

## **THE PRECIPITATION OPERATION**

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### **1 Introduction**

The crystallization of poorly soluble substances is called crystallization by precipitation or simply precipitation. The oversaturation in which it operates is very high, because the consequence of a chemical reaction that creates a high concentration in a little soluble solute solution. The immediate creation of a high supersaturation implies a very rapid nucleation followed by a not high growth and other phenomena such as agglomeration and changes the chemical and physical properties of the crystals produced over time.

The very high values of relative supersaturation, even a few thousand, which comes to be the product itself give rise to very high speeds of the nucleation phenomenon, which can assume the character of homogeneous nucleation. The enormous speed of nucleation, the order of  $10^{11} \# \cdot m^{-3} \cdot s^{-1}$  It determines the generation of a very large number of nuclei that undergo a strong initial growth. All this leads to a fast consumption of the initial supersaturation, so that after a few seconds or tens of seconds has reached the supersaturation of the low values so as not to be able to increase significantly the crystals in suspension, taking into account the extremely high surface that they exhibit.

A second important element for the examination of the phenomenon is the mixing between the reagent solutions that give rise to the chemical reaction. In the case of perfect mixing of the micron level (micromixing) the reaction will occur at the maximum possible concentration of the reactants and will give rise to maximum concentration of the solute product, ie to its maximum supersaturation. In the case of deficient local mixing, the concentration of one of the reactants can be lower than the maximum possible value, and consequently also the solute product and its supersaturation will be lower, even in a very relevant. From the foregoing it is evident the importance that the hydrodynamic plays in determining the performance of the precipitation. In fact, a bad mixing of the reagent solutions, preventing complete mixing, involves on the one hand a smaller number of nuclei produced, on the other a residual supersaturation, linked to a lengthening of reactant mixing time, which determines a considerable dimensional distribution of the crystals produced, and a worsening of unwanted phenomena such as agglomeration. In summary, if you achieve micromixing of conditions it is possible to obtain a very large number of crystals, of the order of  $10^{11} - 10^{16}$  particles per  $cm^3$  of micron or submicron size, including in a narrow interval of dimensions, if this is not the case there is the production of a less high number of crystals that have a considerable dimensional inhomogeneities and a non-negligible amount of crystalline aggregates. The high speed of the phenomena of nucleation and growth of the nuclei determine, finally, the inability to control the crystal habit that often develops in a very irregular way. In addition, the large number of crystals and their small size leads to secondary phenomena such as Ostwald ripening and aggregation, which strongly affect the particle size distribution of the final pellet.

The importance of the precipitation process has been increasing gradually that has grown the need to dispose of materials of very small size, ie of a few tens or hundreds of nanometers. Currently, this interest is very high both in the production of nanopowders and nano-structured particles. Among the areas of greatest industrial interest are the materials used for the magnetic recording and those photos, in the first case it is iron oxide and chromium, and in the second case of silver halide. Of great importance are the ceramic materials used to produce pigments and pharmaceuticals. There are, moreover, precipitation processes, which involve well-known inorganic materials and are often produced in large quantities such as calcium carbonate,

environmental field, such as flue gas desulfurization with lime or the elimination of soluble phosphate present in the wastewater again by means of lime.

In many cases it leads to the precipitation of polymorphism phenomena, ie to chemicals having the same composition, but different crystalline form and functionality. In this case it prompted a greater attention to the operating conditions.

In the paragraphs that follow will be described, at first, the peculiar fundamental aspects of the precipitation process, then it will be examined the influence that the hydrodynamics may have on the nucleation speed, which in this context assumes a far greater compared to ' growth,

Finally, we will describe the equipment that enables the intensification of the mixing process and therefore the optimization of the process of precipitation.

## 2. Supersaturation and solubility

The pushing force of the precipitation is determined by an oversaturation reaction between two reagents, both in the liquid phase or one in liquid phase and the other in the gaseous phase, which are mixed together. To determine the operational oversaturation is necessary to know the solubility of the solute that precipitates. When the precipitate coexists with the solution under equilibrium conditions a parameter that adequately represents the system from a thermodynamic point of view is the solubility product  $K_{sp}$ . For an electrolyte  $A^+ + B^-$  the oversaturation, expressed as the supersaturation ratio  $S$ , it can be defined as the ratio between the product of the activities  $\Pi = \Pi_{TO}$

$\Pi_{TO}$  and the solubility product  $K_{sp} = \Pi_{Aeq} \Pi_{Beq}$ :

$$S = \frac{\Pi}{K_{sp}} \quad (1)$$

An approximate form, more usually employed, the supersaturation ratio is  $S = c / c_{eq}$ ,

where  $c_{eq}$  It is the solubility of the solute.

An embodiment of the least used oversaturation is the concentration gradient, COIE  $\Delta c = c - c_{eq}$ .

For submicron crystals may become important to take into account the effect of the size of the crystals on the solubility expressed through the equation of Gibbs- Thomson:

$$\ln \left( \frac{c}{c_{eq}} \right) = \frac{2\sigma}{rRT} \quad (2)$$

Where the values of the concentrations refer to the very high king size crystal and the other symbols represent:  $\sigma$  the surface energy,  $V_m$  the molecular volume,  $R$  is the gas constant and  $T$  is the absolute temperature. The Gibbs-Thomson law states that there is an inverse relationship between the solubility is the crystal radius. This happens practically only if the surface energy between solid and solution is very high. For the 50 nm AgBr crystals have a solubility greater than 15%. The surface energy, in turn, is inversely proportional to the solubility (see Fig.

1), for which it is particularly high for very little soluble compounds object of the precipitation phenomenon. The remarkable effect that, for these compounds, the variation in size has on solubility involves the so-called Ostwald ripening phenomenon that, under certain operating conditions, the solubilization of the smallest crystals (always smaller than one micron), the increase in supersaturation and consequently the growth of larger crystals. This phenomenon, ultimately, leads to the disappearance of the smallest crystals in favor accretion of large crystals.

### 3. The surface chemistry and stability of colloids

Consider the crystalline solid particles in solution. If we are in the presence of the solid species which behave differently, both for their size that for the crystalline phase, from a thermodynamic point of view, the less stable phase will be transformed into more stable phase. The stability of a solid species is measured on the basis of its stability, in the sense that the more soluble species is less stable than less soluble. For example, the amorphous iron hydroxide is more soluble form  $\alpha$  (goetite) and shape  $\beta$  (akagonite), and the latter is more soluble form of hematite. In this case the less stable form is that amorphous and the more stable is the hematite. The stability also depends on the temperature, in each case when two different species of stability coexist in a solution that is less stable transformed into the more stable. It assists in this case to two distinct processes of dissolution of the species less stable (the most soluble) and to the growth of the more stable (less soluble). The phenomenon less faster of the two will determine the final concentration of the solution. If the dissolution rate is much higher than that of growth, the slow phase is the deposition and the concentration of the solution will move close to the higher solubility,

Ripening or Ostwald Ripening is a transformation process that leads to the disappearance of very small crystals, less than a micron, in favor of larger crystals. The phenomenon behind this process is the bond that exists between the solubility of a solute in solution and the crystalline solid dimension,  $L$ , according to what has already been described in paragraph 2. In this case the smallest crystal is, in fact, the most unstable because it corresponds to a greater solubility.

To further quantify this effect please note that the solubility of crystals of  $Mg(OH)_2$  40 nm is 10% higher than that relating to hundreds of microns crystals. The link between solubility and size of crystals sanctioned by the equation of Ostwald part from the fact that a relatively large crystals saturated solution may be undersaturated with respect to crystals of tens or hundreds of pressure gauges, which therefore is dissolved by increasing the concentration of the same solution that is supersaturated with respect to large crystals, which consequently increase. From this derives a shift in the particle size distribution towards larger crystals (see Fig. 2).

The self-recrystallization It is another phenomenon of change of a solid crystalline species into another due to the different speed of growth of the crystal faces. If a crystal face has a much greater growth rate than the others, in a closed system the first face will disappear while the other will remain. Thus, for example particles of AgBr will be transformed from their octahedral form in the presence of 0.5 mol / l of ammonia and 1 mole / l of ammonium nitrate (see fig. 3).

The precipitated suspension features a large number of micro and nano particles having a high surface altogether. In this case both the surface chemistry determines the stability of colloids, namely the constancy of a particle size distribution which allows to retain the solid particles in suspension.

In general, the aggregation between particles, connected to the suspension stability is due to the competition of forces between particles attractive and repulsive.

The attractive forces are of physical nature, those of Wan der Wals, and are inversely proportional to the square of the distance between the particles.

The repulsive forces are of electromagnetic origin and descend from the surface charge that surrounds the particles, the so-called electrical double layer. The layer of electric charges resulting from

ions that are selectively adsorbed on the surface of the particles or from the dissociation of ionic groups on the surface. This part of the bilayer is still. Since the system must be electrically neutral electric charges on the surface of the solid must be offset by charges of opposite sign which are located in the liquid adjacent to the particles. This part of the double layer tends to penetrate the heart of the liquid, it is disturbed by the chaotic motion of the liquid, and is called the circulation layer.

The electrostatic potential that is established in the vicinity of the particle surface is shown in Fig. 4. The thickness of the layer of adsorbed ions is  $\delta$ .

The overall potential gradient,  $E$ , between the surface of the solid and the solution is called Nernst potential and is constituted by the sum of the immobile layer potential,  $\varphi$ , and that of the state diffusional,  $\zeta$ , ie:  $E = \varphi + \zeta$ .

The repulsive forces that take place for the subsisting electrical interactions in the double layer are proportional to the potential  $\zeta$ . The magnitude and sign of the potential  $\zeta$  are functions of the ionic strength, ie the type of ions and their concentration.

When the concentration of ions increases, the ions in the diffusional layer tend to bind with those of the layers of the diffusional adjacent particles and the stability of the particles is reduced. So the value of the potential  $\zeta$  can pass through a maximum (usually in the presence of monovalent or divalent ions), it may be reduced to zero or reach a negative value (in the presence of bi and trivalent ions) (see fig. 5). If the value of the potential is between  $\pm 30$  mV the suspension of particles it is stable. The process which leads to a stabilization of the suspension due to the repulsive forces is called electrostatic stabilization. If the potential  $\zeta$  is within the range indicated the attractive forces prevail there is agglomeration / coagulation of the particles, the suspension is unstable, and the aggregated particle sediment.

To stabilize suspensions may also be used of the polymeric or macromolecular additives that are adsorbed on the surface of the particles. The typical case is that of gelatin that has been used to stabilize the silver halide solutions. The polymers or macromolecules in the solution creates a series of circuits and molecular chains that prevent the aggregation of particles, for this reason the form of stabilization that results is known as steric.

#### 4. The influence of mixing

The mixing and then the hydrodynamics of the stock solution is a very important factor for the precipitation process in respect of both the particle size distribution is apparel crystalline product.

In a real process, the mixing is not instantaneous, especially if placed in comparison with the speed of the reaction and the crystallization processes. Mixing is a complex process that goes through different stages. First, the mixing starts from the fluid supply disintegration into individual volumes of liquid which are distributed in the container and this situation is changing in the course of a dynamic stage of the process with the splitting pushed more and more of the individual volumes. At the end of this stage there is contact between the very thin film of the volumes of individual reactants through which occurs the diffusion process and the reaction between the two reactants begins in a wide manner. It is understandable that this stage can lead to create areas with very different concentrations of the two reagents,

In a turbulent regime of the species present in solution in the apparatus we are transported in groups of several molecules, in the form of entities in a spiral shape, calls in English "eddie" (see fig. 2). The turbulent flow is

three-dimensional and causes, through the formation of vortices, a local velocity fluctuations with a maximum, near the origin of the motion, for example the stirrer to a minimum, where viscous forces predominate (see fig. 3). These entities interact with the

surrounding fluid and generate smaller entities, which in turn produce the interaction with the surrounding fluid sized entities even smaller and so on. The organ that gives rise to the motion of the fluid, eg. the agitator provides the kinetic energy to the entities that transmit larger, subsequently, this energy to smaller entities that they themselves generate. The kinetic energy is expended in the viscous deformation of small volumes of liquid and is transformed into internal energy of the fluid (see Fig. 4). The microscale Kolmogoroff describes the smallest dimension of the entity in the fluid and is the characteristic length for the dissipation of the kinetic energy viscose (see fig. 5).

Summing up, mixing in an agitated volume takes place through three stages:

- 1) A liquid is dispersed in another and you get a constant average composition, but the scale micro there is a segregation between the two liquids.
- 2) The segregation of the liquid is progressively reduced in volume under consideration, so that the area of contact between the two liquids is greatly increased.
- 3) Occurs mixing at the molecular level so that the segregation between the two phases in practice disappears. The mixture reaches conditions of homogeneity at the molecular level.

The first mixing stage is called macromixing, It occurs at scale and the apparatus has a dynamic which has a duration of the order of seconds (see fig. 6). The macromixing is governed by the physical properties of the fluid, the equipment type and the total energy expenditure for mixing. The other two stages described above refer to the micromixing, which as mentioned above, refers to the deformation of the elementary volumes fluids and involves the diffusion of the reactants until the contact and the consequent reaction. The speed of the micromixing depends on the local turbulence, ie the energy dissipated locally, while the apparatus is not dependent on, nor organ that has generated the movement of the fluid. In this regard, taking into account that the energy dissipated locally can vary by more than two orders of magnitude in a container (see fig. 3).

The macromixing the stadium has a characteristic time of:

$$= ? \quad (3)$$

While the time of micromixing is calculated in an approximate way by the proposed report by Baldiga and Bourne (1986):

$$\cong 12 \frac{\nu}{\epsilon} \quad (4)$$

Ove  $\nu$  It is the kinematic viscosity in  $\text{m}^2 \cdot \text{s}^{-1}$  and  $\epsilon$  is the power per unit mass dispersed in  $\text{W} \cdot \text{kg}^{-1}$ .

The scale of the "micromixing" is that assigned by Kolmogoroff the size of the turbulence at the molecular level (eddy):

$$\lambda = \left( \frac{\nu^3}{\epsilon} \right)^{1/4} \quad (5)$$

The Kolmogorov microscale range from a few microns to tens of microns. The micromixing takes place via two different mechanisms: the laminar distribution of segregated regions and the erosion of segregated regions for turbulence (see fig. 7). The reaction takes place

segregated at the interface between the regions and in regions where there is the mixing, from which the importance of micromixing.

In many precipitation processes, the speed of reaction and nucleation are very fast, it follows that must be also very fast the speed of the micro mixing if you do not want that the mixing represents the slow stage of the overall process with the consequence of having concentrations different in different points of the apparatus. In particular, the processes of mixing and reaction, they must be much faster than the nucleation process if you want that they do not influence the latter process and the entire precipitation operation, ie

$$t_m + t_r \ll t_{ind} \quad (6)$$

if  $t_n$ ,  $t_r$ ,  $t_{ind}$  They represent the mixing times, the reaction and the induction time required by nucleation. Because usually  $t_r \ll t_{ind}$  it is necessary to verify that

$$t_m \ll t_{ind} \quad (7)$$

And 'interesting to compare the mixing time provided Eq. 4 with the average time of recirculation of a fluid in a vessel agitated by a Rushton turbine. The latter, denoted by the symbol  $t_c$ , is given by:

$$t_c \cong \frac{V}{Q} = \frac{V}{\pi B^3 N} \quad (8)$$

Where  $V$  is the volume of the container, and  $R_{THE}$  They are the speed of rotation and the diameter of the turbine.  $B$  is a constant that depends on the geometry of the apparatus but does not differ too much from 1. In Figure 8 are compared the two times in question for typical configurations of laboratory equipment and a troubled industrial container. Obviously the micro mixing time does not depend on the apparatus scale, which instead strongly influences the time of circulation of the fluid. As we see the latter ranging from several tens of seconds to fractions of a second by passing an industrial scale to that of the laboratory, while the micro mixing time is of the order of hundredths or thousandths of a second.

In many precipitation processes, especially those aimed at the production of nanopowders, one operates at very high ratios of supersaturation,  $S \cong 1000 \div 10000$ , which involve induction times in the millisecond range, so that the mixing time to be implemented must also be of milliseconds. This is not possible by means of a stirred reactor, so that if you want to achieve micromixing conditions necessary to resort to particular equipment such as reactors colliding jets and rotating discs.

Finally, the mixing may have a great importance on agglomeration phenomena and on the shape of the crystals. With regard to the first point, it should be noted that the precipitation may occur in the presence or in the absence of agglomeration: in the first case are obtained single crystals, while in the second case it may have polycrystalline aggregates of size of one or two orders of magnitude greater. Moreover, it may occur entirely different morphologies in the presence or absence of agitation. Thus, for example, in the precipitation of calcium carbonate at 30 ° C, with gentle agitation you were observed three different morphologies, aragonite, vaterite and calcite (see Fig. 9), while under very thrust agitation was verified only the first form , aragonite.

## 5. Agglomeration and coagulation of particles

Aggregation and caking are two phenomena that are related to the phenomena of flocculation and coagulation. The first is a process that weakly binds the particles to each other through the second physical links occurs when small particles are held together by crystalline bridges or physico-chemical forces. The two phenomena take place usually in the presence of high supersaturation and are effective for particle sizes of less than 50  $\mu\text{m}$  (see figure). The agglomeration is a process that occurs between the solid particles in a colloidal solution and is often preceded by the aggregation. Aggregation is very similar to the process of flocculation, with the difference that the flocculation takes place in an undersaturated suspension while the coagulation takes place in a saturated solution or slightly supersaturated. The rate of agglomeration is proportional to the number of particles per unit volume in suspension and grows with the variance of the crystalline population. When the speed of agglomeration is very high it is more influential in the speed of growth and leads to strong changes in the particle size distribution. The process of aggregation is studied based on the approach of Smoluchowski who considered the agglomeration as a biparticellare mechanism:  $\Gamma_{i,j}$  and  $L_j$  It is given by

$$\Gamma_{i,j} = K(L_{\text{the}}, L_{\text{the}j}) \cdot N_{\text{the}} \cdot N_j \quad (7)$$

in which  $\Gamma_{i,j}$  is the rate of formation of aggregates,  $\# \cdot \text{m}^{-3} \cdot \text{s}^{-1}$   $N_i$  and  $N_j$ , It is the density of the particle size  $L_{\text{the}}$  and  $L_j$  respectively in  $\# \cdot \text{m}^{-3}$   $K(L_{\text{the}}, L_{\text{the}j})$  dimensionally equal to  $\text{m}^3 \cdot \text{s}^{-1}$  It is a constant called essential (kernel) of the kinetics of aggregation.

We can distinguish two different aggregation mechanisms. The pericinetico mechanism is caused by Brownian motion of monodisperse submicron particles subject to collisions controlled by diffusional motion in a solution stops. The second mechanism, the one ortocinetico, is induced by collisions between the particles generated by the motion of the fluid in motion. According to the Smoluchowski  $N/N_0(t)$  is a linear function of time in the case of pericinetico mechanism while for the ortocinetico mechanism is the logarithm of this ratio which is a linear function of time (see tab. 1). The Smoluchowski equations have been confirmed experimentally in laboratory experiments. To take account of the aggregation effect on the particle size distribution must be entered in the population balance, the terms representing the birth of new particles by aggregation and the disappearance to the formation of aggregates. The population balance in this case contains the terms  $B_{\text{aggr}}(L_{\text{the}})$  and  $D_{\text{aggr}}(L_{\text{the}})$ , which respectively indicate the appearance and disappearance of particles of size  $L_{\text{the}}$ , in terms of  $\# \cdot \text{m}^{-3} \cdot \text{s}^{-1}$  which have the following expression

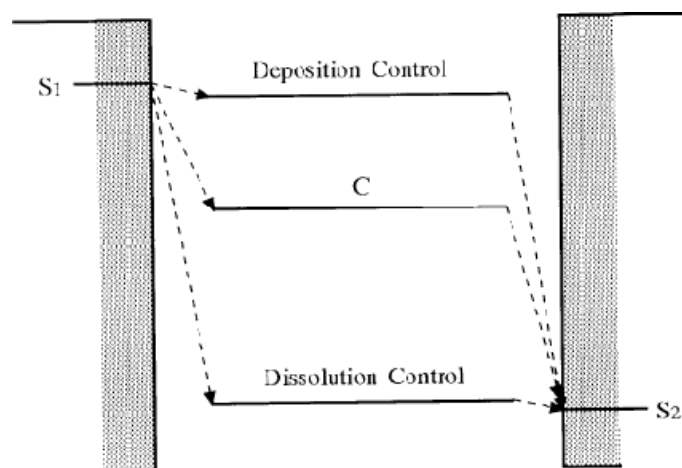
$$B_{\text{aggr}} = \int_0^{L_{\text{the}}} K(L, L_{\text{the}} - L) N(L) N(L_{\text{the}} - L) dL \quad (8)$$

With the  $K(L, L_{\text{the}} - L) = K(L_{\text{the}})$

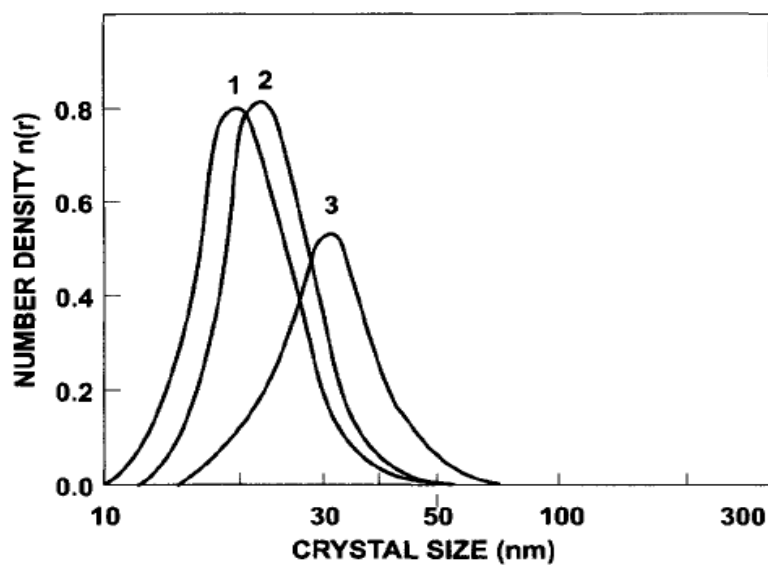
$$B_{\text{aggr}} = K(L_{\text{the}}) \int_0^{L_{\text{the}}} N(L) N(L_{\text{the}} - L) dL \quad (9)$$

in which  $L_k < L_{\text{the}} \leq L_{\text{max}}$ .

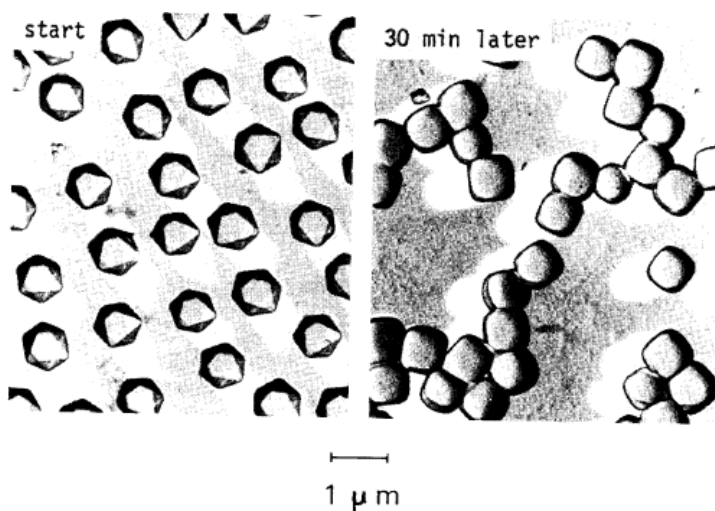
The aggregation coefficients (kernel) may be provided through the expressions shown in Table. 2.



**Figure 1:** Level of the concentration of a solution in a process of transformation

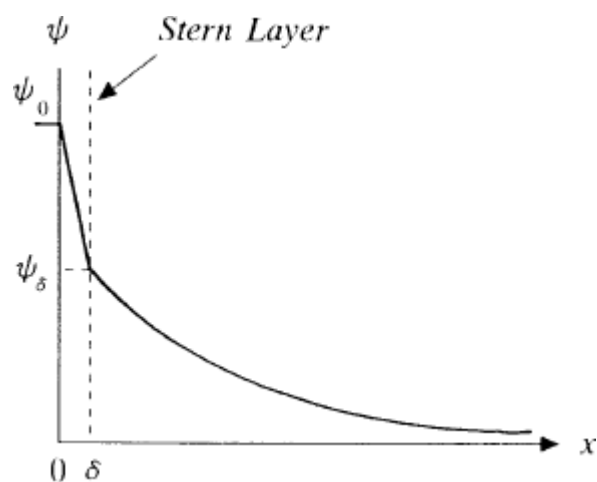


**Figure 2:** Transformation of  $\text{SrSO}_4$  initial CSD crystals 1, 2 after 60 days, 3 after 45 minutes of contact with water

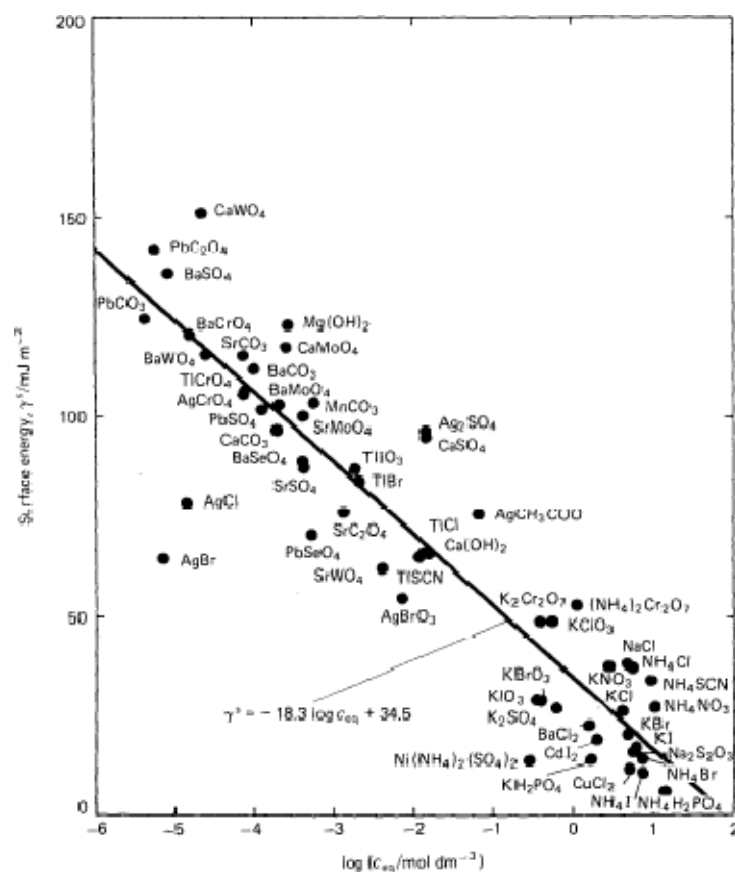


**Figure 3:** Auto recrystallization of octahedral crystals of  $\text{AgBr}$  at  $50^\circ\text{C}$  in the presence of ammonia and ammonium nitrate

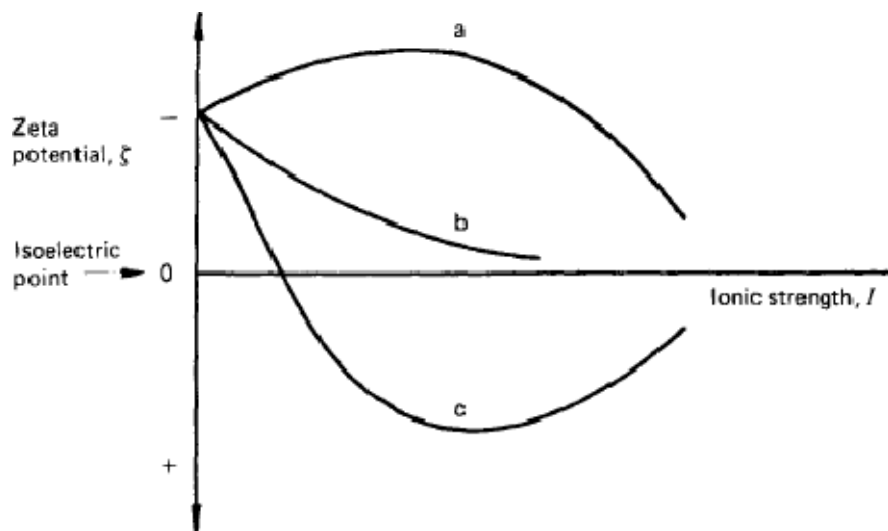




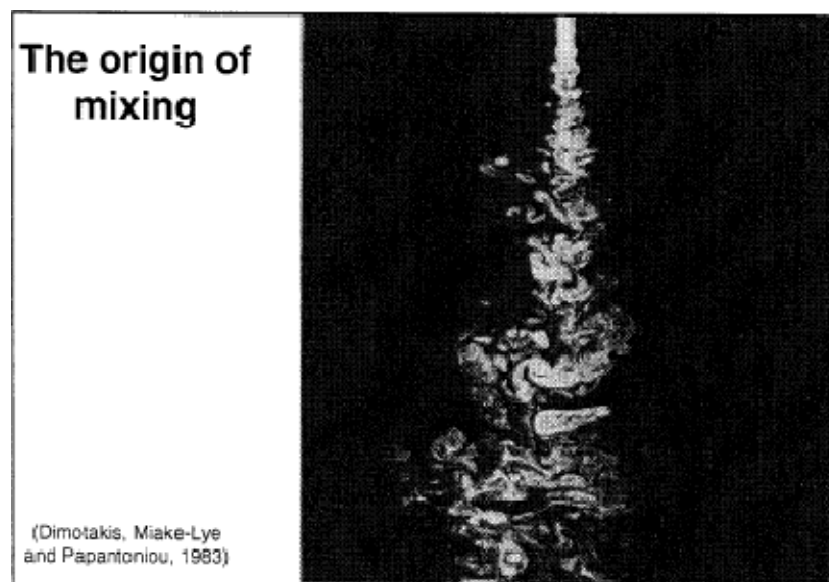
**Figure 4:** The potential in the electrostatic double layer



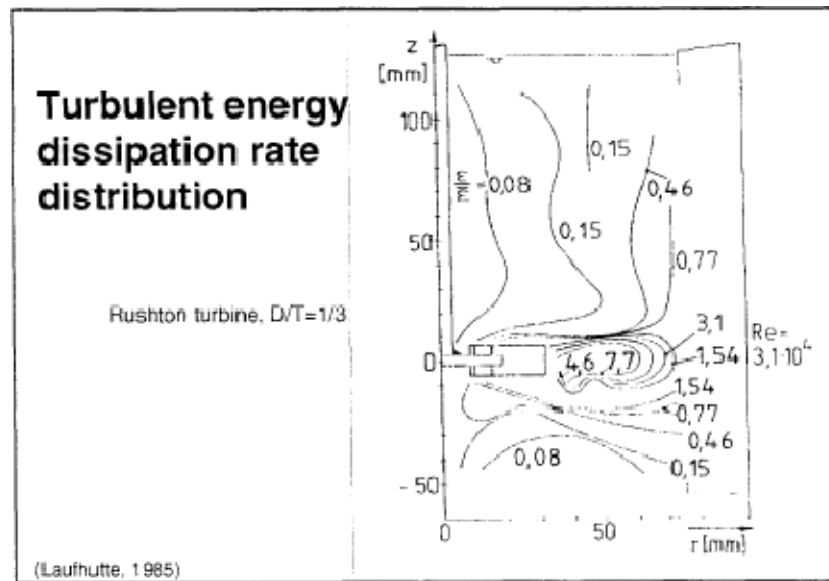
**Figure 5** correlation between the surface energy-crystal solution and the solubility



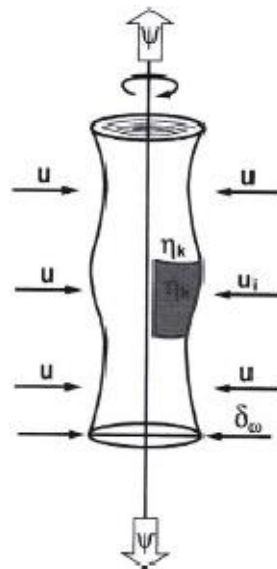
**Figure 6** Trends of the Z potential



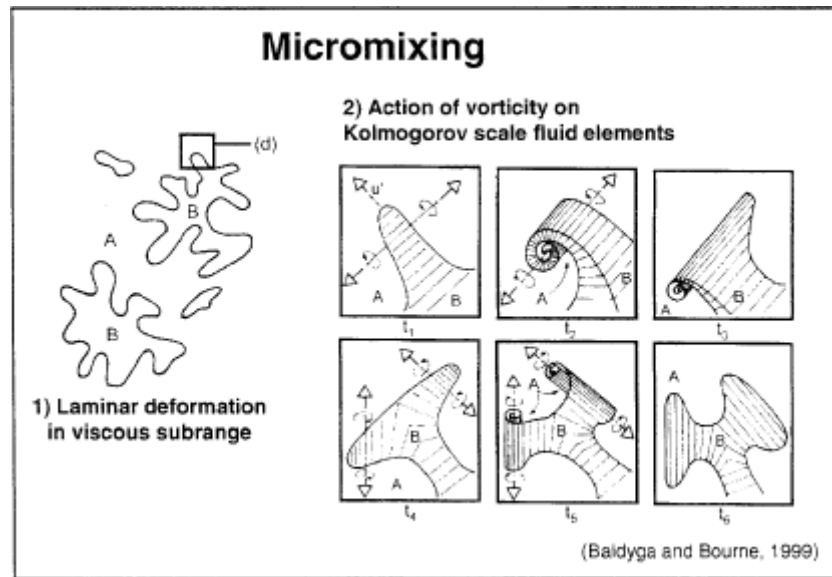
**Figure 7** The entity turbulent formation of the liquid



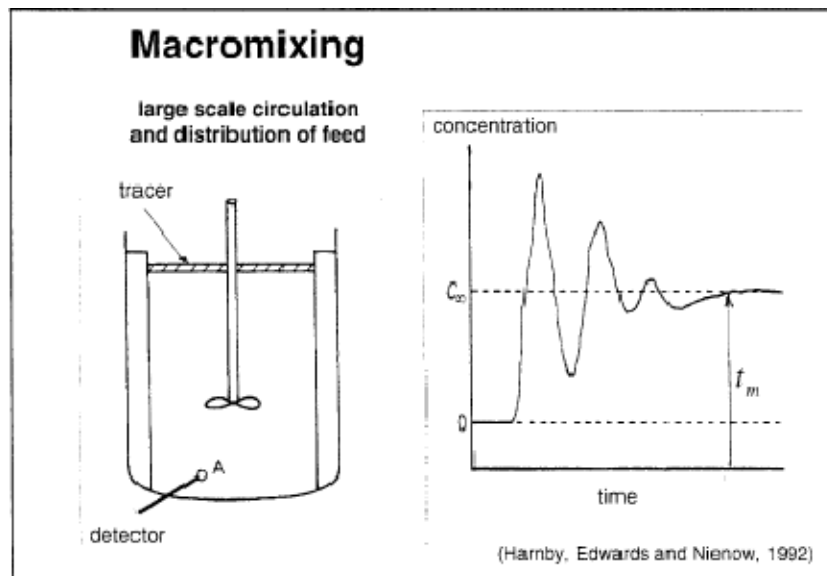
**Figure 8** specific energy distribution in a stirred tank



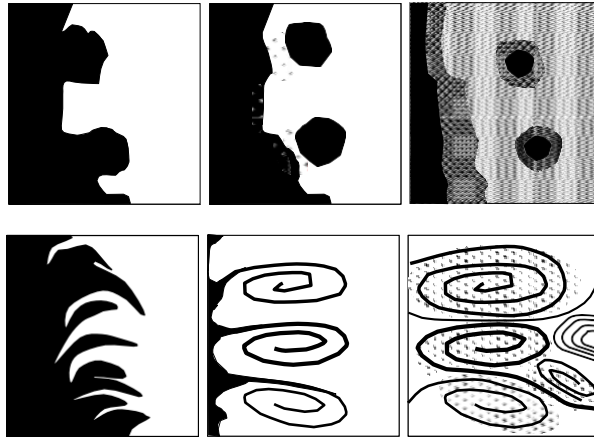
**Figure 9** The viscous deformation of elementary volumes of fluid



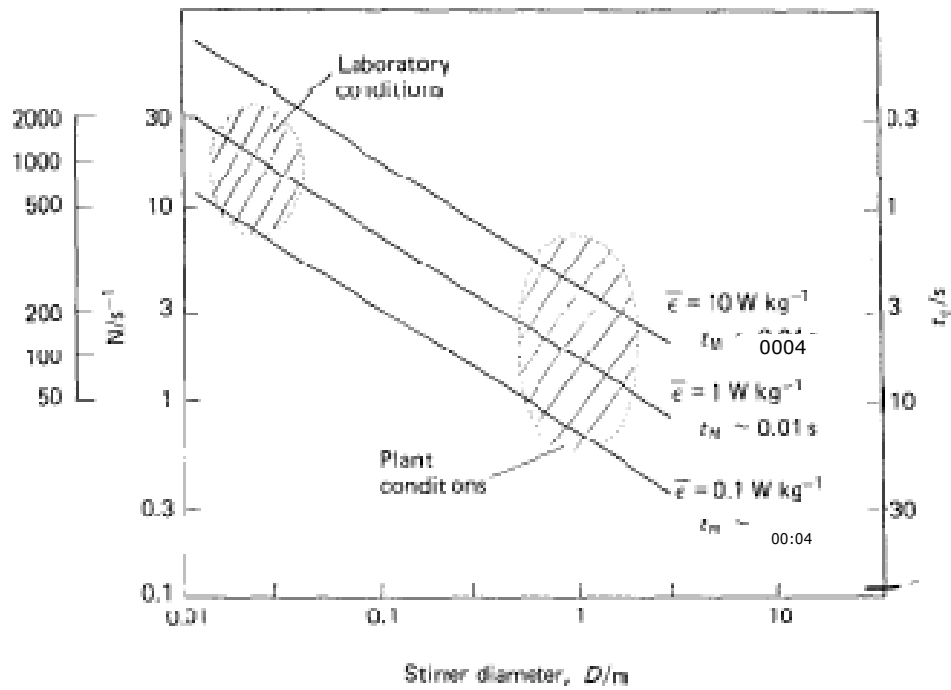
**Figure 10** The action of the vortices at the microscale of Kolomogorov



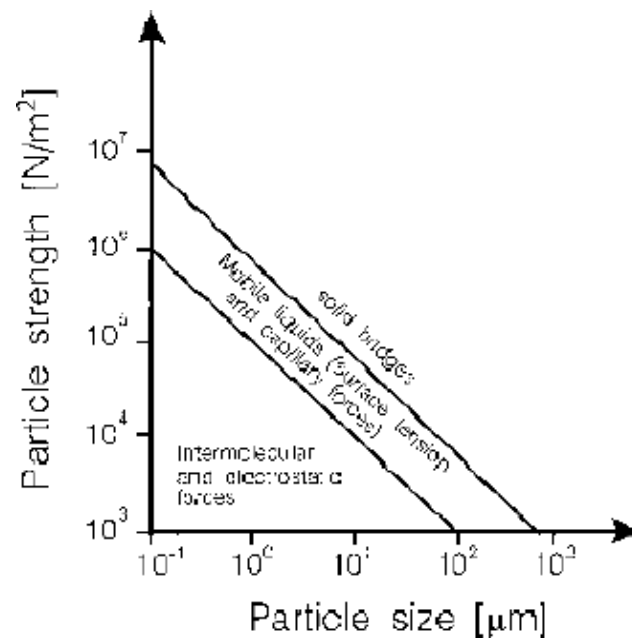
**Figure 11** Dynamics of a macromixing process in a stirred vessel



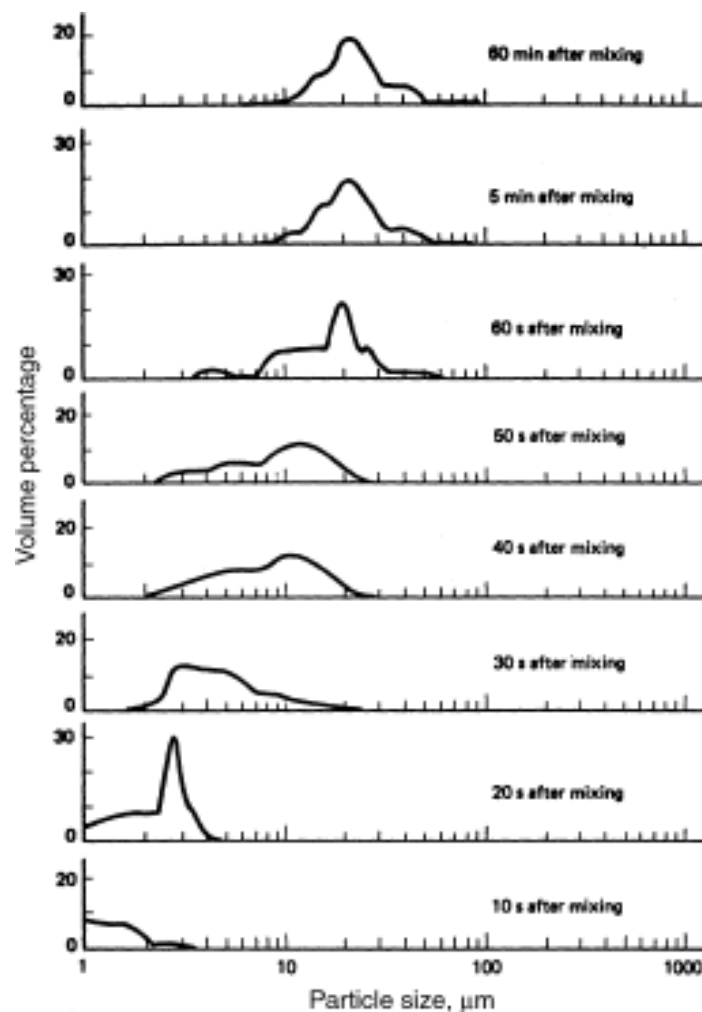
**Figure 12** Fluid mixing models (above "segregation" under "erosion")



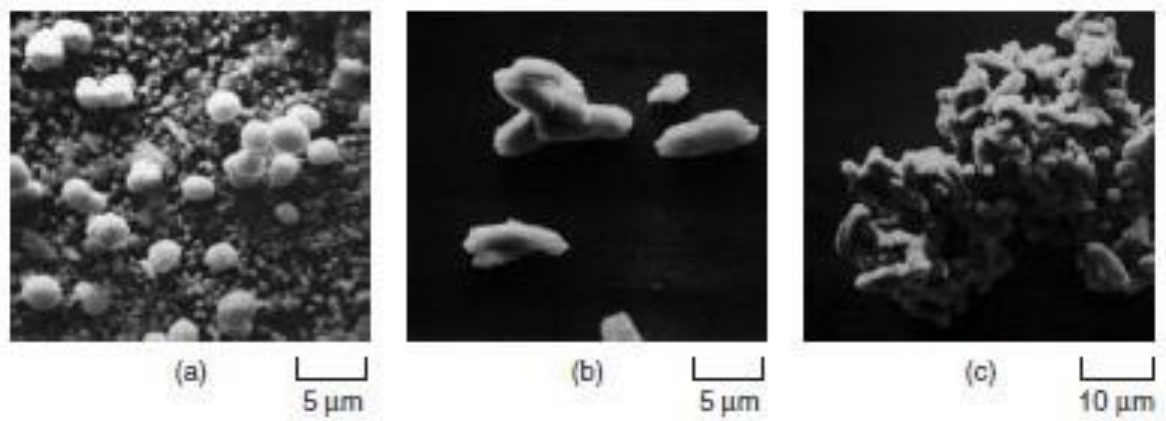
**Figure 13** Comparison between the recirculation time of the fluid and mixing times



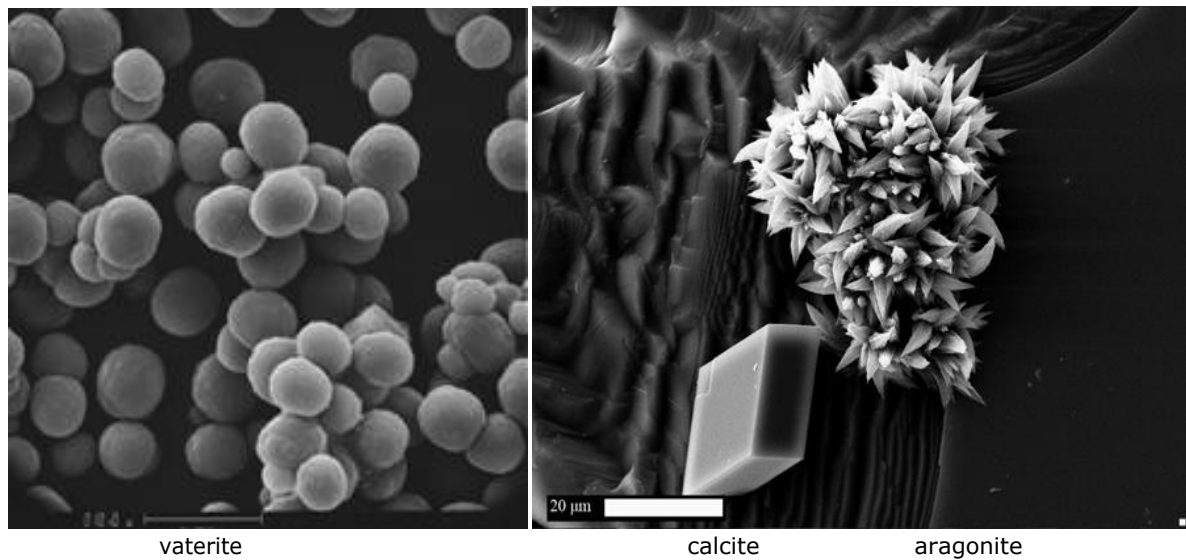
Forces of bonding between the particles as a function of their size



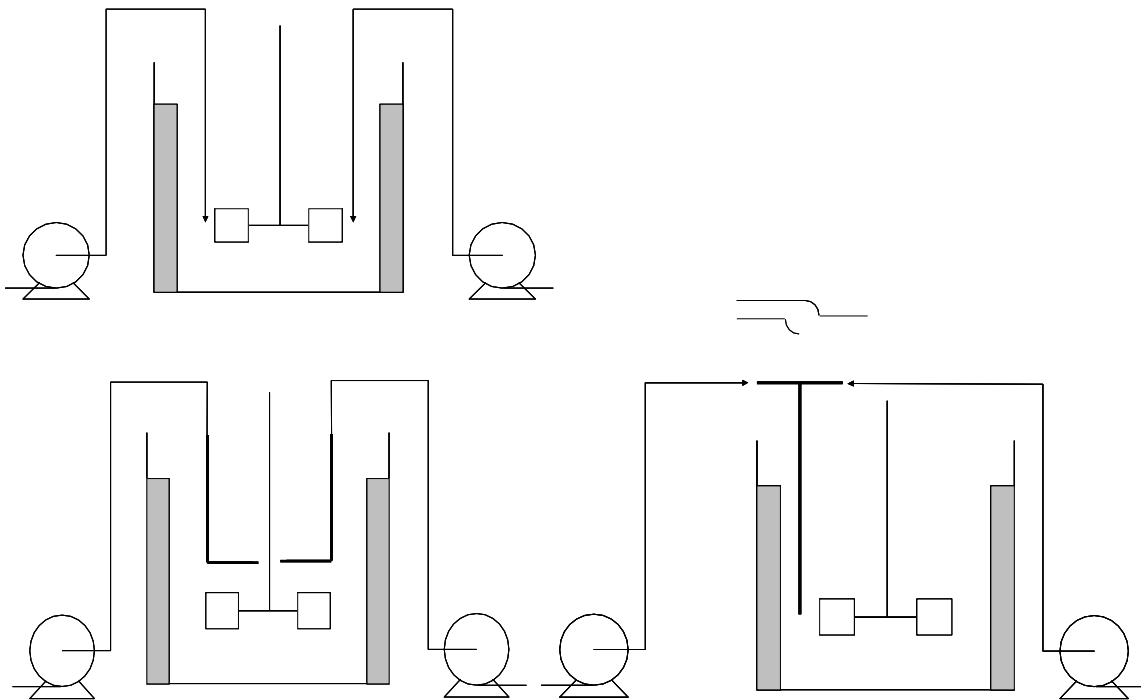
**Figure 8.2.** Volume percentage particle size distribution of  $\text{SrMoO}_4$  particles precipitated batchwise as a function of the time after mixing the reacting solutions. (After Söhnel, Mullin and Jones, 1988)



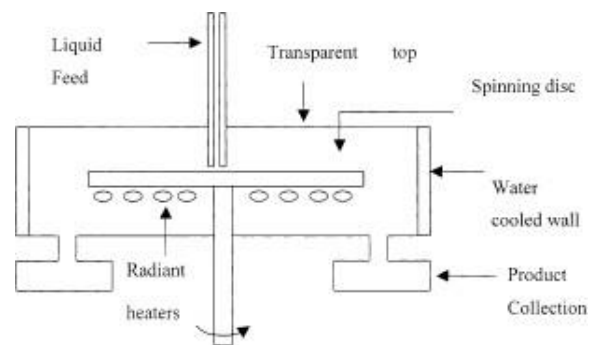
**Figure 8.3.** *Particles of precipitated  $\text{SrMoO}_4$  observed by SEM (a) towards the end of the induction period, (b) after 1 min. and (c) after 30 min. (After Solmel, Mullin and Jones, 1988)*



**Figure 14** Polymorphism of the calcium carbonate.



**Fig. 3:** Equipment for the precipitation.



**Fig. 4:** Spinning Disk (by Cafiero et al., 2002).

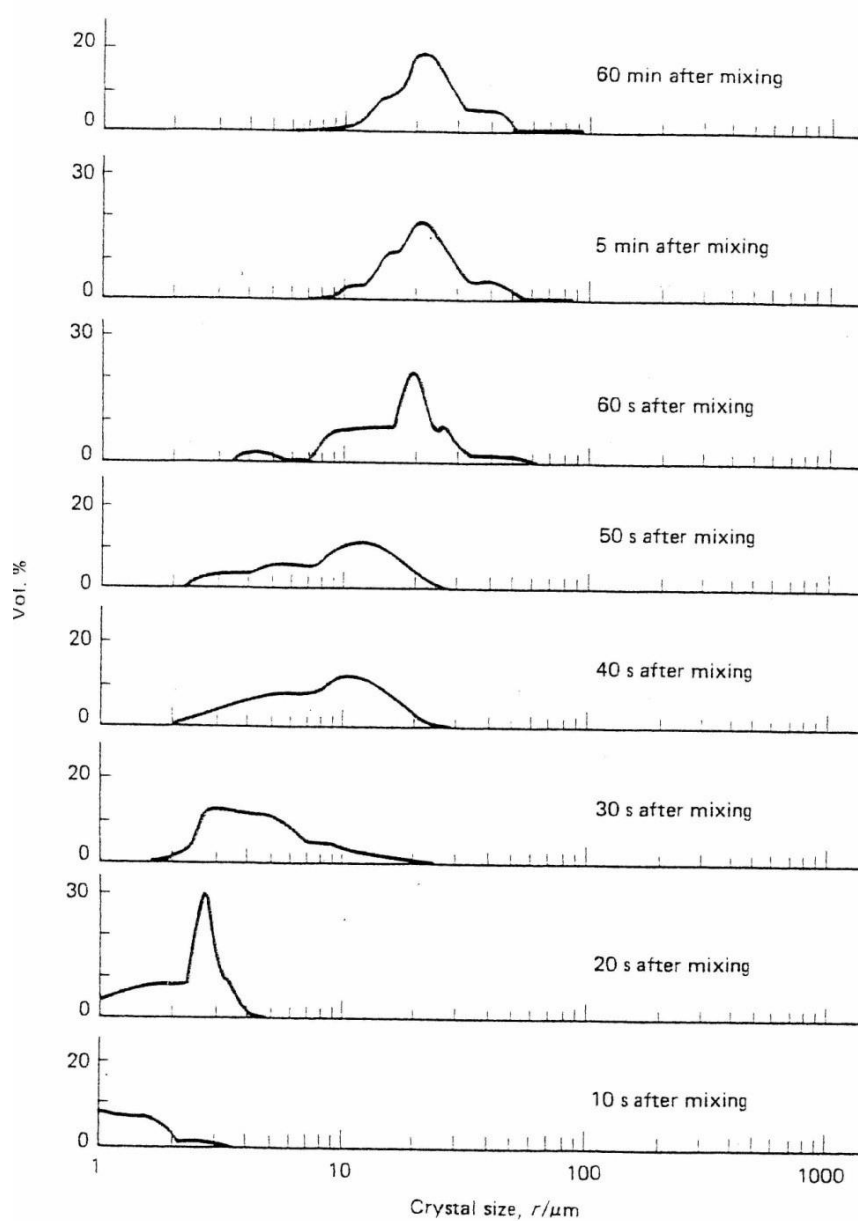


**Tab. 1:** Agglomeration pericinetica and ortocinetica.

Perikinetic agglomeration	
$\frac{dN(t)}{dt} = -4\pi D_{AB} L N^2$ or $\frac{d(1/N)}{dt}$	
$= 4\pi D_{AB} L$	
$\frac{dZ}{dt} = \frac{d}{dt} \left( \frac{N_0}{N(t)} \right) = 4\pi D_{AB} L N_0$	
$Z \equiv \frac{N_0}{N(t)} = 1 + 4\pi D_{AB} L N_0 t$	
$N(t) = \frac{N_0}{1 + 4\pi D_{AB} L N_0 t}$	
Orthokinetic agglomeration	
$\frac{dN(t)}{dt} = -\frac{2}{3} A_{agg} \dot{\gamma} L^3(t) N^2(t)$	
or with volumetric holdup $\varphi_T = \alpha L^3(t) N(t) \neq f(t)$ :	
$\frac{dN(t)}{dt} = -\frac{2}{3\alpha} A_{agg} \dot{\gamma} \varphi_T N(t)$	
$Z \equiv \frac{N_0}{N(t)} = \exp\left(\frac{2A_{agg} \dot{\gamma} \varphi_T t}{3\alpha}\right)$	
$N(t) = \frac{N_0}{\exp(2A_{agg} \dot{\gamma} \varphi_T t / 3\alpha)} = \frac{\varphi_T}{\alpha L^3(t)}$	

**Tab. 2:** agglomeration Kernel.

Literature	$K(V_{Pu}, V_{Pv})$ with $V_{Pu}^{1/3} = L_u$ ; $V_{Pv}^{1/3} = L_v$
Brownian motion (von Smoluchowski, 1917)	$\frac{2kT}{3\eta_L} (L_u + L_v) \left( \frac{1}{L_u} + \frac{1}{L_v} \right)$
Laminar shear, $\dot{\gamma} = \frac{dw_L}{dy}$ (von Smoluchowski, 1917)	$\frac{4}{3} \dot{\gamma} (L_u + L_v)^3$
Turbulent diffusion (Low, 1975)	$k_1 \dot{\gamma}_S (L_u + L_v)^3$
Turbulent inertia (Drake, 1972)	$0.2 \frac{\rho_c(\bar{\epsilon})^{3/4}}{\rho_L \nu_L^{5/4}} E_i (L_u + L_v)^2 (L_u^2 - L_v^2)$
Gravitational settling, $L < 50 \mu\text{m}$ (Drake, 1972)	$K \frac{\rho_L g}{\eta_L} E_i (L_u + L_v)^2 (L_u^2 - L_v^2)$
Gravitational settling, $L > 50 \mu\text{m}$ (Berry, 1967)	$C_{agg} E_i (L_u + L_v)^2  L_u - L_v $
Gravitational settling (Thompson, 1968)	$C_{agg} \frac{E_i (L_u^3 - L_v^3)^2}{L_u^3 + L_v^3}$



Volume percentage size distribution of  $\text{SrMoO}_4$ , precipitated batchwise by mixing solutions of  $\text{SrCl}_2$  and  $\text{Na}_2\text{MoO}_4$ , as a function of the time after mixing the solutions (after Söhnel, Mullin and Jones, 1988)

**Fig. 5:** Ostwald ripening.