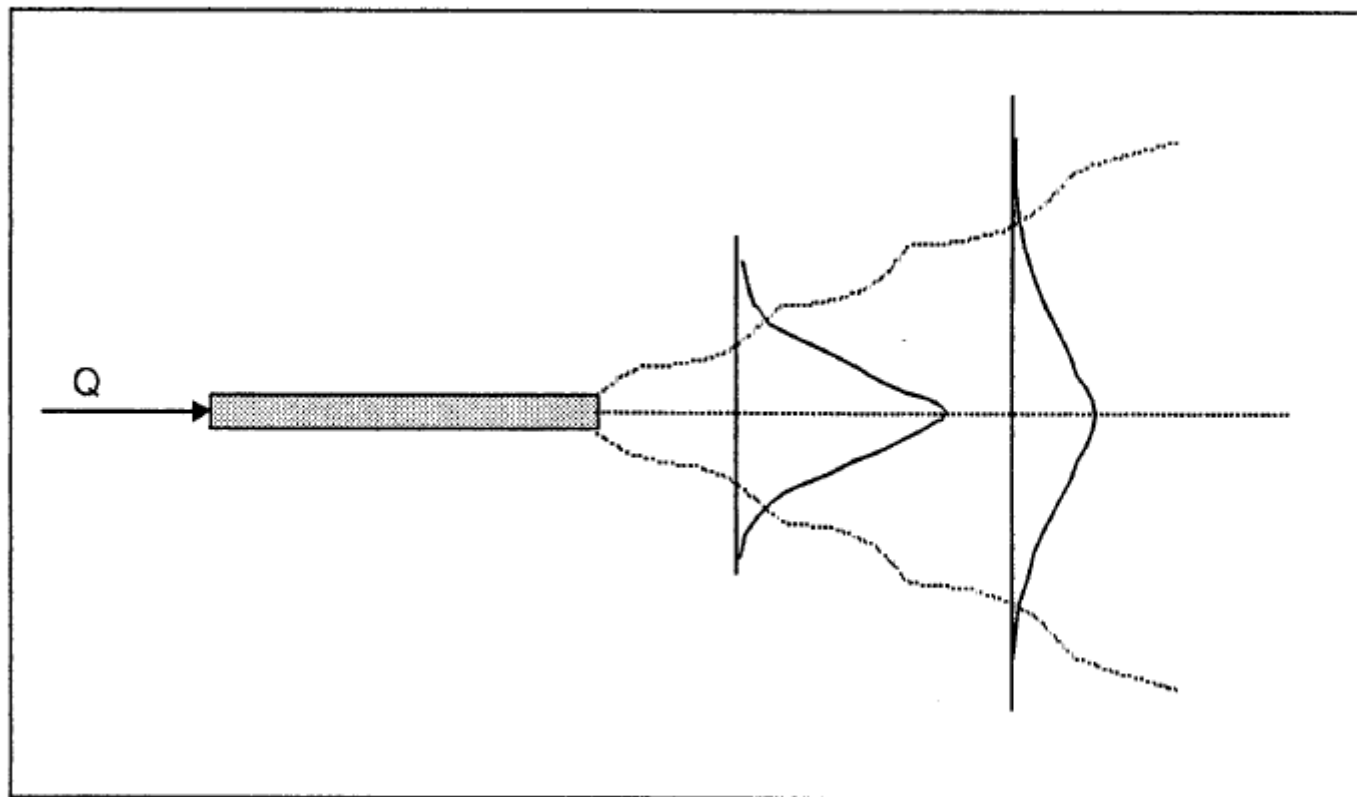
Reactor circulation time

$$t_{macro} = \frac{V}{bNd_{stir}^3}$$

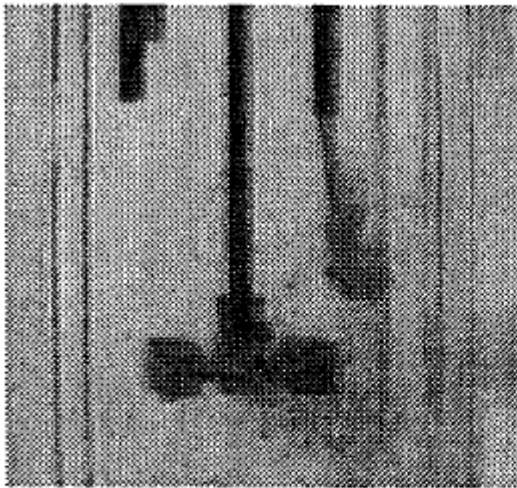


Depends on average energy dissipation $\bar{\epsilon}$

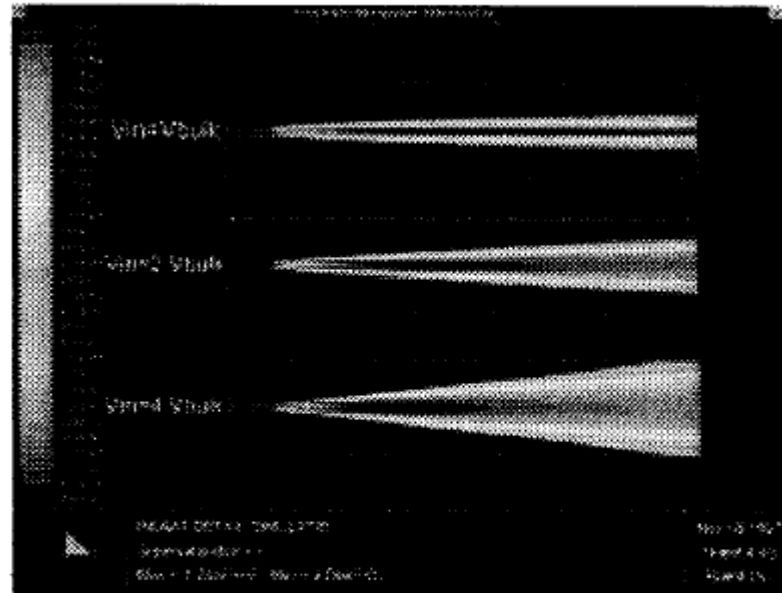
MESOMIXING



FIGURES OF MESOMIXING



Visualization of inlet flow

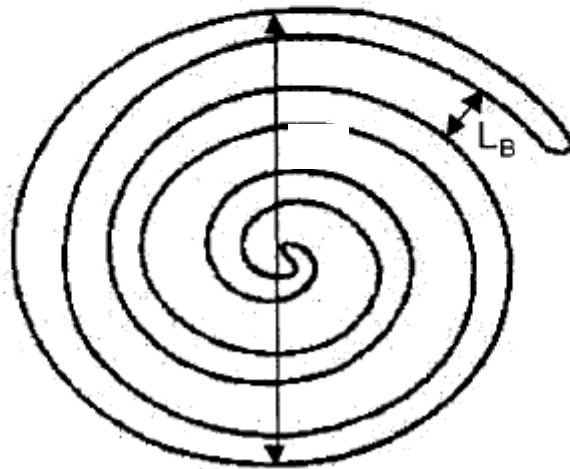


CFD-simulation of supersaturation
different relative velocities

MICROMIXING

Depends on local energy dissipation ϵ

$$t_{micro} = 12 \left(\frac{v}{\epsilon} \right)^{1/2}$$



In case of knowledge of the micromixing scale, λ_k :

$$t_{micro} = 0.5 (\lambda_k^2 / D)$$

where D is the diffusion coefficient

MIXING TIMES

1 **Macromixing**

- process: recirculation
- scale: vessel size 1-10 m
- time: recirculation time 10 - 50 s

2 **Mesomixing**

- process: mixing at feed inlets
- scale: inlet diameter: 1-10 cm
- time: engulfment time 1-10 s


3 **Micromixing**

- process: vortices and diffusion
- scale: vortex ~30 μm
laminar layer thickness ~ 1 μm
- time: vortex lifetime ~10 ms

4 **Diffusion**

- process: diffusion over lamellae
- scale: half of laminar layer thickness ~ 1 μm
- time: penetration time ~ 1 ms

KINETIC TIMES

Reaction time	$t_r = \frac{1}{k c_0^{n-1}}$	$\ll 10^{-5} \text{ s}$	
Nucleation time	$t_n = \frac{6 d_m^2 n^*}{D_i \ln S}$	$\sim 10^{-4} \text{ s}$	
Growth time	$t_G = \frac{M}{\rho G a} \Delta c$	$\sim 10^0 \text{ s}$	
Induction time	$t_i = (J G^3)^{-\frac{1}{4}}$	$\sim 10^{-4} - 10^0 \text{ s}$	

SELECTION OF A PRECIPITATION REACTOR

- The major objective is to develop a precipitation reactor, which intensifies the mixing between the reagents, in order to produce nanoparticles in a very narrow size range.
- The so called T-mixer reactor and rotating disc reactor are adopted. Both the reactors may assure conditions of micromixing which induces homogeneous nucleation, but the first reactor needs a very high energy.
- For sake of comparison the stirred tank reactor is also considered.
- It is examined the production by precipitation of undermicronic particles of barium sulphate, a model system generally used for the techniques evaluation.

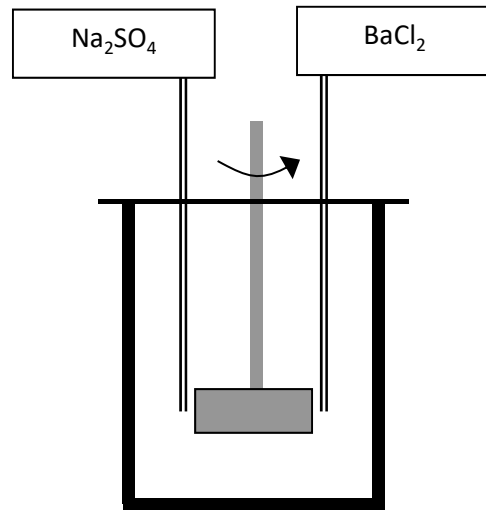
EXPERIMENTAL

- The reaction adopted to produce barium sulphate is as follows :



The equilibrium concentration of the product in the mother solution is equal to 10^{-5} M at 20°C.

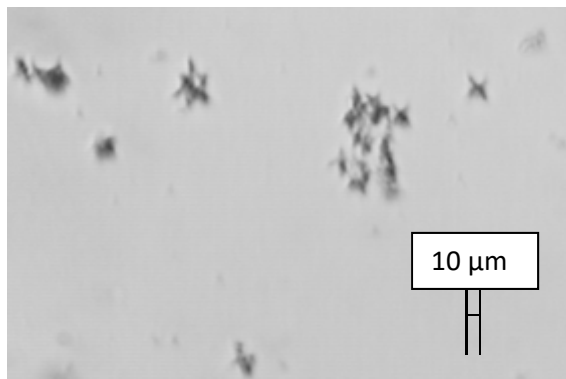
- The precipitation was performed by feeding the two reactants streams at a volumetric rate of 50 ml/s into a 1000 ml stirred tank reactor. The reactant concentration of each stream was 0,1 M.



The vessel was preliminary filled with 300 ml of distilled water. The stirring rate was equal to 2000 rpm.

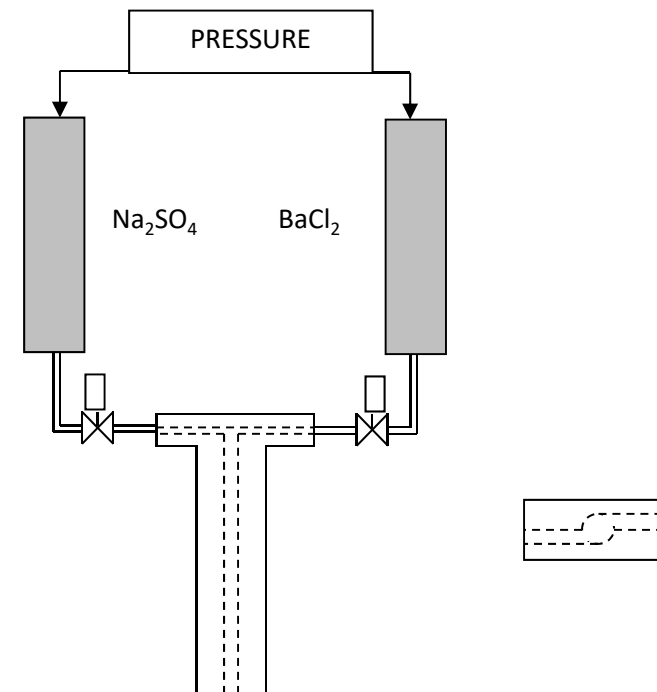
EXPERIMENT EVOLUTION

- The values of the supersaturation ratio decreased from 5000 at the run start.
- Due to low grade of mixing at macro and micro scale smaller values of S were locally attained in the solution bulk.
- During each run, 2 ml of the slurry were sampled and quickly poured into 20 ml of 0.02% wt. gelatine solution. This procedure avoids the agglomeration and settling of the particles.
- At the adopted operating conditions, the produced crystals exhibits a star-like shape, a mean size of 15 microns and a crystal number density , measured by a haemocytometer of $3 \cdot 10^8 \text{ \#/cm}^3$.



T-MIXER REACTOR

- The T-mixer consists of two small injection pipes, 1 mm in inner diameter, which are not coaxial but shifted each other in order to increase the micromixing through a vortex effect.
- The outlet leg is a pipe 30 cm in length and 2 mm in inner diameter.
- The pipe diameters were chosen such that the same Re number in all sections of the T-mixer was attained.



T-MIXER REACTOR PERFORMANCES

- Some preliminary measurements with water were performed in order to determine the effect of the pressure in the reactant tanks on the outlet flow rate of the suspension and the relevant Re number.

Tanks Pressure [bar]	Flow Rate [ml s⁻¹]	Re number
1	4,12	2624
2	5,96	3796
3	6,74	4292
4	7,66	4878

- In order to estimate the micromixing time, a colorimetric test was successfully performed.
- At the applied pressure condition, the mixing time in the T-mixer was estimated to be equal to 0,76 ms.

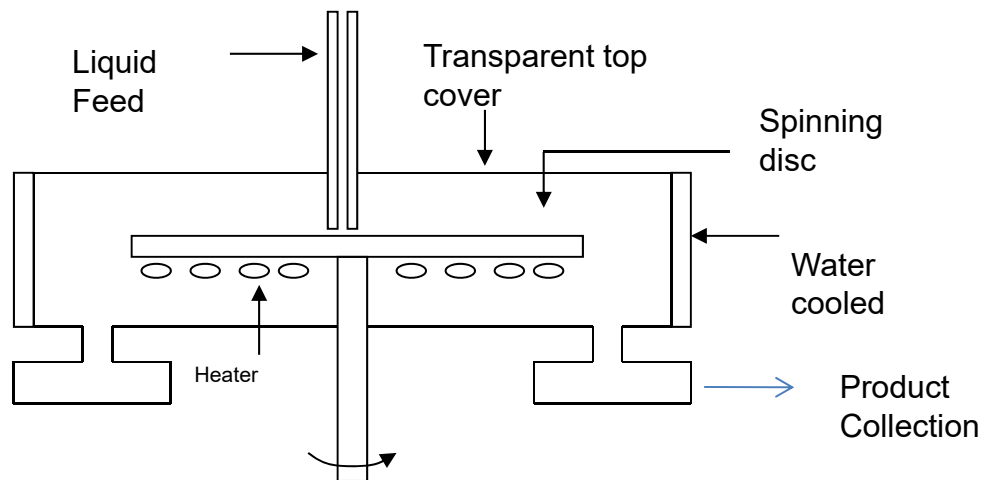
CRYSTALS PRODUCED BY THE T-MIXER

- By this instrument, it was possible to observe that most of the solid particles were in the under-micronic range, i.e. $0,7 \div 1\mu\text{m}$.
- The smallest crystals appeared almost spherical in shape, whereas the largest ones exhibit a star-like habit.
- The crystal number density in the slurry produced by the T-mixer was evaluated to be $6,5 \cdot 10^9 \text{ \#/cm}^3$



THE ROTATING DISC REACTOR

- The rotating disc , made by brass, is 0.5 metres in diameter.
- A variable speed motor was used and the motor drive was connected to the bottom of the disc via a central shaft. The speed of the disc was varied by using a control regulator between 100 and 1000 rpm.
- The two aqueous reagent solutions were fed onto the disc surface by means of two 56 ml burettes, which were located at a radial distance of 0,05 metres from the centre of the disc.
- Experiments were carried out at $25 \pm 0,5$ °C.

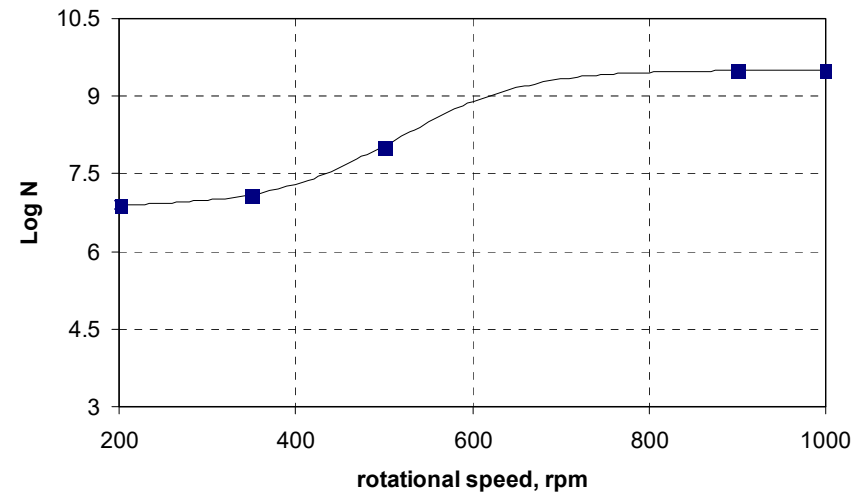


PERFORMANCES BY THE SDR

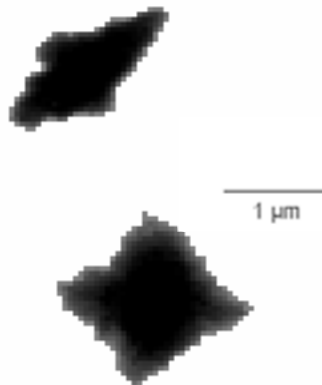
Effect of Supersaturation

Supersaturation ratio	Number of crystals per cubic centimetre
100	$6,9 \cdot 10^7$
2000	$3,2 \cdot 10^9$
2500	$4,0 \cdot 10^9$

Effect of Rotational speed



CRYSTALS



COMPARISON BETWEEN THE OBTAINED PERFORMANCES

	Stirred Tank Reactor	T-mixer	Spinning Disc
Operating conditions	$N = 2000 \text{ rpm}$ $S_0 = 5000$	$P = 4 \text{ bar}$ $S_0 = 2000$	$N = 1000 \text{ rpm}$ $S_0 = 2000$
Number of crystals per cm^3	$2 \div 4 \cdot 10^8$	$6,5 \cdot 10^9$	$3,2 \cdot 10^9$
Crystal size (μm)	$10 \div 15$	$0,7 \div 2$	$1 \div 2$
Specific dispersed power (W/kg)	661	197596	115
Mixing time (ms)	N/A	0,76	0,9

COMPARISON BETWEEN THE SPECIFIC POWERS

- T-Mixer (expression from Mohanty):

$$\varepsilon = \frac{\Delta p \cdot Q_L}{\rho_L \cdot \frac{\pi \cdot d^2}{4} \cdot L}$$

- Stirred tank:

$$\varepsilon = \frac{N_P \rho N^3 D^5}{V}$$

- Spinning Disc Reactor:

$$\varepsilon = \frac{1}{2 \cdot t_{res}} \cdot \left\{ \left(r^2 \cdot \omega^2 + u^2 \right)_o - \left(r^2 \cdot \omega^2 + u^2 \right)_i \right\}$$

where t_{res} denotes the residence time of the liquid solution on the spinning disc, r the radial distance from the centre of the disc, ω the angular velocity of the disc and u the average velocity of the liquid solution on the disc, subscripts "o" and "i" indicate outer or inner radius of the disc.

VELOCITY AND RESIDENCE TIME FOR THE SDR

- The average velocity, u , of the liquid solution on the disc is given by:

$$u = \left(\frac{\rho_L \cdot Q_L^2 \cdot \omega^2}{12 \cdot \pi^2 \cdot \mu_L \cdot r} \right)^{1/3}$$

where Q_L denotes the flow rate on the disc, ρ_L the density of the solution, and μ_L the viscosity of the solvent.

- The residence time of the solution on the disc can be calculated as:

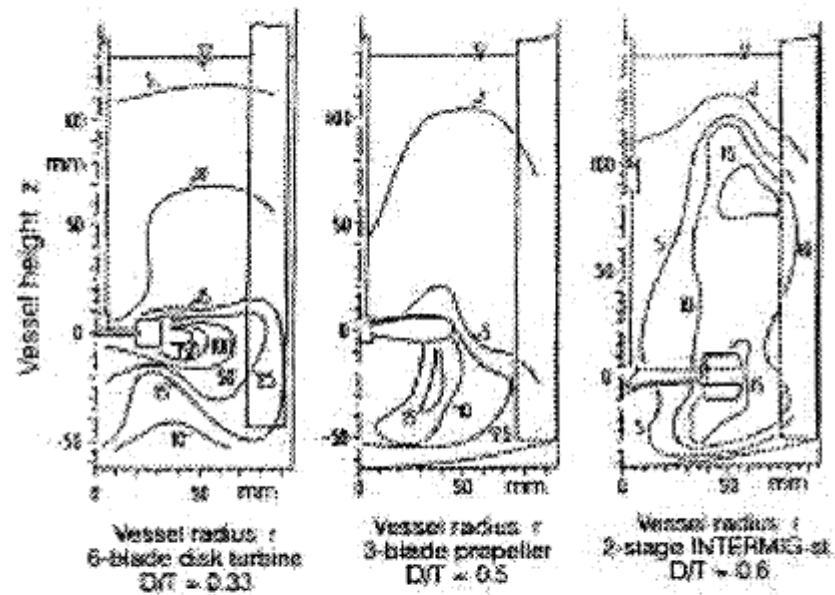
$$t_{res} = \frac{3}{4} \cdot (12 \cdot \pi^2)^{1/3} \cdot \left[\frac{\mu_L \cdot (r_o^4 - r_i^4)}{\rho_L \cdot \omega^2 \cdot Q_L^2} \right]^{1/3}$$

CRITERI PER LO SCALE UP

- Per incrementare la capacità dell'apparecchiatura si può operare su 3 parametri:
 - Il diametro del disco
 - Il numero di dischi in parallelo su una stessa pila
 - Il numero di pile di dischi
- La condizione operativa da mantenere costante è il valore dell'energia dispersa localmente nel punto di immissione dei reagenti.
- Il criterio di ottimizzazione è la minimizzazione dei costi di investimento, salvaguardando la stabilità della struttura rotante.

POWER INPUT

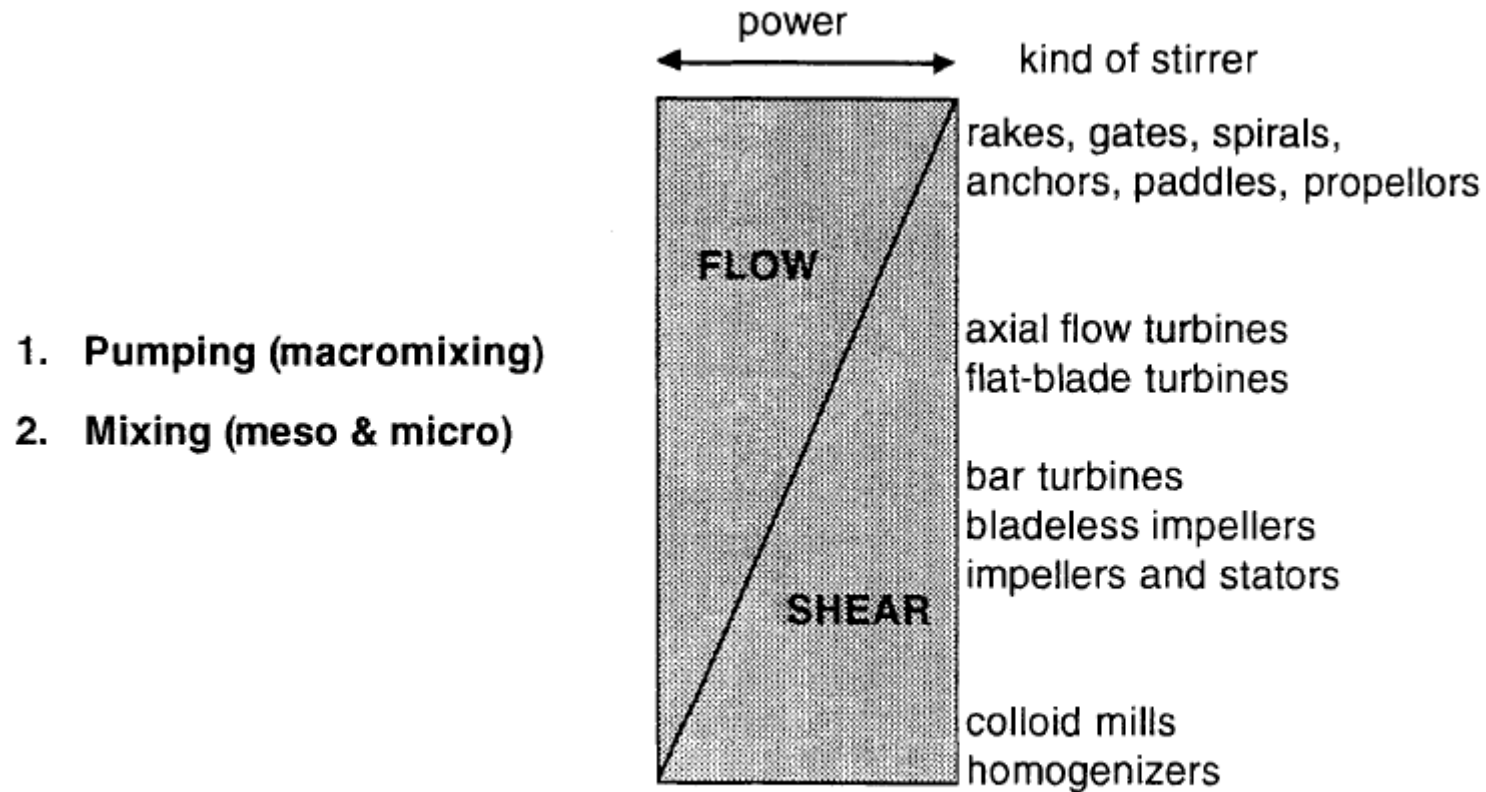
Different stirrers



local energy dissipation \Rightarrow micromixing

average energy dissipation \Rightarrow macromixing

STIRRER FUNCTIONS



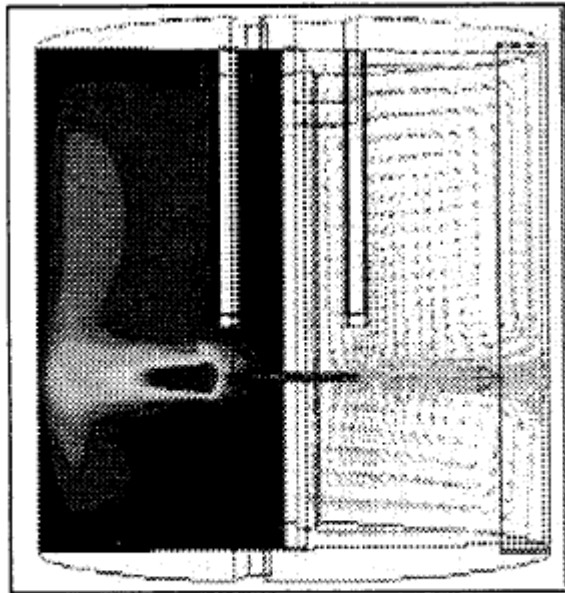
Characterization of impellers
(Oldshue 1983)

SCALE UP

Same average energy dissipation $\bar{\epsilon}$ $\xrightarrow{\text{Different impellers}}$ Different local energy dissipation ϵ

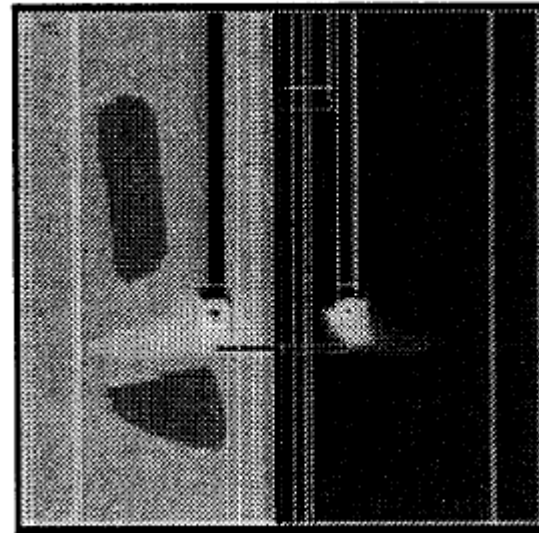
Same average energy dissipation $\bar{\epsilon}$ $\xrightarrow{\text{Different reactor scales}}$ Different local energy dissipation ϵ

HYDRODYNAMICS AND PRECIPITATION IN A STIRRED TANK



Left: energy

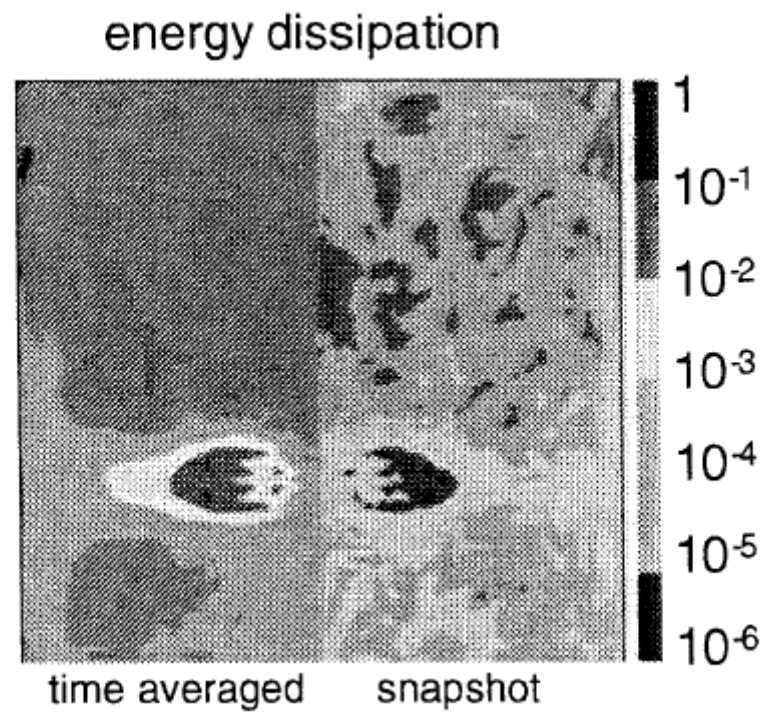
Right: flow



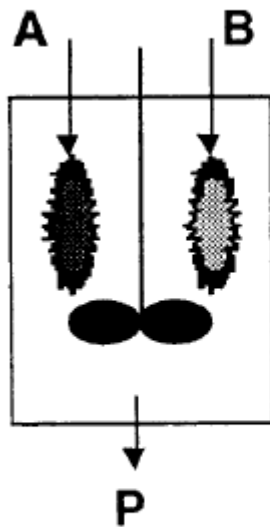
Left: supersaturation

Right: nucleation rate

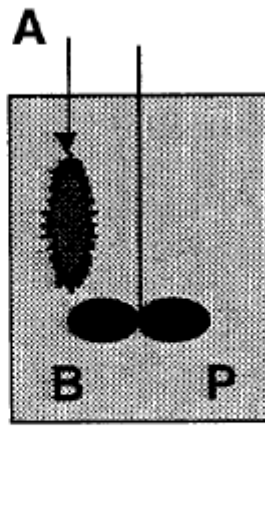
HYDRODYNAMICS AND PRECIPITATION



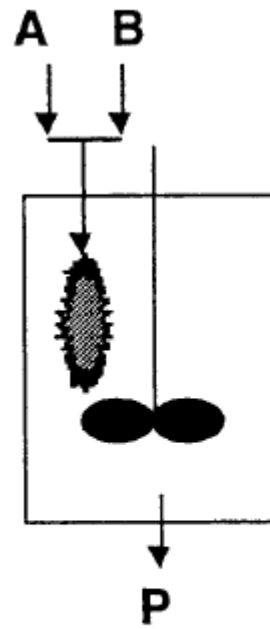
OPERATION MODE



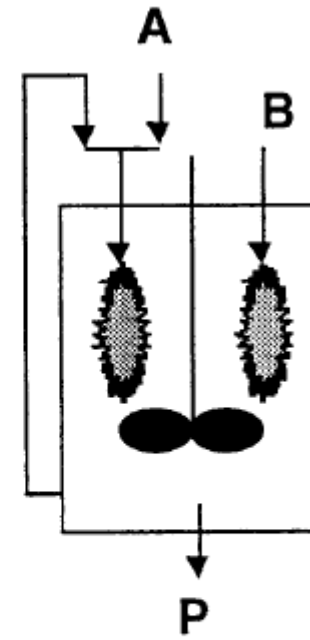
double feed
continuous



fed batch

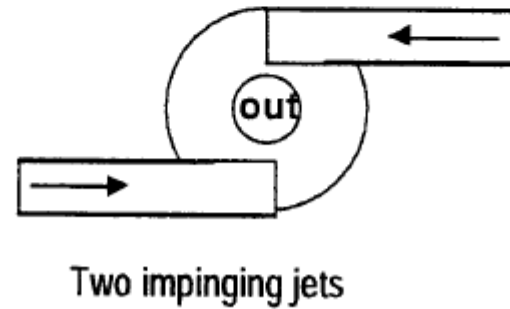
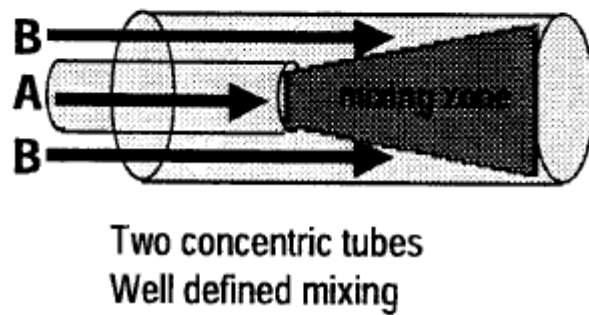
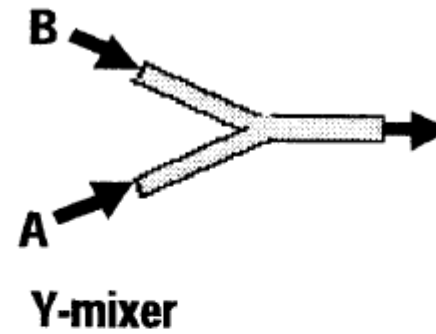
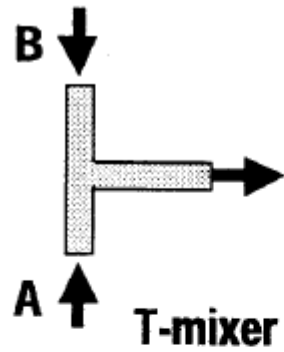


continuous
with
T-mixer

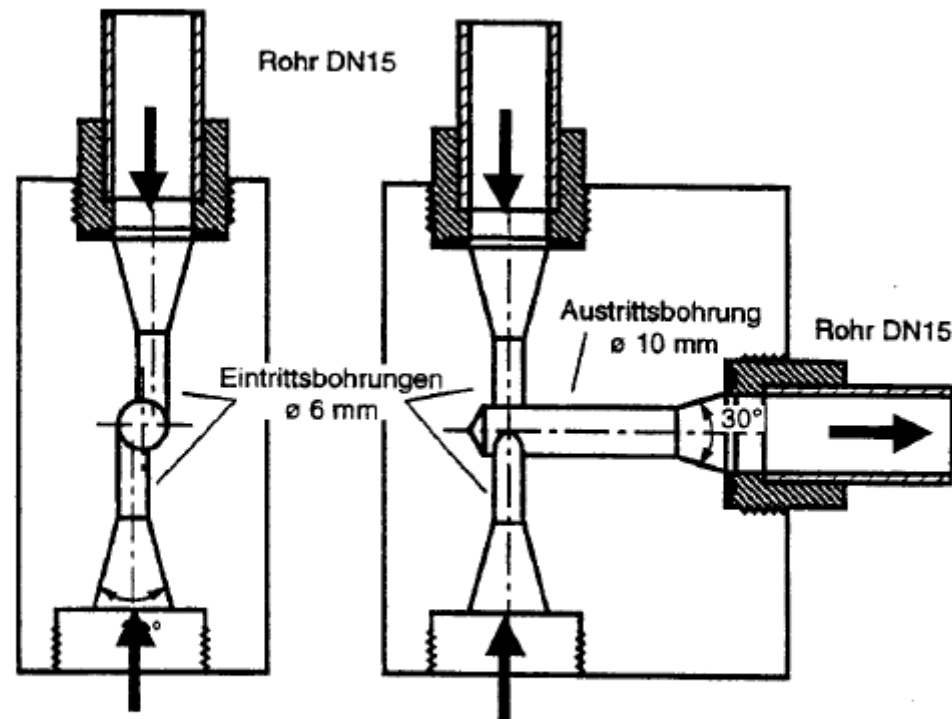


continuous
with
feed dilution

INLET MIXERS



INLET MIXERS IN PRACTICE



Two impinging jets - Stephan Kabasci (1997)
High efficiency mixing

Spinning Disc Reactor



Internally Cooled Spinning Disc Reactor

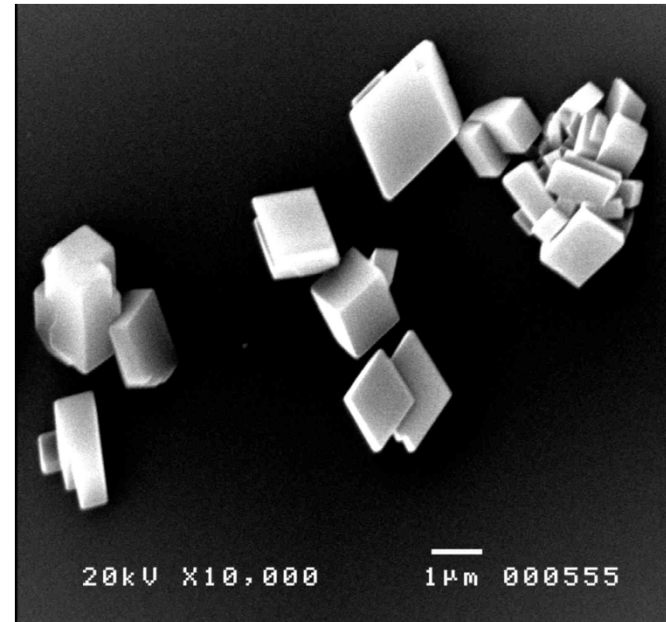
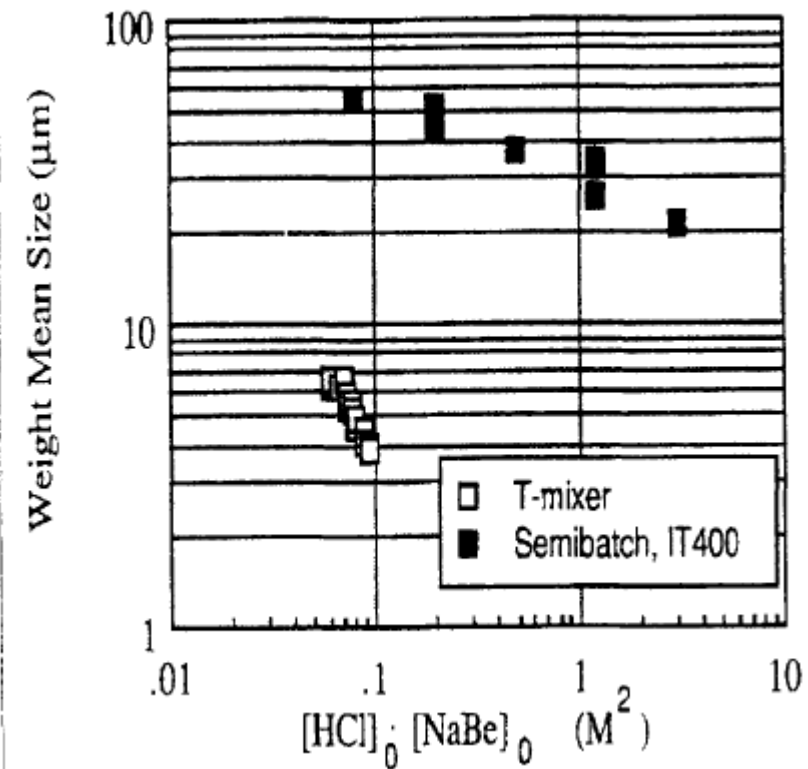
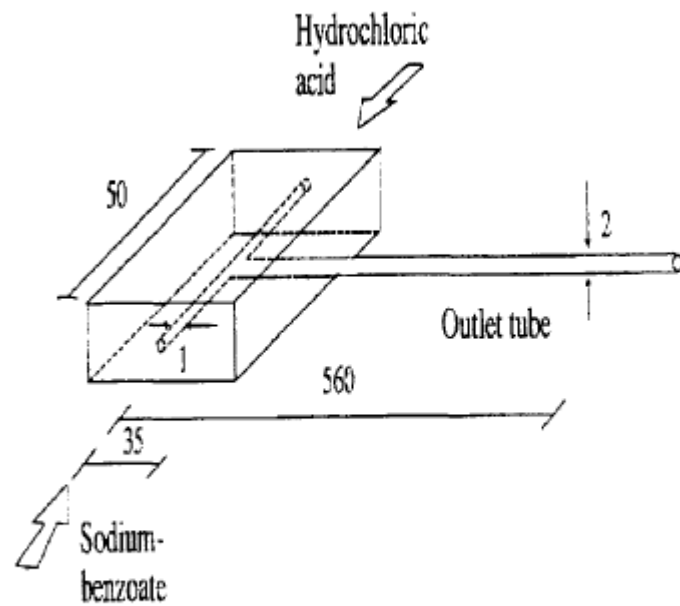


Figure2. Calcium Carbonate crystals produced using the SDR technology

Reference

- Process Intensification: Spinning Disc Reactor for Styrene Polymerisation, K. Boodhoo & R. Jachuck, Applied Thermal Engineering, Vol. 20 (2000) 1127-1146.
- Precipitation of Barium Sulphate Using a Spinning Disc Crystallizer, L.M. Cafiero, A. Chianese and R. Jachuck, 14th International Symposium on Industrial Crystallization, Cambridge October 1999

PRECIPITATION OF BENZOIC ACID



FLUIDISED BED PRECIPITATORS

- **Problem:**

- Compound to be removed is present in low concentration (<1 wt%)
- Often large flows

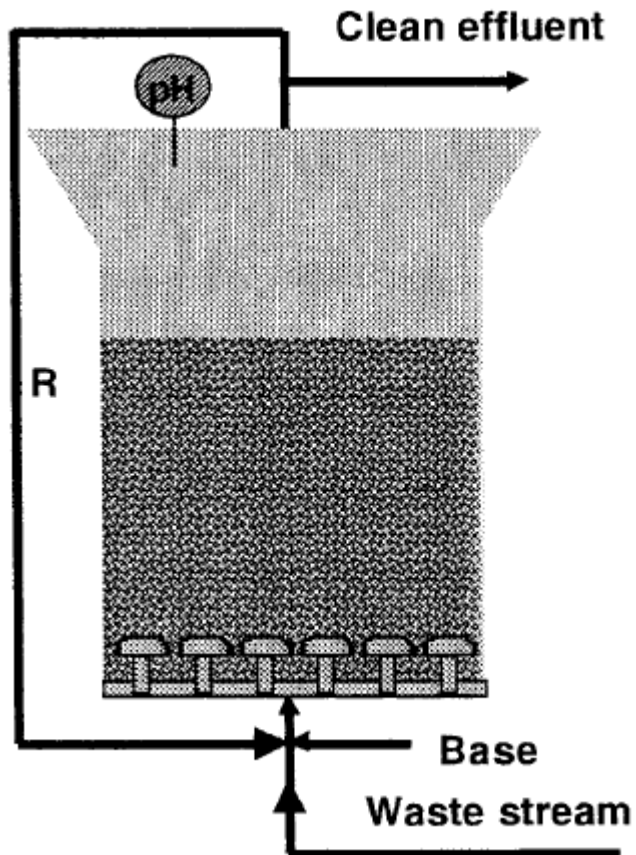
- **Requirements**

- Low residence time (≈ minutes)
- Large particles, easily separable from waste or process stream

- **Solution:**

- Fluidised bed precipitator

WASTE WATER TREATMENT



- **Compounds removed:**

- Ca as Calcium Carbonate
- P as Amorphous Calcium Phosphate
- Heavy metals as carbonates or hydroxydes

- **Fluidized bed characteristics**

- seeds: sand grains
- $H = 5 \text{ m}$
- $v_{\text{sup}} = 1 \text{ cm/s}$
- $\tau_{\text{particles}} \approx 1 \text{ year}$
- $\tau_{\text{liquid}} \approx 10 \text{ min}$

WASTE WATER TREATMENT

Fluidised bed precipitator
Phosphate removal from wastewater

