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Course:
**Production technologies of micro / nano
particles**

CRYSTALLIZATION

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1 GENERAL ON CRYSTALLIZATION FROM SOLUTION

The crystallization is the process of separation between the components of a fluid (liquid solution, molten or vapor) which leads to obtain a final liquid phase of the component that is separated and a solid phase consisting essentially by the component that is intended to be separated. Crystallization from solution is the most common application of this operation is done chemical and petrochemical industry.

A solid contacting compound with a solvent enter into solution until the chemical potential of the compound in solution, referred to as the solute, is less than the solid chemical potential: it defines solubility the concentration value for which the solute in solution is in equilibrium with the solid phase. The solubility value mainly depends on the solvent composition and the temperature and, to an extent often negligible, by pressure.

A solution in which a solute is present in higher concentrations than that of balance is defined supersaturated: in this case you create conditions suitable to the birth of the solute crystalline germs, which will gradually increase until reaching sizes that can also be a few millimeters .

The supersaturation in the solution can be obtained in various ways:

- for cooling or heating of the solution, according to which the temperature increases or decreases the solubility;
- by evaporation;
- by chemical reaction with production of the solute;
- by adding to the solution of a solvent or a solute which reduces the solubility of the solute that is meant to separate (salting-out phenomenon).

The process of crystallization products are the residual solution, said mother liquor, and a solid material, formed from different crystals for dimension and appearance (crystal habit). The performance of the process affect not only the chemical composition of the obtained crystals or mother of water, but also the particle size distribution of the crystals and their shape, in fact, very often the most important variable in the conduct of an industrial crystallizer is the particle size distribution of the crystalline product. In fact, there are no specific constraints for the sale of the product regarding the percentage of fine crystals or crystals of high greater size of a maximum size. Furthermore, it is generally desirable to reduce the percentage of purposes in a crystalline product,

The particle size distribution and shape of the crystals obtained are numerous consequences of the phenomena involved in the process of crystallization, as shown in the diagram in Fig. 1.1. Among them the most important are the nucleation, or the generation of new crystals, and the growth of the individual faces of the crystals present in the suspension.

In turn, these two phenomena are influenced by the operating temperature and pressure conditions, by the hydrodynamic conditions of the equipment and strongly by the presence of specific additives and impurities, even at the level of parts per million. From what has been said, one can understand the difficulties that are encountered in predicting the evolution of the crystallization process, and then in the design and / or in the verification of industrial equipment.

Indeed the crystallization from solution, while being an operation practiced for thousands of years (eg. for the production of sodium chloride), only recently has found a scientific approach methods that have provided satisfactory results in the industry.

Note, finally, that the characteristics of the final solid of a production process based on crystallization depends not only on the operation of crystallization, but also from downstream operations (centrifugation, filtration, drying, etc.) As illustrated by the sequence of process shown in fig. 1.2.

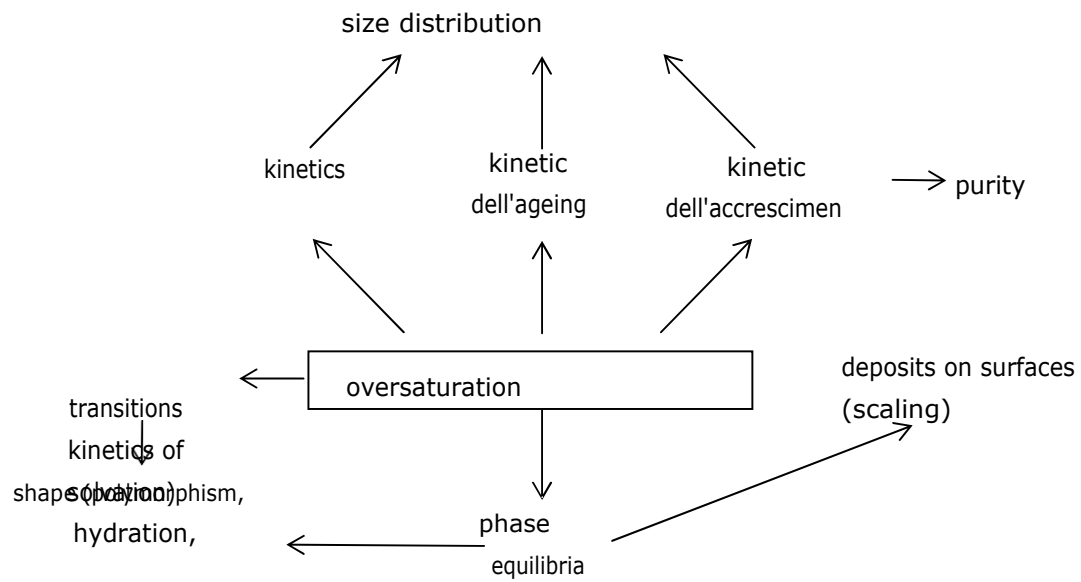


Fig. 1.1: The role of supersaturation in crystallization processes.

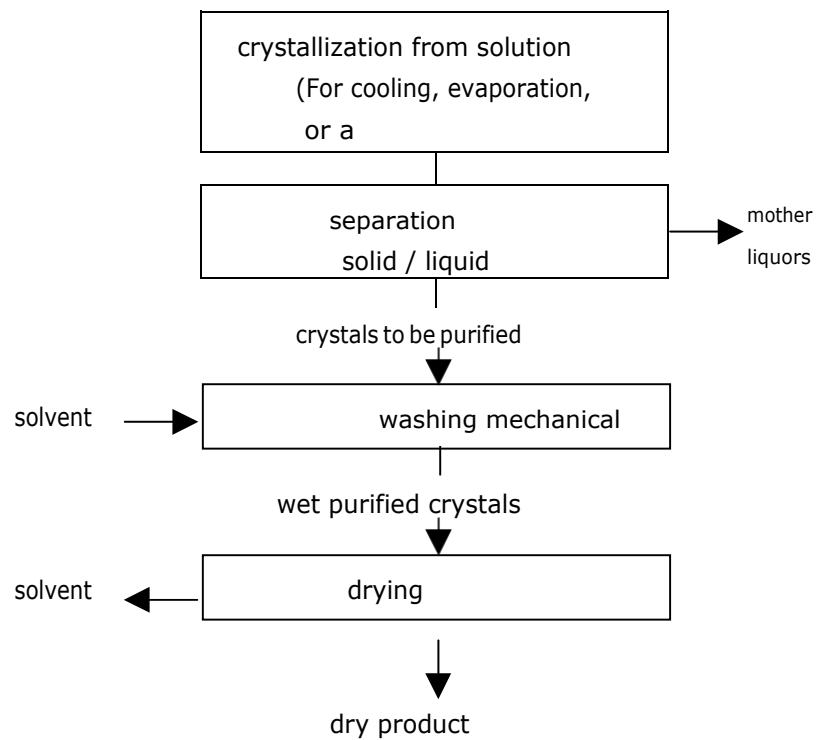


Fig. 1.2: Crystallization and subsequent operations (downstream processing).

2 STRUCTURE AND SIZE OF SOLID MATERIALS

2.1 Design and characterization of crystalline solids

The crystals are solids in which the elementary particles occupy ordered and periodic positions. The spatial arrangement of the particles is called lattice. The structural unit that is repeated in the lattice according to the three spatial dimensions is said elementary cell. The elementary particles can be atoms (eg. Diamond), ions (eg. Sodium chloride) or molecules (eg. Sucrose). A particular chemical species can form crystals with a different structure (polymorphism phenomenon). An example of polymorphism in nature is the carbon, which can form the diamond or graphite.

The lattice may have one-dimensional imperfections (substitutions, interstitial defects, gaps), two-dimensional (planar and screw dislocations) or three-dimensional (inclusions and voids). In fig. 2.1 shows the point and linear defects.

The lattice, and the elementary cell that composes it, are defined by:

- the spatial conformation of the atoms in the unit cell;
- the size of the edges of the elementary cell a , b , c ;
- the angles between the edges of the elementary cell, α , β , γ .

There are 14 different possible conformations for the elementary cells, as demonstrated by Bravais in 1848 (see Fig. 2.2).

To characterize the lattice of a crystalline material is, generally, used the X-ray diffraction. The X-ray wavelengths, between 10 and 0.1 nm, are comparable with the dimensions of the distances of the particles in the lattice, for which undergo a diffraction when passing through the crystals. The diffraction angle, θ . It depends on the wavelength of the beam, λ , and the distance between the particles, d , according to the Bragg law:

$$2d \sin \theta = n\lambda \quad (2.1)$$

By rotating a crystal without flaws and measuring the diffraction angle of a known wavelength range you can evaluate the distances between atoms in the various directions.

The directions within the lattice are generally defined using the Miller indices, which represent the triad of components that identify a direction in a Cartesian system (see fig. 2.3); by convention we adopt the set of three minimum value integers and writes them in parentheses without any separator; the bar above a whole indicates a negative value. The Miller indices are also used to define the planes perpendicular to the directions defined by the corresponding vectors (see Fig. 2.4): the macroscopic shape of the crystals, called crystal habit, it can be characterized using the Miller indices of the faces that delimit them (see fig. 2.5).

The habit of a crystal depends both on the lattice structure, both from the external conditions in which crystallization occurs (pressure, temperature, concentration, possible presence of impurities).

2.2 Characterization of the particle size

The individual particles of a granular solid can be formed by a mono-crystal, more crystals from aggregates with each other or may present an amorphous structure. A qualitative classification of the macroscopic form of granular solids, crystalline or amorphous which are, distinguishes them in spheroidal, planar or acicolari

(needle-like), depending on whether they have none, two, or a prominent dimension. They should also define, form factors with respect to a characteristic dimension L as: surface factor k_s :

$$k_s = \frac{S}{L^2} \quad (2.2)$$

volume factor k_v :

$$k_v = \frac{V}{L^3} \quad (2.3)$$

For example, for a sphere is regarded as characteristic dimension is the diameter and $k_v = \pi/6$, $k_s = \pi/4$. Similarly, for a cube the characteristic dimension is the edge $k_v = 1/6$, $k_s = 1/2$. To forms characterized by multiple dimensions, such as a parallelepiped, generally refers to the second dimension. This is because the measurement of the particle size of a solid and its separation into size classes, are generally carried out by sieving.

The particles that make up a granular solid do not have all the same size: for a solid it is necessary to define the size distribution of the crystalline population (Crystal Size Distribution, CSD, or Particle Size Distribution, PSD).

For a population is defined as the probability density with respect to a quantitative characteristic continues L the function $f(L)$ such that the probability that the value of L for the elements of the population is between L' and L'' is equal to the integral of $f(L)$ between L' and L'' :

$$P(L' < L < L'') = \int_{L'}^{L''} f(L) dL \quad (2.4)$$

The distribution density enjoys the normalization properties:

$$\int_{L_{min}}^{L_{max}} f(L) dL = 1 \quad (2.5)$$

If the probability is expressed as the number of particles on the total of the particles, it is called numerical distribution; if, on the other hand the probability is expressed as a volume, or weight, on the total of the particles, it is called volumetric distributions. The CSD is often expressed in cumulative terms:

$$L(\vec{r}) = \frac{1}{2} \left(\frac{d\vec{r}}{dt} \right)^2 + U(\vec{r}) \quad (2.6)$$

You define the following parameters (see fig. 2.6)

- more likely or fashion size: it corresponds to the peak of the distribution density function. If the $f(L)$ presents a single peak, the distribution is called single-mode, if the peaks are two bimodal etc.

- average size:

$$\bar{L} = \frac{\int_0^\infty L \cdot f(L) \cdot dL}{\int_0^\infty f(L) \cdot dL} \quad (2.7)$$

- median size is that size which corresponds to a cumulative distribution of 50%

$$\int_0^{L_{50}} f(L) \cdot dL = 0.5 \quad (2.8)$$

- distance between quartiles: $L_{75} - L_{25}$
- coefficient of variation:

$$CV = \frac{L_{84} - L_{16}}{2 \cdot L_{50}} \quad (2.9)$$

CV for a Gaussian equals σ / μ , and sometimes even for different distributions it is evaluated as the ratio between the standard deviation and the average value.

In the industrial field The CSD of granular products are expressed in terms of weight. In addition it tend to characterize the distribution by means of a reduced number of parameters, such as the median and the coefficient of variation or the distance between the quartiles. For scientific applications, in particular for the modeling of crystallization processes, it is appropriate to express the CSD in numerical terms: in particular, it defines population density $n(L)$ that function such that the number of crystals per unit volume characterized by a size between L and $L + \Delta L$ is:

$$\frac{dN}{V \cdot dL} = n(L) \quad (2.10)$$

The population density is obviously related to the probability density by the equation:

$$n(L) = \frac{N_{tot}}{V} \cdot f(L) \quad (2.11)$$

A special importance attaches to the population density moments $M_n(L)$: it defines the moment of the integral order

$$M_n = \int_0^\infty L^n \cdot n(L) \cdot dL \quad (2.12)$$

It is:

$$\frac{1}{\rho} \int_0^\infty L(nVN) dM_0 \quad (2.13)$$

$$\text{average} \frac{\int_0^\infty L(n(L)) L dL}{\int_0^\infty L(n(L)) dL} = \frac{1}{M M_0} \quad (2.14)$$

Furthermore, if k_s and k_v do not depend on L , it is

$$\frac{L(A n k_s)}{\int_0^\infty} \cdot \frac{1}{2} = \frac{L}{M} = M k_s \quad (2.15)$$

In which A_T It is the total surface of the crystals per unit volume, and the value of the average surface area for the crystals of the population is

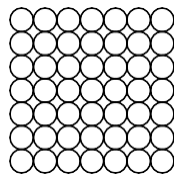
$$\text{average} = \frac{k_s A}{M M_0} \quad (2.16)$$

is

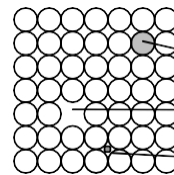
$$\frac{L(n k_v M)}{\int_0^\infty} \cdot \frac{1}{3} = \frac{L}{M} = M k_v \quad (2.17)$$

In which M_T It is the total volume of the crystals per unit volume and

$$\text{average} = \frac{k_v V}{M M_0} \quad (2.18)$$



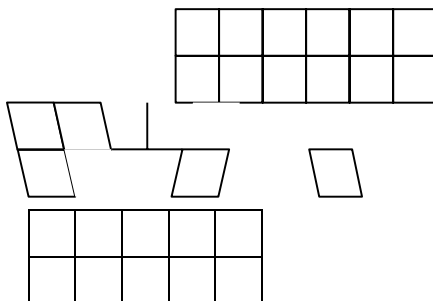
perfect lattice



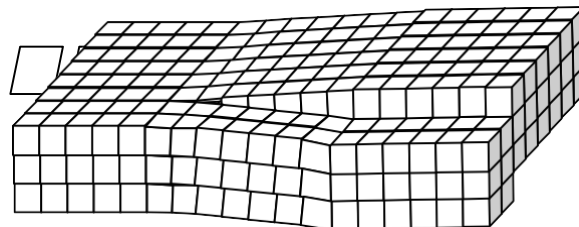
replacement

defect interstitial gap

point defects



planar dislocation



screw dislocation

Fig. 2.1: The lattice defects.

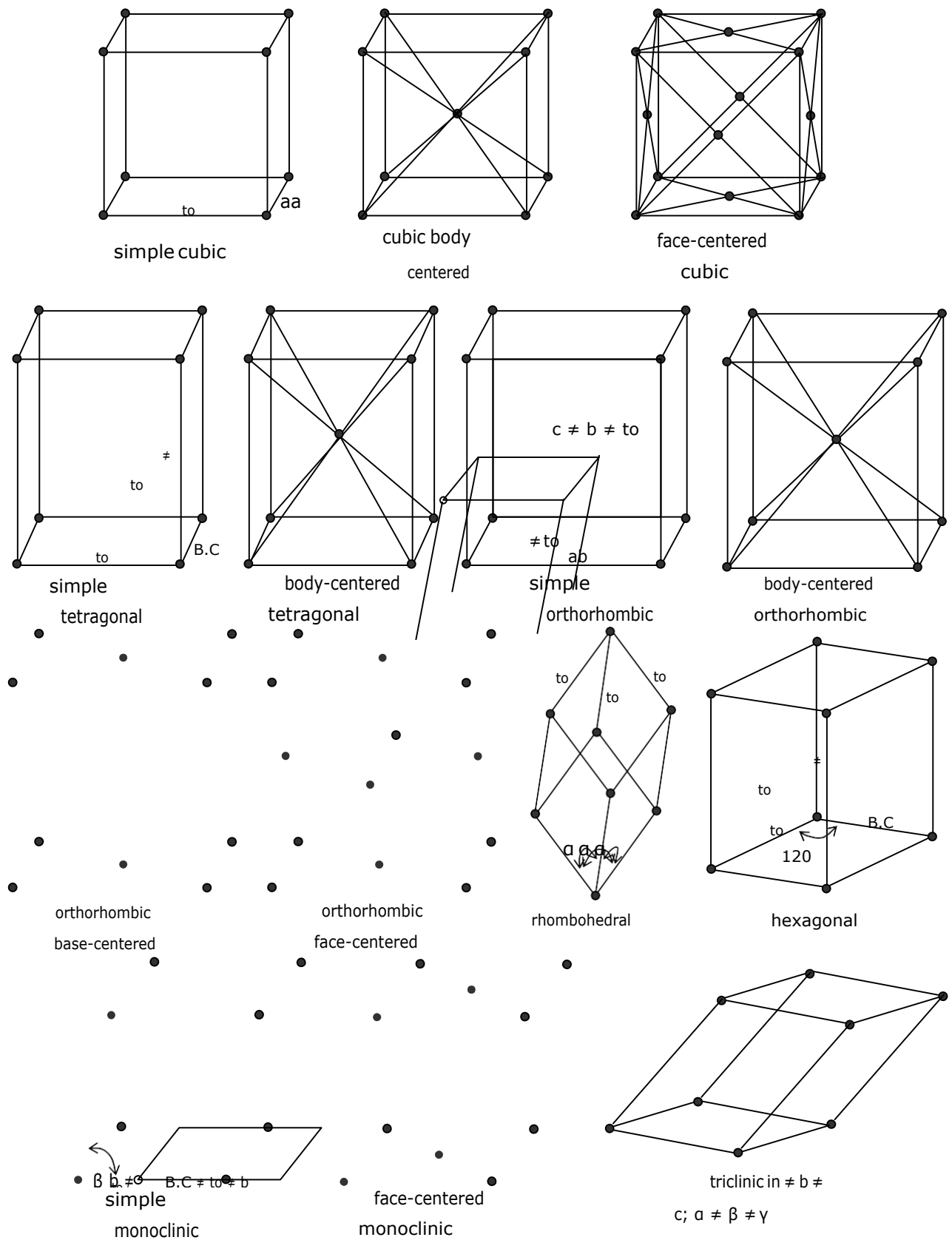


Fig. 2.2: The 14 elementary cells.

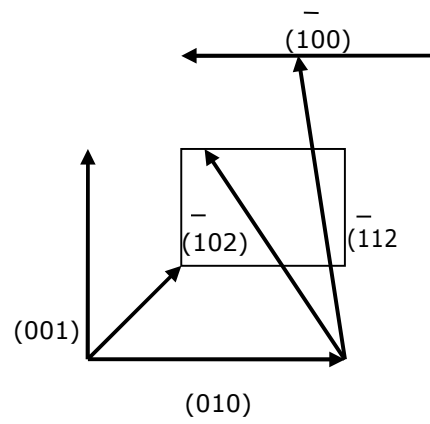


Fig. 2.3: The Miller indices of the directions.

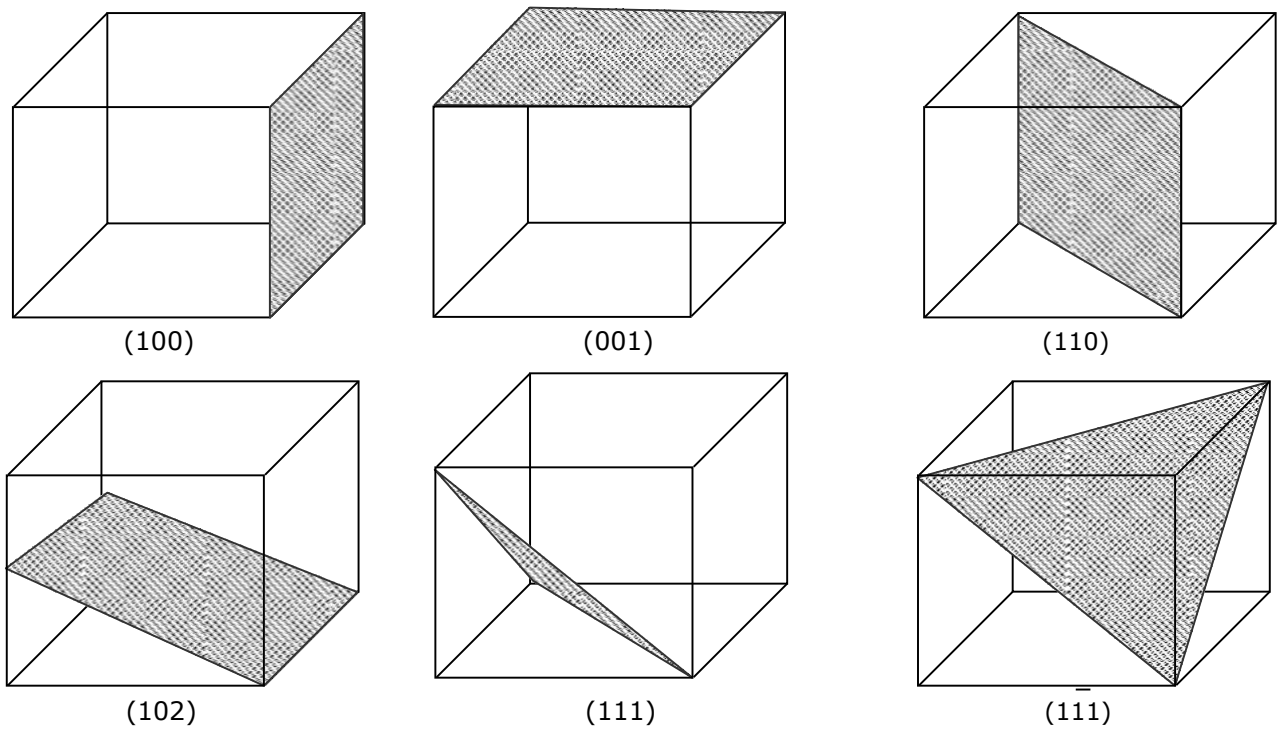


Fig. 2.4: The Miller indices of the surfaces.

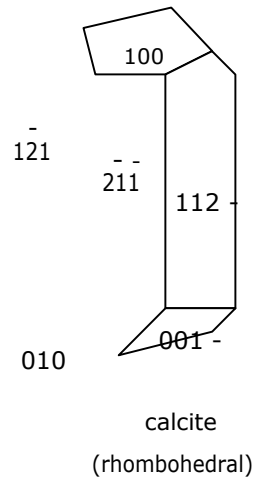
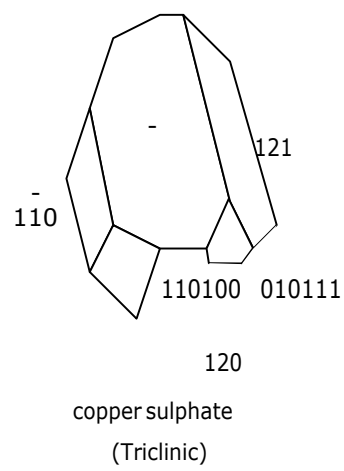
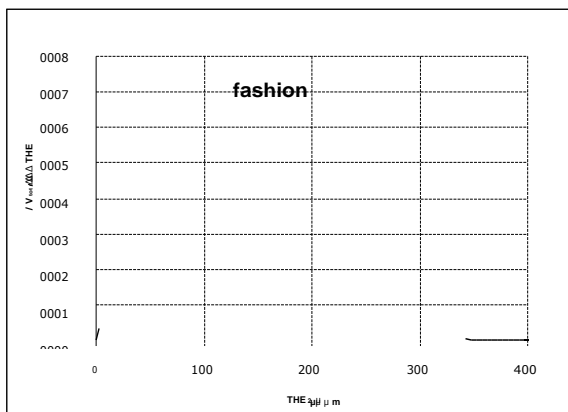
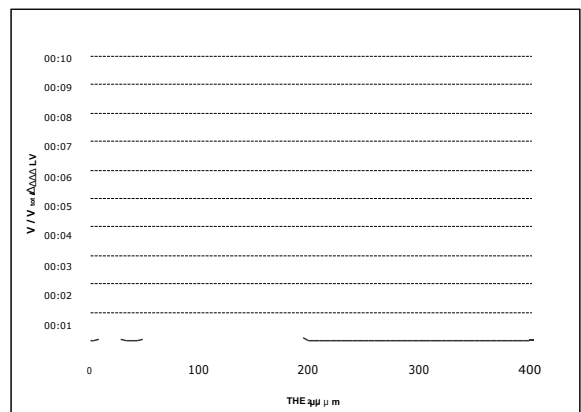


Fig. 2.5: Description of the crystals through the Miller indices.



singlemode distribution



bimodal distribution

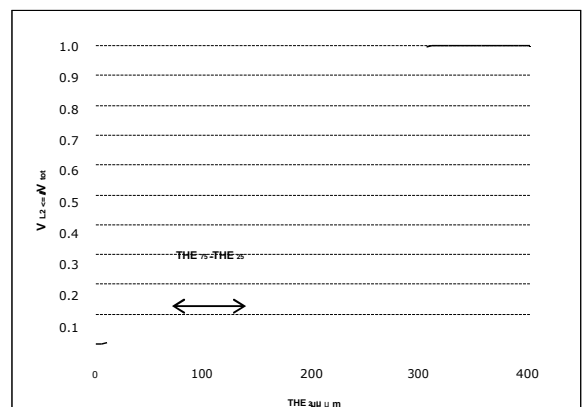
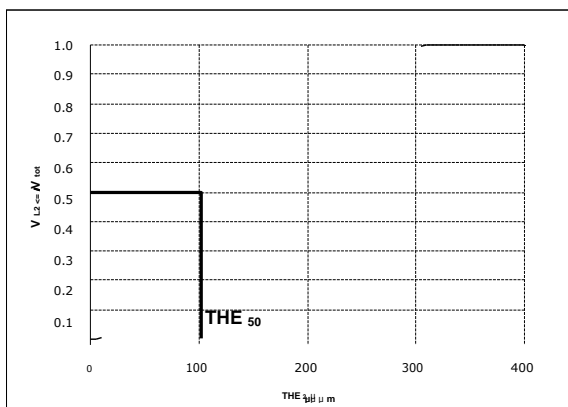


Fig. 2.6: Parameters of the size distribution functions.

3 THE REGION metastable

The level of supersaturation of a solution can be expressed in various ways:

- concentration difference

$$\text{volumetric } \Delta c = c - c_{eq} \quad (3.1)$$

$$\text{mass } \Delta w = w - w_{eq} \quad (3.2)$$

where c is the concentration in kg/m^3 , w the mass fraction of solute in kg/kg solution, and the subscript eq indicates the equilibrium conditions;

- ratio of supersaturation

$$S = \frac{c}{c_{eq}} \quad (3.3)$$

Wherein x is the mole fraction of the solute in solution

- relative supersaturation

$$\frac{\mu_{s,L} - \mu_{s,S}}{RT} \quad (3.4)$$

In which $\mu_{s,L}$ is $\mu_{s,S}$ They are, respectively, the chemical potential of the solute in solution and in the solid phase, R is the gas constant, T the temperature in Kelvin. Under equilibrium conditions, the chemical potential of the solute in the solid phase and in solution are equal, so that (3.4) can be written in the form

$$\frac{\mu_{s,L} - \mu_{s,S}}{RT} = \ln(\gamma_{s,L} \sigma_{s,L}) \quad (3.5)$$

Where to $\gamma_{s,L}$ is $\sigma_{s,L}$ indicate, respectively, the activity and the coefficient of activity of the solute in solution. For

simplicity, the subscripts if L is implying: since it is usually

$$\frac{\mu_{s,L} - \mu_{s,S}}{RT} = \ln(\gamma_{s,L} \sigma_{s,L}) \quad (3.6)$$

In a supersaturated solution the generation of crystal nuclei occurs only after a well-defined time, called the

induction time. The induction time decreases with increasing supersaturation and tends to zero for a precise value of said maximum supersaturation that is normally expressed in terms of concentration difference, Δc_{\max} , and, more rarely, in terms of weight, Δw_{\max} . This value is

function of the hydrodynamic conditions of the system, the speed with which the supersaturation and the temperature was varied. If the first two conditions are fixed, Δc_{\max} It is a function of temperature only, and the curve formed by points (c_{\max}, T) is called the start of nucleation curve.

In the plan concentration - temperature, the nucleation curve is entirely above or below the solubility curve depending on whether the solubility of the trend is positive or negative with temperature: in fig. 3.1 are represented the solubility curve and the start nucleation for a system with a trend of increasing solubility with temperature, which is the case by far the most common. The region between the two curves is called metastable region of the system.

The metastable region is of utmost importance as it delimits the scope of operational variables of crystallizers. In fact, at concentrations less than solubility of the crystallization process it does not take place, but rather takes place the dissolution of any crystals present; on the other hand at concentrations greater than that corresponding to the curve start of nucleation, ie in the so-called lability area, each minimum disturbance triggers an intense nucleation, with consequent lowering of the concentration of the solute in solution that brings the operating conditions inside the zone metastable. The identification of the metastable region is also useful for evaluating the optimal operating conditions for a crystallization. A location of the operating point (c, T) near the nucleation curve indicates a preponderance of nucleation compared to the growth, with the production of many crystals that may be small in size, while its close proximity to the solubility curve can mean a difficulty both in the generation of crystals in their growth. The best working conditions, ie those that combine a sustained rate of growth with a reduced rate of nucleation occur for points in the central part of the metastable zone.

The metastability range varies from system to system and, for the same system, may vary with temperature. Moreover, the presence of additives or impurities in the solution can affect more or less markedly the range of metastability field demonstrating the effect that they make solid-solvent interaction. The values of the maximum temperature difference which corresponds to the Δc_{\max} , ranging from a few tenths of a degree for some salts in aqueous solution (eg. potassium chloride and ammonium chloride) to a few tens of degrees for many organic crystals.

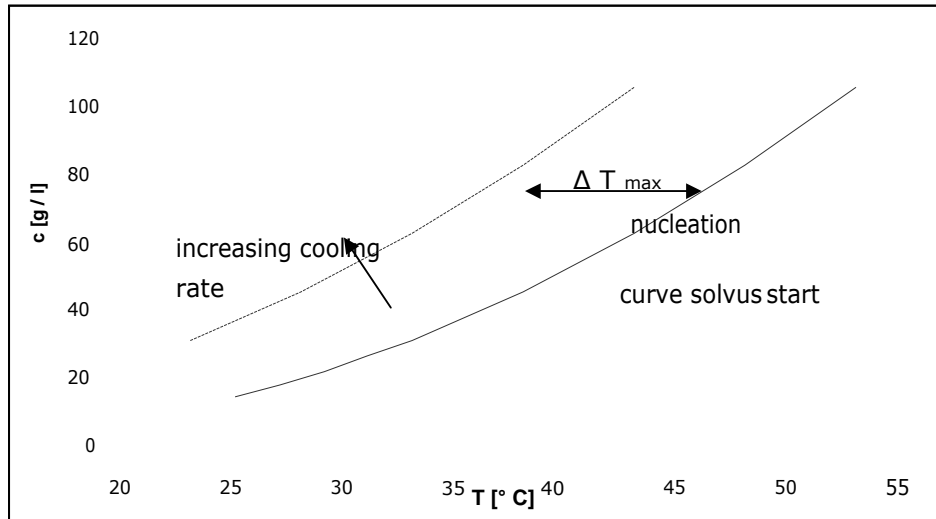


Fig. 3.1: metastable range.

4 THE nucleation

It is intended for any nucleation phenomenon that ports to the production of new crystals. A distinction is made between nucleation that occurs in the absence of crystals (primary nucleation) and the one that takes place in the presence of crystals (secondary nucleation). In turn, the primary nucleation is divided into homogeneous and heterogeneous, depending on whether the formation of crystal nuclei within the solution occurs spontaneously or in the presence of foreign substances (eg. Atmospheric dust). The secondary nucleation, however, can have a dual nature:

1. the birth of nuclei in the heart of the solution, thanks to the presence of aggregates of molecules that have been removed from the adsorbed layer on the surface of the crystals and because of the entrainment of the fluid in motion (catalytic mechanism);
2. the production of crystalline fragments due to collisions of the crystals on the surface of the crystallizer, the agitator paddles or on another crystal (collisional mechanism).

relate to the birth of a new crystal or the detachment of a fragment from an existing crystal due to a mechanical stress. A brief overview of the different nucleation phenomena is represented in fig. 4.1.

With regard to the primary nucleation, it is possible to hypothesize that the "aggregate" of solute molecules that are in a supersaturated solution as a result of collisions grow greater, giving rise to "embryos", which probabilistically can assume a size greater than a said critical, function of supersaturation at which is located the solution, and in any case appreciably lower than $1 \mu m$. When this happens the embryo stabilizes to become "core", and then, for accretion effect, a crystal size gradually greater.

Embryos that, however, do not reach a size above the critical one can not originate a crystalline nucleus.

The rate of formation of nuclei, said speed of primary nucleation, is usually expressed with the Volmer equation:

$$J = \frac{16 \pi \gamma^3 V_m}{3 k T \ln S} \exp \left(- \frac{\Delta G^*}{k T} \right) \quad (4.1)$$

Where:

- J nucleation rate expressed in number of nuclei per unit volume of solution and per unit of time
 $[\# \cdot m^{-3} \cdot s^{-1}]$
- γ preesponenziale factor experimental nature $[\# \cdot m^{-3} \cdot s^{-1}]$
- V_m interfacial tension solid-solution $[J / m^2]$
- V_m molecular volume $[m^3]$
- k Boltzman constant, equal to $1.38 \cdot 10^{-23} [J / K]$
- T absolute temperature $[K]$

the supersaturation ratio

It should be noted that, according to (4.1) there is a direct proportionality between the J logarithm and the logarithm of high S to -2 .

In the case of heterogeneous primary nucleation it is necessary to take into account the reduction of the interfacial tension due to the presence of solids, such as atmospheric dust. In this case

$$J = \frac{16 \pi \gamma v^2}{kT} \exp \left(-\frac{\Delta G^*}{kT} \right) \quad (4.2)$$

where the reduction factor ϕ is function of the angle of wettability between the solid and liquid: if the solid is not wet by the liquid, ϕ It is equal to 1 and the nucleation rate is not influenced by the presence of the solid. By contrast, the greater the affinity between the solid and the liquid, the more ϕ It is reduced and the nucleation speed increases.

The nucleation rate, in a less rigorous, can also be expressed as a mass of crystalline nuclei per unit volume and per unit time, R_N ; in this case the link with the oversaturation is expressed with a power relation of the type:

$$R_N = k \sigma^m \quad (4.3)$$

The secondary nucleation is defined as that which occurs when they are already present crystals in suspension. It may be attributed to the following two classes of mechanisms:

- **catalytic mechanisms** : The layer of solute, in the form of molecular aggregates adsorbed on the crystal surface can be partially moved in the heart of the solution; as a consequence increases the concentration of the aggregates in solution and the nucleation phenomenon is thus catalyzed. The nuclei that are generated have size less than one micron.

The secondary nucleation speed for catalytic mechanism, $B_{N, cat}$, It is generally expressed by the relation:

$$B_{N, cat} = k_{N, cat} \sigma^m \quad (4.4)$$

In which $B_{N, cat}$ is the speed expressed in nucleation crystals per unit volume of solution and per unit of time [$\# / m^3 / s$], and the exponent m is experimental in nature.

- **Collision Mechanisms** : The crystals are subjected to impact with the walls and the interior of the crystallizer, and between them. The voltages that are generated as a result of each shock can lead to the production of fragments of small dimensions (friction phenomenon) or fragments of size comparable with

the size of the original crystal (the fracture phenomenon). In addition, the fluid stream can detach dendrites present on the surface of the crystals giving rise to fragments of small size (abrasion phenomenon).

The secondary nucleation speed for collisional mechanism is generally expressed by a type of empirical relation:

$$B_{N, \text{coll}} = B_{N, \text{et al}} \sigma = K \tau^r \epsilon^i \quad (4.5)$$

In which $B_{N, \text{et al}}$ is expressed in crystals per unit volume of solution and per unit of time [$\# / \text{m}_3 / \text{s}$], ϵ is dispersed by the agitator power per unit volume of the solution (between 0.3 and 1.5 W / kg) and M_T the concentration of the crystals in the solution, expressed in kg of crystals per m_3 of solution. The exponents r , i and j are of an experimental nature. Their field of variation is, in a first approximation, the following:

$$r = 1 \div 4 \quad j = 1 \div 2 \quad i = 0.4 \div 1.0$$

The coefficient K depends on several factors:

- the nature, the crystal habit and size of crystals;
- the geometry, the capacity and the hydrodynamics of the crystallizer;
- the temperature and the nature of the solution, including the impurities and additives present.

From what has been said it can be inferred that the rate of nucleation is difficult to extrapolate a magnitude for the same system by an apparatus to another, even if geometrically similar. It's instead possible to make predictions about the distribution of the fragments that are obtained by collisions up to a size of $100 \div 150 \mu\text{m}$: Recently Chianese and Mersmann (Chianese, 1996) have proposed to adopt, for crystals consisting of brittle material such as those of inorganic nature, the following generalized expression for the distribution of the fragments:

$$f(L_f) = \frac{N(L_f)}{N_{\text{TF}}} \quad (4.6)$$

where $f(L_f)$ is the distribution density function defined as

$$f(L_f) = \frac{N(L_f)}{N_{\text{TF}}} \quad (4.7)$$

where $N(L_f)$ is the number of fragments per unit volume having an average size L_f and size range ΔL_f and N_{TF} the total number of fragments per unit volume. The distribution density enjoys the normalization properties, so:

$$\int_{L_{f, \text{min}}}^{L_{f, \text{max}}} f(L_f) dL_f = 1 \quad (4.8)$$

On the basis of equations (4.4) and (4.6) it is possible to determine the value of the parameter A as a function of the parameter b of the limits of the fragments considered; by the following expression:

$$TO = \frac{b + 1}{L_{f \max}^{b+1} - T_{Hf \min}^{b+1}} \quad (4.9)$$

The equation (4.6) is therefore a function of only one parameter b. From the analysis of fragments obtained by collision phenomena of several organic and inorganic systems Chianese and Mersmann they showed that for a value of b equal to -2.82 you have a good agreement between prediction curve and the experimental data (see Fig. 4.2).

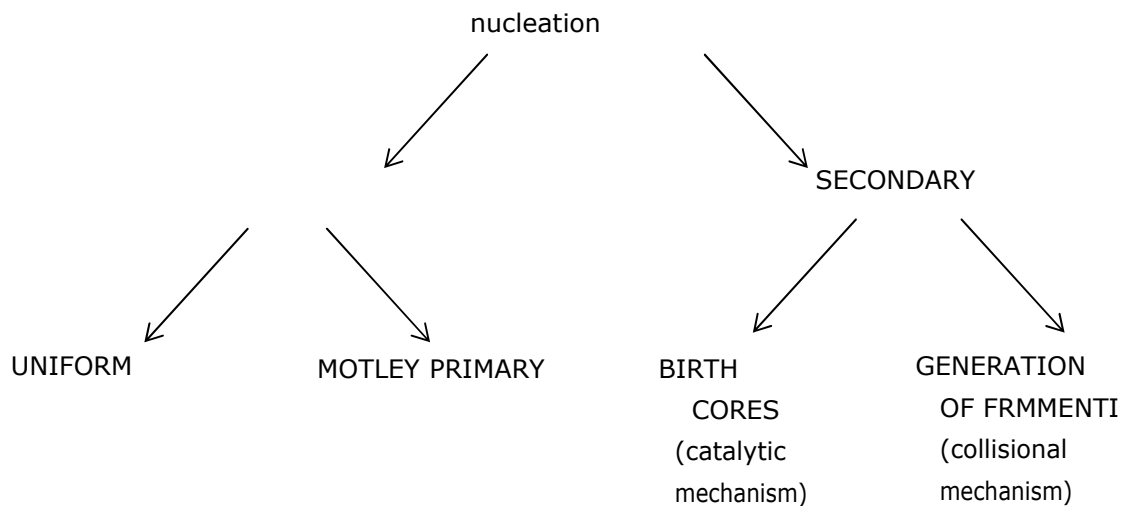


Fig. 4.1: Diagram of nucleation mechanisms.

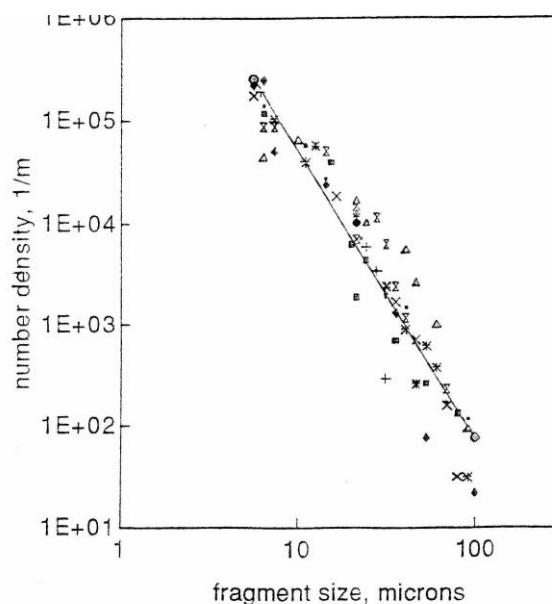


FIGURE 6 Fragment distribution of the organic compounds from impact experiments: thiourea (●) $L_c = 1000-1180 \mu\text{m}$, (+) $L_c = 500-600 \mu\text{m}$; tartaric acid (*) $L_c = 1000-1180 \mu\text{m}$, (□) $L_c = 500-600 \mu\text{m}$; sorbic acid (×) $L_c = 1000-1180 \mu\text{m}$, (◇) $L_c = 500-600 \mu\text{m}$; citric acid (Δ) $L_c = 1000-1180 \mu\text{m}$, (×) $L_c = 500-600 \mu\text{m}$.

Fig. 4.2: Distribution of fragments (Chianese et al., 1996).

5 GROWTH OF CRYSTALS

5.1 Definition of the speed of growth

A crystal immersed in a supersaturated solution grows because the solute tends to be deposited on its surface. Not always this phenomenon is isotropic: the faces that delimit a crystal may have different structural characteristics, both in terms of density of elementary particles, both in terms of their orientation: therefore the surface aggregation may be energetically favored, then the accretion more fast, on one face with respect to another. Another factor that may cause a different speed of growth is the presence of impurities in solution which will selectively adsorb on some of the faces, causing a slowdown in the aggregation phenomenon only on these. Due to the anisotropy of the surface aggregation phenomenon,

For each of the crystal face can be defined as a specific feed rate, said linear speed of growth of the face:

$$G = \frac{dL}{dt} \quad (5.1)$$

where ds denotes the infinitesimal advancement of the face object in the direction perpendicular to the face itself. In studies related to industrial crystallization does, however, reference to the overall rate of growth of a crystal, which can be expressed as a linear speed:

$$G = \frac{dL}{dt} \quad (5.2)$$

Eq. (5.2) dL is equal to $2 \cdot ds$ and is to indicate the variation of a characteristic dimension of the crystal (the diameter for spherical particles and usually $2 \cdot r_0$ size for geometric shapes that identify more dimensions). The G growth speed is normally expressed in m/s is twice the speed of growth &

THE

of the face to which it refers the characteristic dimension.

The speed of growth can eventually be expressed in terms of the crystalline mass deposited per unit of the crystal surface and per unit of time:

$$R_G = \frac{1}{A_c} \frac{dM}{dt} \quad (5.4)$$

R_G is the speed of growth usually expressed in $kg/m^2 \cdot s$. It can be shown that between G and R_G have the following relationship:

$$R = \frac{K_s}{\rho} \left(\frac{K_v}{K_s} \right)^{1/3}$$

where ρ is the crystal density in kg / m^3 and K_s and K_v are the surface and volume factors introduced in Chapter 2.

The process of growth of a crystal takes place in two stages (see Fig. 5.2):

- 1) The solute, in the form of molecular aggregates, is transferred from the solution on surface of the crystal, where it is adsorbed.
- 2) The molecular aggregates spread adsorbed on the crystal surface, are structured in elementary crystalline cell and finally integrate in the crystal structure.

The speed of the first stage is a function of the concentration gradient between the breast of the solution and the solid-solution interface

$$R = K_s (c - c_{the}) \quad (5.6)$$

while the second stage may take the classic expression in power of a kinetic phenomenon:

$$R = K_r (c_{the} - c_{eq})^n \quad (5.7)$$

Often the integration stage is much slower than that of transfer for which it can be assumed $c_{the} \cong c$.

To simplify a kinetic discussion that on the basis of the dual stage of the crystallization process would require knowledge of the interface unknown concentration c_{the} , It considers directly the overall speed of growth comprising the two stages and expresses the kinetics of this speed with an expression of the type power:

$$R = K (c - c_{eq})^n \quad (5.8)$$

The order of the growth speed "n" is normally between 1 and 2.

Not always the speed of growth in a given direction is the same for all crystals of a certain compound: for some substances, such as eg. potassium sulfate, has been found experimentally a speed of greater growth for larger crystals. They adopt in this case kinetic expressions which will include the crystalline size. Among the most commonly used is the one proposed by Cannon and Randolph:

$$= \frac{(k_R + a_L 1)}{GG} \Delta c^{nb} \quad (5.9)$$

A second effect observed experimentally is a difference in the speed of growth of single crystals, even of the same size (growth rate of the phenomenon of dispersion): this phenomenon has rather obvious physical un'interpretabile, if one considers that the lattice imperfections present on the surface of a crystal modify the energies of adjacent ties.

A more rigorous expression of the growth rate refers to the relative supersaturation rather than to the difference of concentration:

$$R = k \sigma^n \quad (5.10)$$

This is because the pushing force expressed in terms of Δc contains a strong dependence with the temperature because the equilibrium concentration is a function of temperature, while it is not so when the pushing force is expressed in terms of relative supersaturation σ , related to the difference between the chemical potentials through Eq. (3.4).

5.2 aggregation mechanisms on the crystal surface

The growth of the crystal involves the creation of new bonds, thus a decrease of the free energy, and the formation of new solid-liquid interface, which is linked, however, a free energy increase. Consider the units, atoms, ions or molecules, which constitute the surface of a crystal, schematized by cubes geometrically, as shown in Fig. 5.3: the aggregation of a unit in a shallow gap, indicated by A in the figure, involves new bonds of 5 of the unit faces that aggregates and a decrease in the surface of the solid 4 faces; the gap on the edge, indicated with B in the figure, it involves new bonds on 4 faces and a reduction of area equal to two faces; The aggregation in position C, or on a concave angle (called kink) involves the formation of new bonds on three faces and no surface change: These three positions are energetically favored for all positive values of supersaturation, for which the new unit will aggregate with great ease. The aggregation of a concave edge, indicated by D in the figure, involves new bonds on 2 faces and an increase in surface area equal to 2 faces, for which the ΔG is negative only starting from a certain value of supersaturation: the supersaturation threshold that makes the negative ΔG is even higher for the aggregation on the flat surface, wherein the surface increases by 4 faces and only on a new bonds are formed (see unit E in the figure).

The probability that a unit is aggregates in solution in a site is the higher the greater is the energy gain that the aggregation involves: when the oversaturation is very high, the ΔG is very negative for all sites and also those on the flat surface are energetically favored, for which the increase takes place in a non-selective and the crystal surface is wrinkled (see Fig. 5.4). For sovrassaturazioni minors, the aggregation on the flat surface becomes very rare and the phenomenon that controls the speed of growth is the birth of a new stable surface layer (two-dimensional nucleation): once a stable portion of the new layer has been formed, it is expands

relatively rapidly because its edges

edges are convex on which the combination is effected with greater ease. E'easy to guess that a crystal that grows according to this mechanism, called birth & spreads, presents rather smooth surfaces (see Fig. 5.5).

In some cases it has been experimentally detected, for low sovrassaturazioni, a speed of accrescimento greater than that expected on the basis of the birth & spreads mechanism: this phenomenon is caused by dislocations screw, as described by Burton, Frank and Cabrera in the 50s. the screw dislocation constitutes a convex step on which the new units are aggregated with ease: the crystal to grow the step which moves along a spiral path without, however, disappear (see fig. 5.6). In the presence of a screw dislocation, therefore, the formation of a new layer does not require any two-dimensional nucleation and the crystal grows at a faster rate.

5.3 methods of measuring the speed of growth

The characterization of the kinetics of a crystalline material accretion presents considerable difficulties: the measurement of the speed of growth can be performed using different methods, each of which has particular characteristics and sources of error, making it more or less suitable depending on the cases. Since the measurement method has a significant influence on the value that is measured, every time that one has to do with data concerning the growth kinetics is important to specify in detail the procedure used to obtain them.

A first classification of the growth speed of the measurement methods divides them into direct and indirect: direct methods in the speed of growth is determined on the basis of a direct measurement of the mass, or the size, of one or more crystals. In indirect methods, however, measure the variation of the concentration of the solution in which the increase takes place.

A second important distinction must be made between those measures which are carried out by taking into consideration the individual crystals and those that determine an average growth. In the first case a variable crystals number from one to a few units is placed in contact with a solution supersaturated and the variation of their size is monitored through the analysis of the image. The typical experimental diagram of the apparatus used is shown in Fig. 5.7d. The growth of single crystals can also be determined gravimetrically, but this second methodology presents obvious problems related to the difficulty of measuring with sufficient precision the weight of the crystals themselves. The methods that measure the growth of a sample of crystals as a whole, also known as accretion mass methods, It makes use of equipment of the type shown in Figs. 5.7a e 5.7b. The operating procedure consists in placing in suspension in a supersaturated solution a known amount of crystals and maintaining the suspension at a constant temperature for a given time interval. The crystals must then be separated from the mother liquor: one must keep in mind that this second part of the operating procedure, which is analogous to downstream processing Industrial crystallization, involves a series of problems related to the following factors:

- difficulty of discharge of the suspension from the crystallizer;

- difficulty of removal of the mother liquors from the surface of the crystal;

- danger of crystallization or secondary dissolutions due to thermal shock at the outlet of the crystallizer.

In this regard, the advantages of the apparatus arrangement shown in Fig.

5.7b compared to that in Fig. 5.7a are evident: the lower discharge cone facilitates and speeds up the handling of the suspension and the thermostating the centrifuge reduces the risk of crystallization and dissolution of the crystals. The removal of the mothers from the surface of the crystals waters can be also facilitated by using a washing liquid in the centrifuge itself.

During the growth the agitation intensity in the apparatus must be sufficient to keep the suspended solid, but not too high in order to avoid - or at least to contain - the secondary nucleation due to collisional mechanisms. For particularly fragile crystals can be advantageous for the adoption of a fluidized bed apparatus (see Fig. 5.7c).

The growth methods in mass can be classified into differentials and integrals, based on the ratio between the quantities of crystals and mother liquor in the game: in the differential method of this ratio is very low, typically of the order of a few percentage units, in such a way You can neglect the variation of supersaturation of the mother liquors. The growth of the crystals can be measured gravimetrically or through the image analysis of a statistically significant sample of crystals. In the integrals methods of seeding crystals represent 10-20% of the suspension. The growth can be measured by a direct way, gravimetrically or by means of image analysis, or in an indirect way, by measuring the variation of concentration of the mother liquors. Recently, the methods of measurement accretion of single crystals have been a great success. These methods are particularly suitable for investigating the behavior of the individual faces of the crystals, the ratio between the speed of growth of a crystal and its original dress and growth mechanisms. However, these measures must be repeated on many crystals in order to obtain a discrete statistical significance and are difficult to use to describe the kinetics of growth in industrial crystallizers. the relationship between the growth rate of a crystal and its original dress and growth mechanisms. However, these measures must be repeated on many crystals in order to obtain a discrete statistical significance and are difficult to use to describe the kinetics of growth in industrial crystallizers. the relationship between the growth rate of a crystal and its original dress and growth mechanisms. However, these measures must be repeated on many crystals in order to obtain a discrete statistical significance and are difficult to use to describe the kinetics of growth in industrial crystallizers.

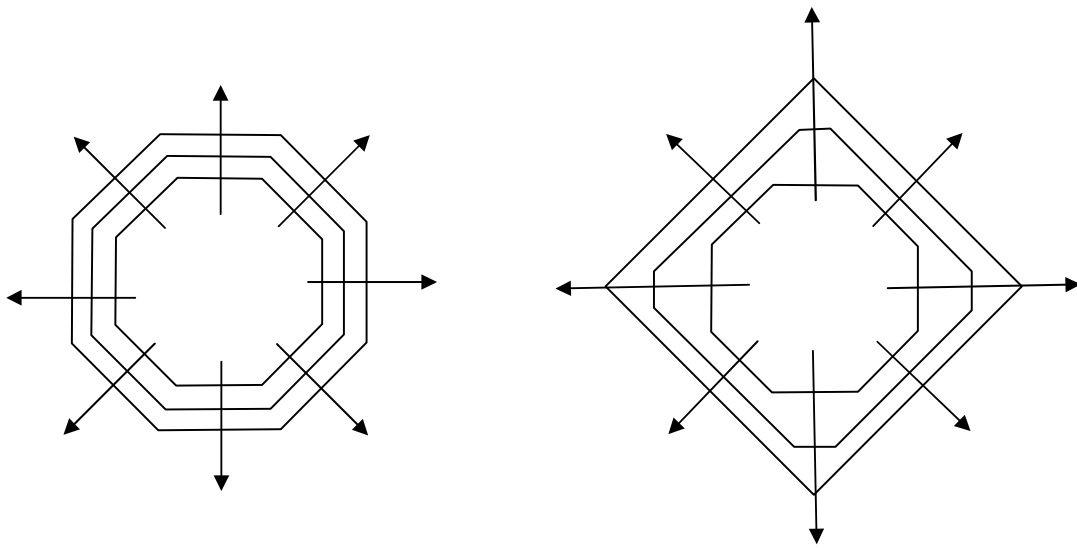


Fig. 5.1: Example of anisotropic growth.

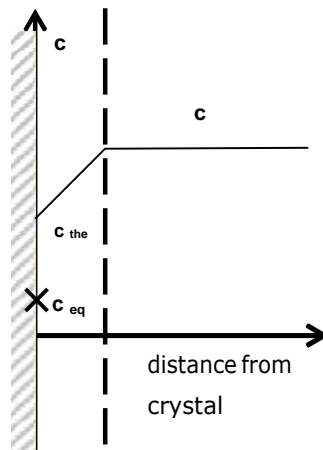


Fig. 5.2: concentration profile in the vicinity of a crystal.

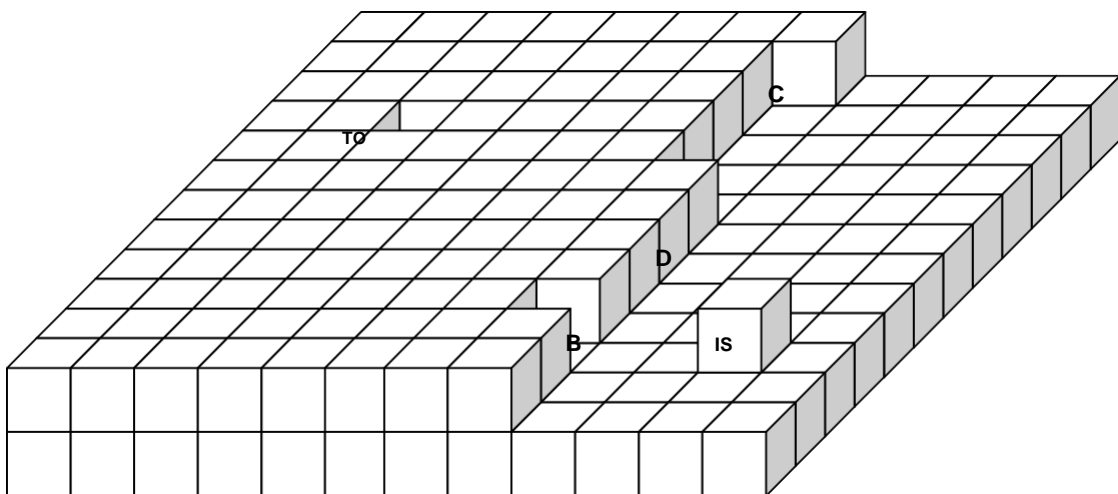


Fig. 5.3: Diagram of the surface of a crystal.

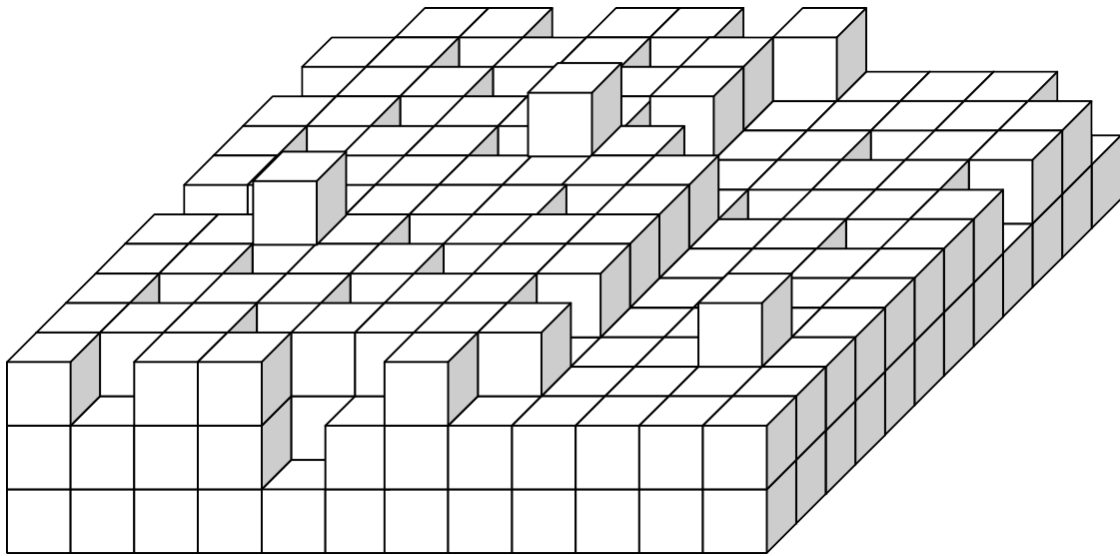


Fig. 5.4: Grafting with high supersaturation.

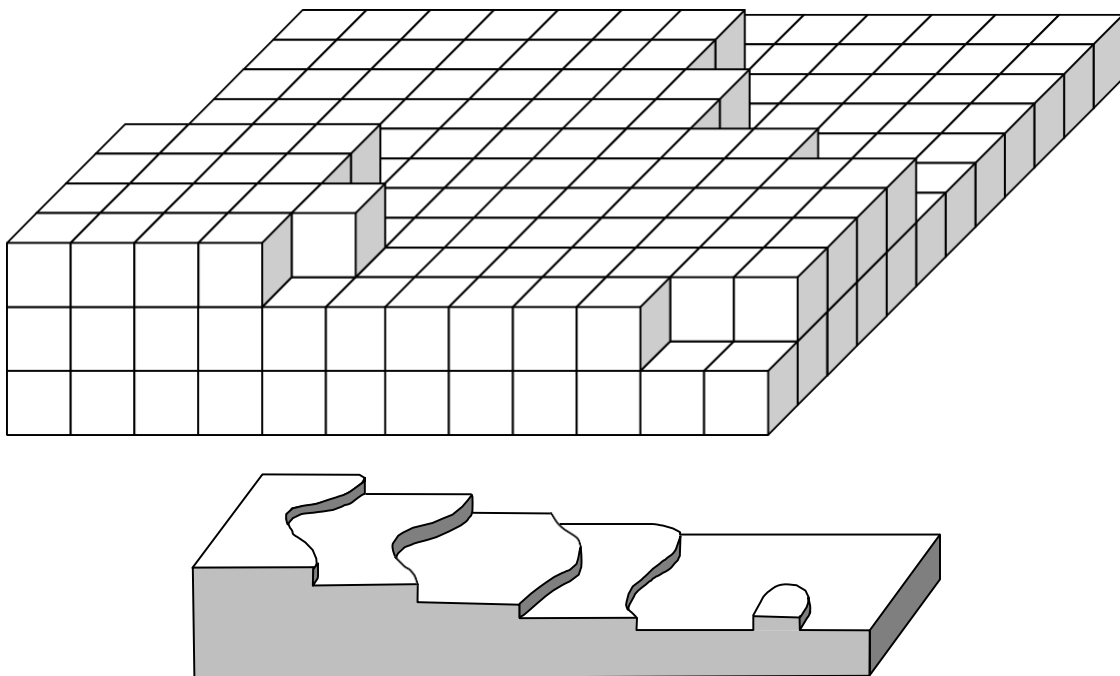


Fig. 5.5: Grafting with low supersaturation.

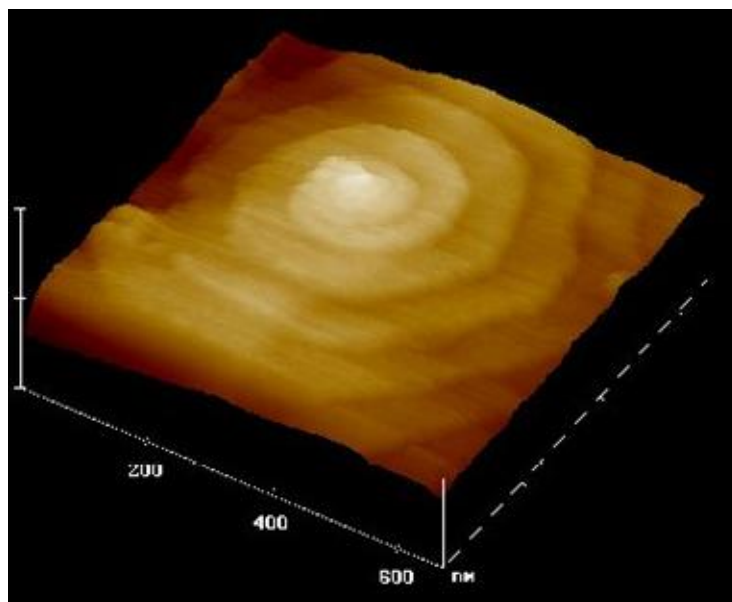
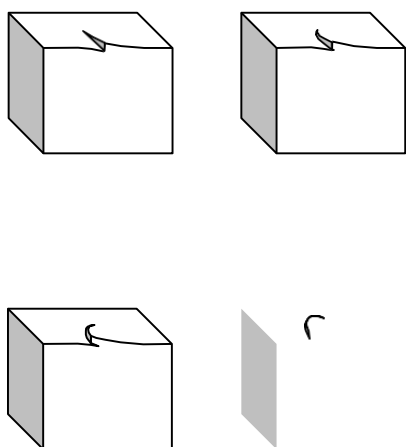
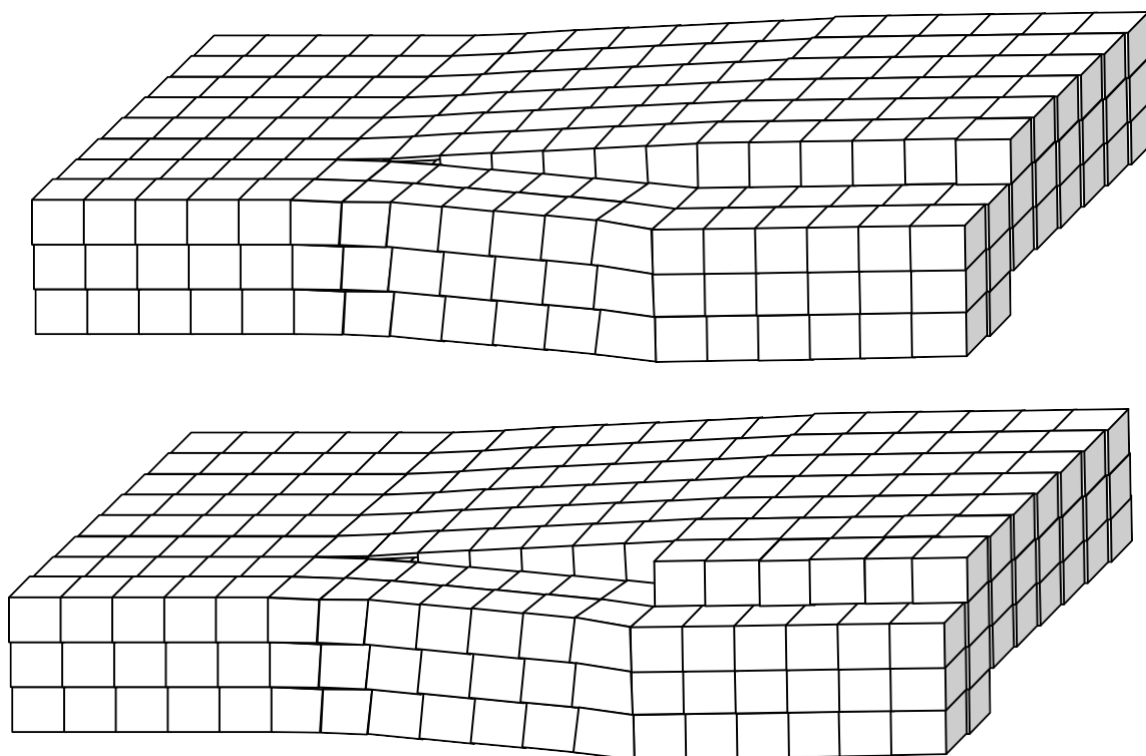


Fig. 5.6: Grafting mediated by a screw dislocation.

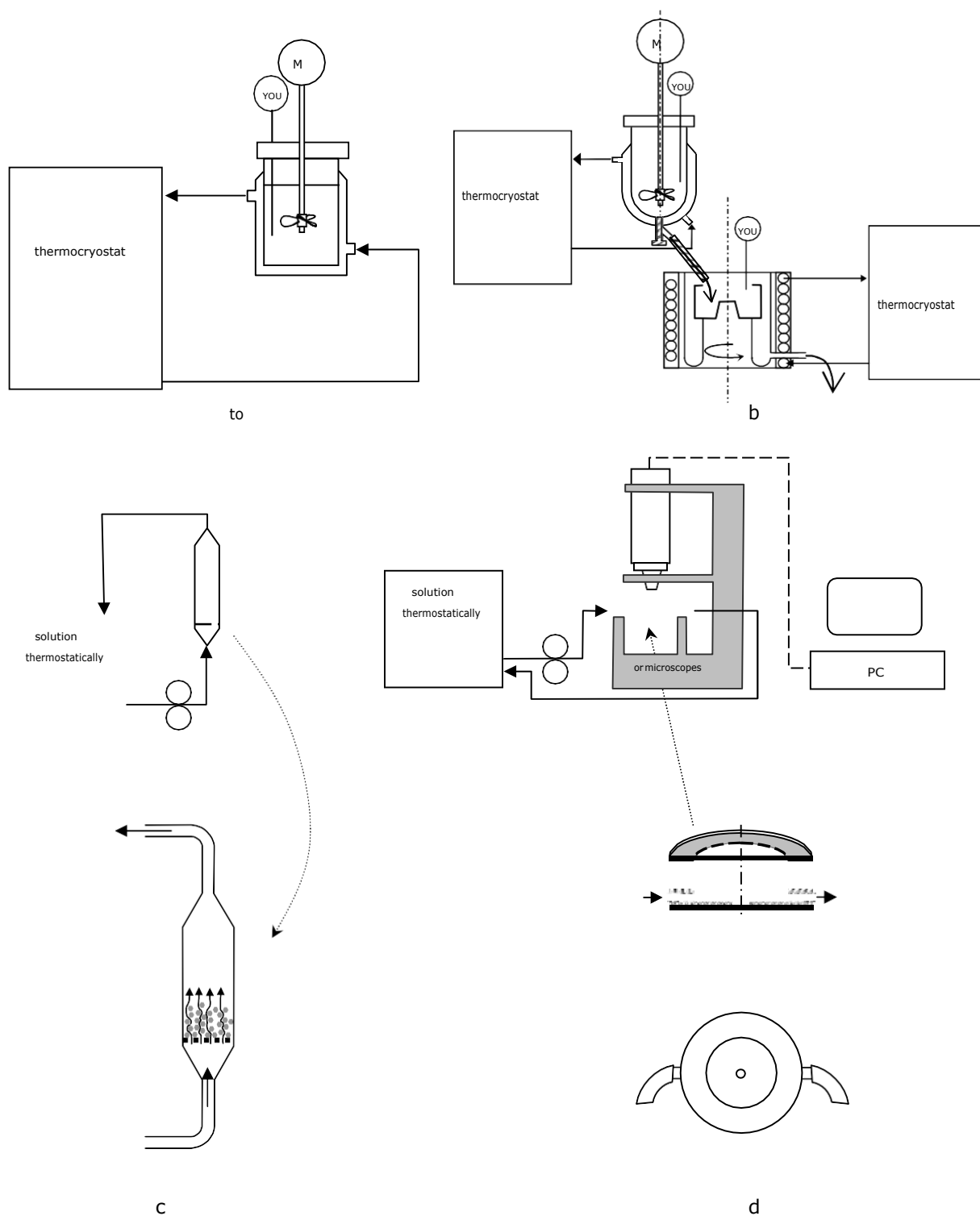


Fig. 5.7: Equipment for measuring the speed of growth: a) simple batch crystallizer; b) batch crystallizer with bottom discharge and thermostatic centrifuge; c) crystallizer fluidized bed; d) apparatus for the growth of single crystals.

6.1 The population balance in a MSMPR

The phenomenological models of unit operations are based on the balance sheets of matter and energy, which are expressions of the principle of conservation of these two entities in the crystallizer is also applicable on the balance sheet of the crystalline population aimed at determining the size distribution of the crystals produced. Consider a crystallizer perfect blending, in which even distribution of the crystal population is uniform throughout the volume. For the assumptions of perfect mixing the suspension in the crystallizer it has the same output current characteristics. Such an apparatus is called MSMPR crystallizer (Mixed-Suspension, MixedProduct-Removal crystallizer) and is represented schematically in Fig. 6.1. The material balance can be as follows:

$$\rho_c \frac{dV}{dt} = \rho F - \rho_c V \frac{dV}{dt} = \rho F - \rho_c V \frac{dV}{dt}$$

where M is the mass of suspension contained in the crystallizer ($M = \rho_c \cdot V$), the volumetric flow rate F, ρ_c the density of the crystals and the subscript "1" refers to the input current. The enthalpy balance can be represented as follows:

$$\rho_c \frac{dV}{dt} h = F h_1 - \rho_c V \frac{dV}{dt} h + Q \quad (6.2)$$

where h is the specific enthalpy and Q the thermal energy transferred to the suspension in the crystallizer unit of time for crystallization effect of heat or from an external source. If the crystallizer is adiabatic, usually you neglects the heat crystallization.

The population balance formula is based on entirely analogous considerations: consider a dimensional class L_{av} characterized by an average size in a size range with the lower end L_1 and upper L_2 , are n_1 and n_2 the population density and G_1 and G_2 the linear growth speed corresponding to the extremes of the same. In a time interval Δt the number of crystals which enter dimensional range are:

$$V n_1 G_1 \Delta t \quad (6.3)$$

Similarly, those who leave the dimensional range for the growth of the crystals which are located at the upper end interval are:

$$V n_2 G_2 \Delta t \quad (6.4)$$

They must be, then, considered the crystals entering the crystallizer with the input current volumetric flow F_{the} :

$$F_{the} n_i \Delta L \Delta t \quad (6.5)$$

where n_i is the average density of population in the range $L_1 - L_2$.

They go, also considered the crystals coming out of range with the output current from the crystallizer volumetric flow F . They are:

$$F n \Delta L \Delta t \quad (6.6)$$

where n is the density of population in the class $[L_1, L_2]$. Taking into account the terms stated above, the population balance in stationary conditions can be written as follows:

$$F_1 n_1 \Delta L \Delta t + V n_1 G_1 \Delta t = F n \Delta L \Delta t + V n_2 G_2 \Delta t \quad (6.7)$$

By eliminating the variable to all terms Δ You grouping terms with G variable first member, you get the following equation form of the population balance:

$$V (G_2 n_2 - G_1 n_1) = (F_{the} n_1 - F n) \Delta L \quad (6.8)$$

Passing by finite differences to those infinitesimal, the average values of n and n_i become the density of population that refer to a precise size and population balance takes the form:

$$V d(G n) / dL = F_{the} n - F n \quad (6.9)$$

In the case where Q_i is equal to Q , that is complied with the volumetric balance between the two currents and G is independent of L (McCabe's law), and finally placing $V / F = \tau$, the residence time of the process, the equation takes the form:

$$G \tau (dn / dL) + n = 0 \quad (6.10)$$

The integration of the equation in stationary conditions (6.10) can easily be resolved by applying the integration to separate variables:

$$\int_{n_0}^n \frac{dn}{n} = - \frac{1}{G \tau} \int_0^L dL \quad (6.11)$$

where n_0 is the population density for the size L which tends to 0. We have:

$$n = n_0 e^{-\frac{L}{G}} \quad (6.12)$$

The boundary condition for $L \rightarrow 0$ can be put in relation with the speed of nucleation B_0 , defined as the number of nuclei that are formed per unit volume and time:

$$n_0 = \frac{B_0}{G} \quad (6.13)$$

n_0 is the population density of crystalline embryos, whose size L_0 . It can be considered tending to 0.

According to (6.12), under the assumptions made, the numerical distribution of the product of a continuous crystallizer is of exponential type. Note the residence time is possible to evaluate the speed of growth of the crystals, G , and nucleation, B_0 , on the basis of the measure of the population density in output, n .

The equation (6.12), considering Eq. (6.13) and passing to logarithms, it becomes:

$$\ln(n) = \ln\left(\frac{B_0}{G}\right) - \frac{L}{G} \quad (6.14)$$

For interpolating the data which $\ln(n)$ Vs L is obtained by a straight line of slope equal to $-\frac{1}{G}$ and of

intercept equal to $\ln\left(\frac{B_0}{G}\right)$ (See Fig. 6.2).

When the growth rate is a function of size, for example according to Eq. (5.9), the graph $\ln(n)$ Vs L is not straight, but has a concavity upwards for increasing G with L .

Regardless of the simplifying assumptions used to derive the expression of the population density, the density of the magma is obtained by the integral:

$$M_p = \rho \int_0^{L_{max}} n(L) dL \quad (6.15)$$

in which the density of the magma is expressed in m^3 solid for m^3 of suspension. If k_v It does not depend on the L (6.15) is

$$M_p = \rho \int_0^{L_{max}} n_0 e^{-\frac{L}{G}} dL \quad (6.16)$$

The concentration of solute in the mother liquor in output is calculated from the partial balance of the solute. In steady-state assumption, the absence of seeding feeding and neglecting the variation of density of the suspension is

obtained:

$$C = C_{the} - M_T / p_c \quad (6.17)$$

For some systems, the growth speed is not constant with the size of the crystals, but variable. One of the most frequent expressions to indicate this variability is that suggested by Abegg:

$$G = G_0 (1 + \gamma THE)_b \quad (6.18)$$

In this case the integration of the population balance in a semilog plan is no longer a straight line, but a curve as shown in Fig. 6.3.

6.2 Effect of the geometry of the crystallizer on the particle size distribution

The industrial crystallizers can be configured so as to reduce the amount of fines present in the final product. This objective is achieved by means of two different techniques:

A removal of ends from the crystallizer by withdrawing a stream containing only the crystals with a smaller size L_F (see fig. 6.4). The crystals are removed and the solution is recycled to the crystallizer.

A decantation of the crystals before the withdrawal of the final product, through a column of elutriation, in order to exclude the ends in the final product (see Fig. 6.5). In both cases, the particle size distribution undergoes the consequences of the geometry of the crystallizer, in the ways indicated below.

Removing ends

In this case it is possible to consider two different populations of crystals, that of the fine crystals respectively ($L < L_F$), n_F , and that of large crystals ($L > L_F$), n . The first population is removed with two currents, the recycling Q_0 and that emerging from the crystallizer Q_u . The budgets of the two populations can be written as follows. For fine crystals:

$$VG (dn_F / dL) + Q_0 + Q_u n_F = 0 \quad (6.19)$$

For large crystals:

$$VG (dn / dL) + Q_u n = 0 \quad (6.20)$$

The residence times for the two populations are therefore: for the

fine crystals $\tau_F = V / (Q_0 + Q_u)$

for large crystals $\tau_P = V / Q_u$

The integration of the differential equation (6.19) with the boundary condition $n = n_0$ to $L \rightarrow 0$, leads to

exponential expression:

$$n_F = n_0 \exp(-L / G \tau_F) \quad (6.21)$$

while integrating the equation for the large crystals by $L = L_F$, you have

$$n = n_0 \exp(-L_F / G \tau_F) \exp(-L / G \tau_P) \quad (6.22)$$

In the semi-logarithmic plot n vs. L , the particle size distribution assumes the pattern shown in Fig. (6.6). The population of large crystals intersects the ordinate axis at a different point from n_0 , called n_{0EFF} .

Crystallizers with classification of large crystals

When we adopt an elutriation leg is made in such a way that the fine crystals have a much longer than that of large crystals of residence time, so if the fine crystals of the residence time is equal to τ , that of large crystals is equal to a fraction of that time equal to $\tau_P = \tau / z$. This leads to two distinct populations characterized by the equations:

$$n_u = k_1 \exp(-L / G_2 \tau) \quad \text{for } L < L_p$$

$$n_u = k_2 \exp(-L / G_2 \tau_P) \quad \text{for } L > L_p$$

The representation of the particle size distribution in the semilog plane is provided by the figure (6.7).

while greater than or equal to L_p -sized crystals have a

6. 3 Budget population in the presence of the collision phenomena of crystals

If you also take into account the secondary nucleation collision the balance equation in differential terms assumes the expression:

$$\frac{d(n_{out} L)}{dt} = \frac{Gen_{out}}{L} + \frac{1}{L} (n_{in} V_F) - \frac{n_{out} L}{V_F} \quad (6.23)$$

where $b(L)$ represents the rate of generation density of fragments of size L , whose unit of measurement is $\# / m^4 s$, while $d(L)$ is the density of the rate of disappearance of the crystals due to their breakage, expressed in the same units of measure. The integration of equation (6.23) is done numerically.

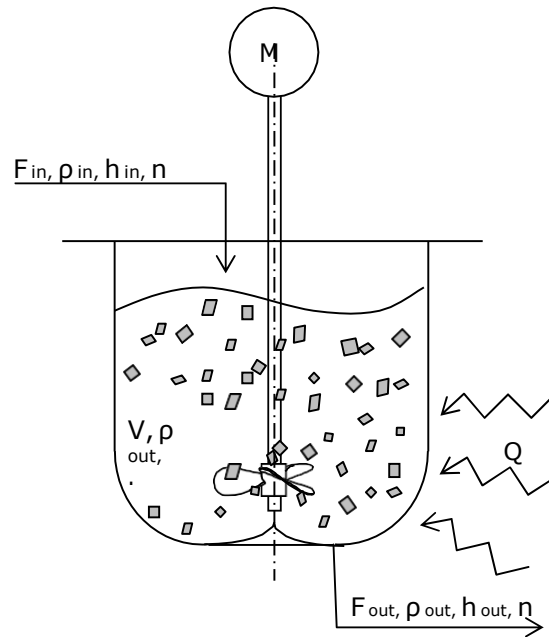


Fig. 6.1: MSMPR Crystallizer.

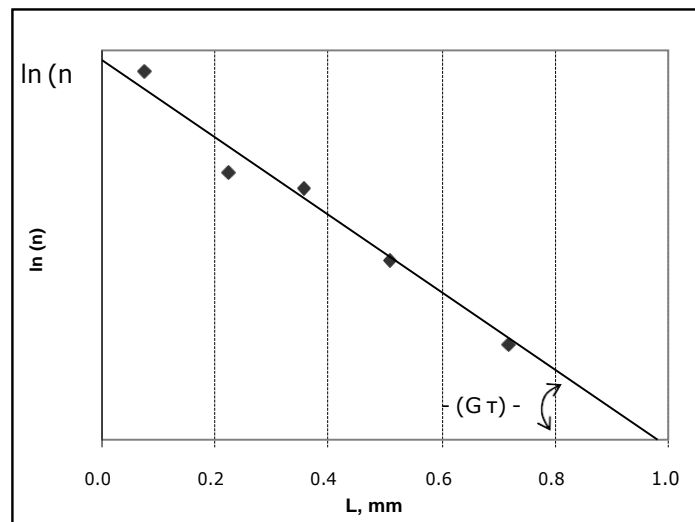


Fig. 6.2: semi-logarithmic plot of the population density in a crystallizer MSMPR.

7 THE BATCH COOLING CRYSTALLIZATION

The concept on which is based the batch crystallization is to generate an initial distribution of crystals and let them grow in a closed system until reaching the final dimension. From a technological point of view the only transfer from the outside to the closed system is therefore energy nature (or subtraction of heat input). The extent and the energy transfer mode determines the evolution in time of the supersaturation and consequently of the nucleation and growth phenomena. The interaction between the transfer of energy, the phenomena into play and the distribution of the crystals is well represented by the diagram reported by Jancic and Grootsholten (see Fig. 7.1). Path

1, 2, 6, 7, 5 is the one that triggers the event that you have, in the absence of seeding, the primary nucleation in the solution. Once the nuclei generated is appropriate that the crystallization evolve with the growth of crystals according to the path 1, 2, 3, 4, 5. In fact the growth of existing crystals is always accompanied by the generation of new crystals for secondary nucleation for where both paths 2, 3, 4 and 2, 6, 7 are followed by the process. A good run of the batch crystallization should aim to follow a curve such that the supersaturation achieve sustained growth speed of the crystals present and to minimize the phenomena of nucleation.

7.1 Statements of the solute material in the crystallizer

During the running of the crystallizer the variation of concentration of the solute is transformed into a growth of existing crystals or in the generation of new crystals by nucleation. The primary balance of the solute material can thus be expressed by the following equation:

$$\frac{dC}{dt} = - \frac{1}{V} \left(\sum_i R_i V_i + \sum_j N_j \right) \quad (7.1)$$

where a is the surface of the crystals present per unit volume of solution. Expressing the speed of nucleation and accretion in the typical form in power as a function of supersaturation in terms of concentration gradients

$$G = C (k \Delta R)^n \quad (7.2)$$

$$N = C (k \Delta R)^m \quad (7.3)$$

and substituting in eq. (7.1) the concentration with the following expression:

$$C = C_{eq} + \Delta C \quad (7.4)$$

you have

$$\overline{\Delta} = \frac{1}{\Omega} \int_{\Omega} \Delta \, dx = \frac{1}{\Omega} \int_{\Omega} \Delta \, dx \quad (7.5)$$

E' should be explicit in the derivative of the equilibrium concentration of the variation of temperature with time, that is, put

$$\frac{dc_{eq}}{dT} = \frac{dc_{eq}}{dT} \left(\frac{dT}{dt} \right) \quad (7.6)$$

where $b(t)$ is the cooling rate at time t .

Finally Substituting in eq. (7.6) the expression obtained by dc_{eq}/dt is obtained by the equation that provides the trend of the supersaturation of the solute over time

$$\frac{d\Delta c}{dt} = \frac{dc_{eq}}{dT} \left(\frac{dT}{dt} \right) - \Delta c \left(\frac{d\ln N}{dt} \right) \quad (7.7)$$

Eq. (7.7) is associated with the condition to the starting point:

$$\Delta c(0) = \Delta c_0$$

The eq. (7.7) indicates that the variation of supersaturation in time is a function of the difference between the generational term, $b(t) (dc_{eq}/dT)$, and the two terms involving the consumption of oversaturation same effect for accretion of crystals present and the birth of new crystals

7.2 Particle size distribution of the crystals of the Forecast

One of the objectives of crystallization is to obtain a crystalline product in accordance with the specific particle size required, and thus it is important to be able to predict the distribution of the size of the crystals produced. If you adopt a high initial seeding of N_{L0} size crystals is possible in a first approximation, neglecting the birth of new crystals, ie $R_N = 0$ and eq. (7.7) becomes

$$\frac{d\Delta c}{dt} = \frac{dc_{eq}}{dT} \left(\frac{dT}{dt} \right) - \Delta c \left(\frac{d\ln N}{dt} \right) \quad (7.8)$$

In order to develop a crystallization model that enables the prediction of the particle size distribution of the crystalline product should be replaced in eq. (7.8) to the expression of the mass accretion rate R_G that in terms of linear growth speed arising from Eq. (5.5), is obtained as a result of the equation

$$\frac{d\Delta c}{dt} = \frac{dc_{eq}}{dT} \left(\frac{dT}{dt} \right) - \Delta c \left(\frac{d\ln N}{dt} \right) \quad (7.9)$$

Assuming that each seed crystal is not subject to phenomena of breakage but only accretion phenomena, its characteristic dimension evolve over time according to the following equation:

$$T(t) = \int_0^t T'(GL) dt \quad (7:10)$$

The knowledge of the crystal size over time allows the prediction of the crystalline surface per unit of volume, it has in fact:

$$(a) \quad T_2(L) = k N_s \quad (7.11)$$

The resolution of the system of differential algebraic equations (7.9) - (7.11) is used to predict a first approximation the trend of oversaturation over time as a function of cooling rate and consequently operate the optimum choice with regard to the cooling policy to be applied.

7.3 Techniques of oversaturation control in a batch crystallization

For batch crystallizers operating for cooling, there are two techniques to influence the performance of supersaturation in time: the use of seeding and cooling modes. The effect of these operational techniques will be described below, referring to an application case concerning the crystallization of potassium sulphate in a crystallizer of 15 l capacity, equipped with a draft-tube and baffles and an agitator three nautical blades (see fig. 7.2). In this case, the crystallization was carried out by lowering the temperature of the suspension from 60 to 30 ° C in 155 minutes. The initial supersaturation was between 30 and 40 g of potassium sulfate per kg of water.

- weighted average Size

$$W_M = \frac{\sum_{ii} L_{ii}}{\sum_{the} W_{LL_{ii}}} \quad (7.12)$$

- Coefficient of Variation

$$CV = \frac{\left(\sum_{the} (W_{WM_{ii} LL}^2) \right)^{0.5}}{\sum_{the} W_{the}} \quad (7.13)$$

- Percentage of ends ($L_j < 250 \mu m$)

$$= \frac{\sum_j L_j}{\sum_{the} W_{ij}} \quad (7.14)$$

7.3.1 Use of sowing

The use of the seed is fundamental to prevent it from occurring in the solution, during the cooling, a

conspicuous nucleation; this fact would affect in a manner

determining the particle size distribution of the final product. E', therefore, always advisable to use, at the beginning of cooling, a seed whose mass can be calculated based on the size of the seed crystals of the desired crystalline product. Assuming that the crystals produced have a uniform size, L_p , the mass of crystals of size L seeding 0 It will be equal to:

$$\frac{MM}{\left(\frac{\Delta M}{L_p} \right)^3 - 1} \quad (7:15)$$

where ΔM is the mass precipitated during the crystallization. Obviously eq. (7:15) does not take account of the generated crystals for secondary nucleation and consequently it is to be expected at the end of the crystallizer march an average size of a little less than in crystals that L_p considered.

With reference to the case in question, the use of sowing is considerably advantageous. From the comparative data reported in tab. 7.1, it can, in fact, observed that the adoption of the sowing almost halves the percentage of fine and significantly increases the average size of the final product. The particle size distribution in the two cases, compared in fig. 7.3, is very different: in the absence of seeding the maximum of the distribution occurs between 0.3 and 0.6 mm due to the considerable nucleation occurred, while in the presence of seeding the maximum of the distribution, very pronounced, falls in the range of the desired size for the product, ie between 1.4 and 1.65 mm.

7.3.2 Cooling Mode

In a batch crystallizer for cooling (or heating) the oversaturation is a direct function of the speed with which the temperature varies the instant solution for instant. To maintain the supersaturation within an appropriate range of values, situated in the central band of the metastability field, it is necessary to generate sovrassaturazioni not in excess of those able to be discharged on the surface of the crystals in suspension due to the growth phenomenon. Therefore beginning of the operation, when the entire surface of the crystals is low, the cooling rate should not be high, while at the end of the transaction, being available to the growth a large mass of crystals, the cooling rate can be high. The performance of the cooling rate, if you do not perform any of its control mode, it is exactly the opposite of what is desirable, so in case you wish to adjust the oversaturation is necessary to avoid cooling the so-called "natural". Among the possible cooling mode that there is linear and that with increasing speed over time, so-called "constant-nucleation", as it should ensure a supersaturation almost constant during the march. The consequence of the three cooling policies, shown in fig. 7.4, on the progress of oversaturation and on the final product are shown respectively in Fig. 7.5 and tab. 7.1. then if you want to adjust the oversaturation it is necessary to avoid cooling the so-called "natural". Among the possible cooling mode that there is linear and that with increasing speed over time, so-called "constant-nucleation", as it should ensure a supersaturation almost constant during the march. The consequence of the three cooling policies, shown in fig. 7.4, on the progress of oversaturation and on the final product are shown respectively in Fig. 7.5 and tab. 7.1. then if you want to adjust the oversaturation it is necessary to avoid cooling the so-called "natural". Among the possible cooling mode that there is linear and that with increasing speed over time, so-called "constant-nucleation", as it should ensure a supersaturation almost constant during the march. The consequence of the three cooling policies, shown in fig. 7.4, on the progress of oversaturation and on the final product are shown respectively in Fig. 7.5 and tab. 7.1. shown in fig. 7.4, on the progress of oversaturation and on the final product are shown respectively in Fig. 7.5 and tab. 7.1. shown in fig. 7.4, on the progress of oversaturation and on the final product are shown respectively in Fig. 7.5 and tab. 7.1.

The fig. 7.5 shows that in the case of operating with natural cooling is obtained at the beginning of the march a

very high value of supersaturation (close to the maximum corresponding to the primary heterogeneous nucleation), while operating with mode

cooling at a constant nucleation are obtained values of supersaturation and considerably lower content in a narrow range of values. The consequence on the particle size distribution is in the case of a high percentage of natural cooling purposes.

In the case considered the best cooling policy appears to be the linear cooling; in other cases reported in the literature and relating to crystallizers larger the best policy is that of a cooling at a constant nucleation.

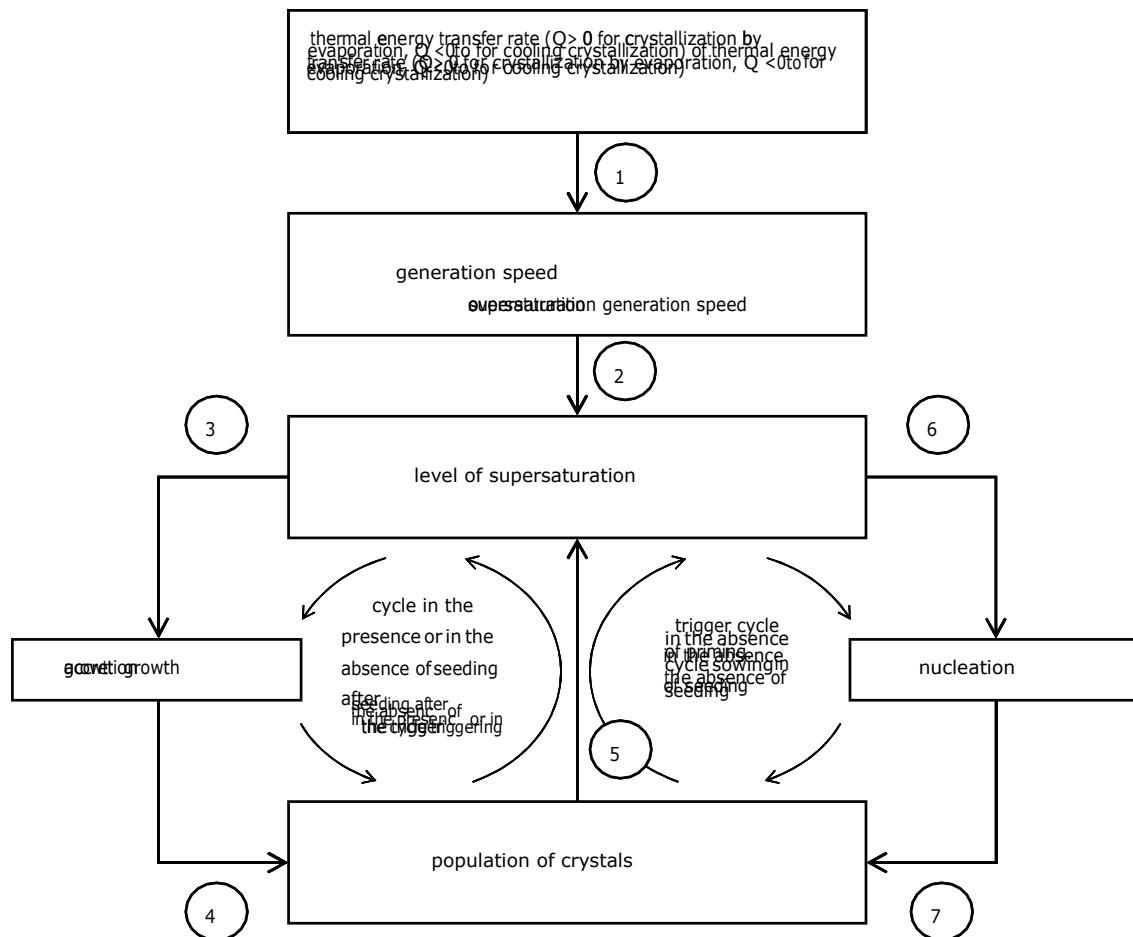


Fig. 7.1: Schematic representation of the events that determine the distribution particle size in a batch crystallization.

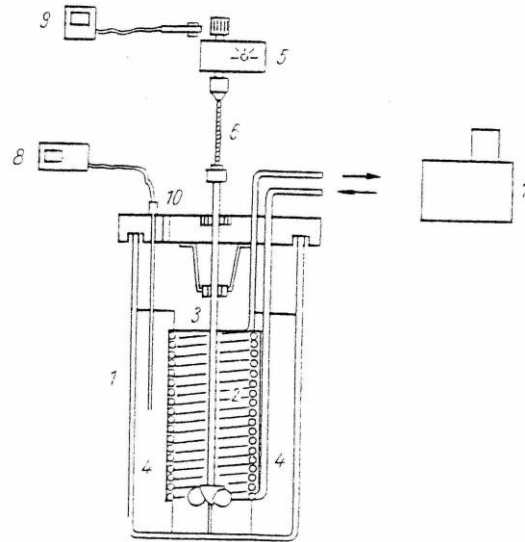


Fig. 1 Experimental crystallizer. 1 crystallizer. 2 heat exchanging draft tube. 3 stirrer shaft. 4 baffles. 5 variable speed electric motor. 6 flexible connection. 7 thermostatic bath. 8 electric thermometer. 9 stroboscopic rpm meter. 10 sample port.

Fig. 7.2: Batch Crystallizer used by Chianese et al. (1986).

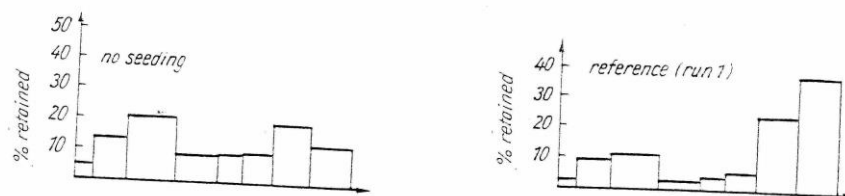


Fig. 7.3: particle size distribution of crystals of K_2SO_4 in the presence (run 1) and in the absence seeding.

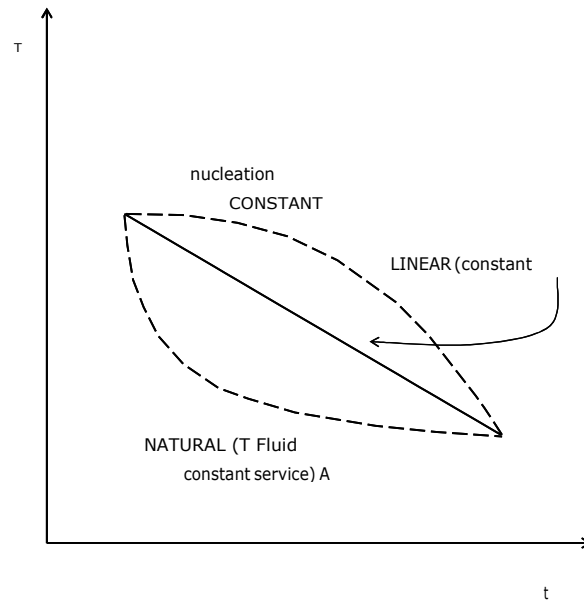


Fig. 7.4: Different modes of cooling.

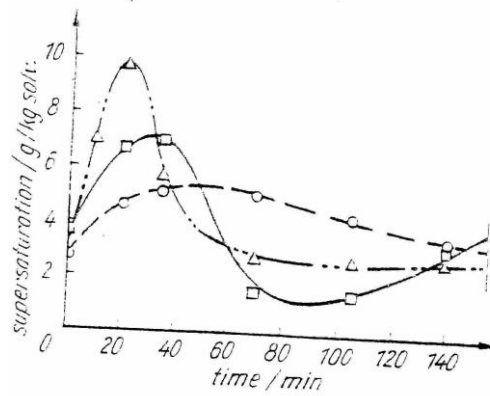


Fig. 7.5: Performance of supersaturation in correspondence of: (o) cooling nucleation constant; (□) linear cooling (Δ) natural cooling.

SOWING	THE _{WM} , mm	CV	Fini, weight%
NO	0.83	00:57	48.4
YES	1:10	00:46	28.0

Tab. 7.1: Characteristics of K crystals $_2\text{SO}_4$ obtained from a batch crystallizer with and without the use of sowing.

MODE <u>COOLING</u> <u>DOWN</u>	THE _{WM} , mm	CV	Fini, weight%
constant nucleation	1:10	00:46	28.0
linear	1:24	00:46	16.4
natural	1:05	00:53	34.9

Tab. 7.2: Characteristics of K crystals $_2\text{SO}_4$ obtained from a batch crystallizer adopting different cooling policies.

8 THE MEASURING INSTRUMENTS OF THE CSD

The particle size distribution of a crystalline product is often the most important variable in the conduct of an industrial crystallizer. The industrial crystallizers operating in both continuous and batch mode, should be managed in such a way as to produce crystals having a desired particle size distribution even in the presence of any disorders resulting from changes in the operating conditions and the characteristics of the supply current. To achieve this goal it is necessary to dispose of measuring instruments placed inside the crystallizer (in situ) or immediately on the outlet duct for instant by instant monitor the particle size characteristics of the crystalline product. The in situ instruments are also particularly appreciated because they do not require sampling operations.

The classes of instruments used for the measurement of the particle size distribution of crystals are based on the following techniques: sieving, detection of the electric field, image analysis, diffraction or reflection of a laser beam and finally attenuation of ultrasound or light rays (turbidimetry).

The screening is the most widely used in industrial practice for technical assessments on the quality of products and crystals for their classification.

The procedure on which it is based consists in the separation of the different crystal classes belonging to well-defined particle size ranges using a series of sieves with decreasing mesh sizes. The separation between the crystalline particles is based on the smallest section of the particle itself able to pass it through the sieve mesh. Since the section in question is characterized by the second and third dimension of the particle, this technique allows a measure of the distribution based on the particle size depending on the crystal size.

If the crystals are subjected to separation by sieving tend to a sticking between them, the measurement is not very accurate as it relates to crystalline aggregates rather than single crystals, also in this case, there is a considerable underestimation of the amount of the fine. To overcome these difficulties, it is necessary to realize a wet sieving rather than dry, so as to disperse the crystals in a suspension. A further cause of error in the sieving technique is constituted by the breakage of the crystals during their movement through the various sieves. This implies that in order to have reproducible measurements it is necessary to adopt degrees of shaking such as to minimize disruption of the crystals themselves.

The technique based on the detection of the electric field, created by the passage into a narrow orifice of particles suspended in an electrolyte solution, is that marketed by Coulter Counter. Tools of this type are not used in the continuous monitoring of industrial crystallizers linked to orifice block problems.

The image analysis is the best technique for the characterization of the size and shape of the crystal population.

The crystals to be analyzed are placed on a

slide and examined with a microscope equipped with a video camera. The images captured by the camera are transmitted to a PC that has software for image analysis and their characterization by statistical techniques. The calculation procedure passes through the identification of contours and of the sections of the individual crystals and related measures, in terms of perimeter and area of the figure identified. All the crystals should be examined on each screen. The more crystals, the more precise the produced particle size distribution, which means that we must examine not less than 500 crystals. An obstacle to such a measure is represented by very irregular crystals, for example by fragments of crystals because they are very small and are not easily characterizable from the geometrical point of view. When this happens it is appropriate to previously separate the crystals above of a given size and only refer to the analysis of the image, leaving the latter to another technique the determination of the particle size distribution of the fine.

The image analysis is the only technique able to carry out a proper evaluation of the particle size distribution of elongated crystals (prismatic, acicular, etc.), As it is able to provide information both on the first and on the second dimension.

The measurement techniques of the particles based on the diffraction of a ray of light relate to the analysis of the interactions between the incident light beam and the solid particles. For this purpose, it adopts a laser light beam. The beam passes through a liquid or gaseous suspension of solid particles giving rise to the diffraction of light. The extent of diffraction depends on the size and concentration of particles and the nature of the medium in which the particles are dispersed. The diffracted beams are detected on the focal plane of a lens and their intensity is measured and recorded in function of the angle of diffraction with respect to the optical axis of the instrument, as shown in FIG. 8.1. In most related to industrial crystallization application, the crystals are very large in comparison to the wave length of the incident ray ($= 0.632$ microns for a laser beam). For these particles, the phenomenon to which is primarily attributed to the diffraction of the beam in the direction close to the optical axis is called Fraunhofer diffraction. The major limitation of the measurements performed by the laser beam diffraction is the low volume required concentration, less than 1%, in order to avoid that a ray diffracted already is deflected several times before being detected.

For different particles from the spherical shape is obtained by a particle size distribution as a function of an intermediate size between the two main.

The class of instruments based on the reflection of an optical beam has the sensor on the suspension of crystals and can therefore be used to measure the particle size at any point within the crystallizer. Two different techniques are used for this purpose: one based on the detection of the image of the suspension by means of a camera and one that measures the intensity of the laser beam reflected from each particle as it passes in front of the light source. The suppliers of these types of instruments are essentially two: Lasentec of Mettler-Toledo and MTS Group.

The first type of technique is extremely effective in identifying the crystal habit and the maximum dimensions of

the particles in suspension, but does not appear capable of providing

values realistic size distribution for the difficulty of analysis image of particles which overlap one another. It, therefore, is adopted for research purposes, but has not received a validation for industrial use.

The most promising technique for measuring in-situ of the particle size distribution is that based on the reflection of a laser light beam. Below is described the principle of operation of the instrument produced by said Lasentec FBRM (Focused Beam Reflectance Measurement) (see Fig. 8.2). The source of a laser beam is rotated so as to send the light beam on the perimeter of a circle at a fixed distance from the instrument itself. When the beam strikes a particle is reflected and passes through the sensor window provided with a photodiode detector. The duration of each signal resulting from the reflected light, multiplied by the speed of scanning of the beam is the length of a chord of the particle intercepted by the ray of light. The number and the length of the strings are functions of the concentration of the suspension and the diameter of the particles, as well as crystalline gown of the particles themselves. With this type of instrument they do not then detect distributions of particle sizes but the distribution of particle strings.

An emerging technique for measuring particle size distribution is based on the measurement of ultrasound attenuation intensity crossing a suspension. This method seems to be able to measure the particle size distribution in a range between 0.01 to 3000 microns for solid concentrations up to a maximum of 70% by volume. The operating principle of the instrument is illustrated in fig. 8.3. A high frequency electric generator is connected to a piezoelectric ultrasonic transducer. an ultrasonic pulse, containing a series of cycles of ultrasound at a particular frequency is thus generated. Ultrasound waves passing through the suspension, interact with the suspended particles and, finally, are detected by an ultrasonic detector. λ depends on the thickness of the suspension layer, the size of the particles and from these projected per unit volume of the crystals dimension L. In a polydisperse system, you will then find a distribution density can provide the attenuation detected. This technique is similar to that based on the diffraction of the laser beam with regard to the characterization of the particles. In fact, both techniques detect the areas of particle section in the opposite direction or ultrasonic wave to the laser beam and bring these areas to those of a spherical particle having a section equivalent to that measured. Therefore, the techniques in question do not consider, nor take into account the actual geometry of the suspended particles.

The greatest value of the ultrasonic technique is the ability to operate on a suspension, however, concentrated (up to 60-70% by weight of solid).

The measurement of the turbidity of a suspension is carried out by measuring the intensity of a beam of light that passes through a thin layer of the suspension, "medium", without being diffracted. The transmittance of the medium is the intensity ratio between the transmitted light beam and that of the original incident beam. The relationship

between transmitted light and light

accident is less, the greater is the darkening due to the particles in suspension, ie to their projected surface.

This measurement is usually applied to suspensions of fine crystals of size less than 500 microns. In this case it is unlikely a knowledge of their shape such as to determine their projected area as a function of size, so that the determination of the density of a suspension necessarily passes through a calibration procedure. In fig.

8.4 represents the operating diagram of a turbidimeter recently developed at the Industrial Crystallization Laboratory of the University "La Sapienza" (Bravo et al, 1998). The laser beam is separated by a half-mirror surface in 2 rays with an intensity of 70% and 30%, respectively, in the same direction of the beam and in that perpendicular. The first beam passes through a flow cell in which the test suspension and is subsequently filtered, collimated and its intensity is measured by a photodiode (PD2 in the figure). The intensity of the beam deflected at 90 ° by the half-mirror surface is measured by another photodiode (PD1 in the figure) so as to determine at each instant the intensity of the emitted laser beam, which can be influenced by variation of the temperature reached by the emitting diode. To eliminate the influence on the measurement of the solution is made to the relationship between the transmittance of the suspension and that of the solution.

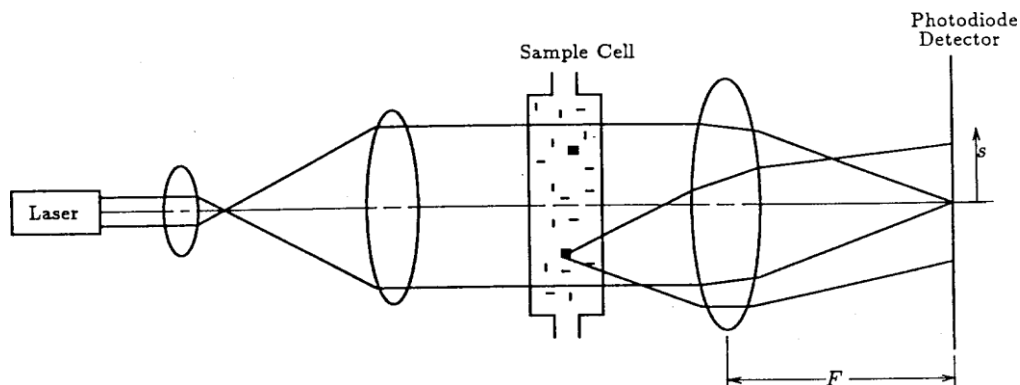


Fig. 8.1: Block diagram of the granulometer based on laser diffraction.

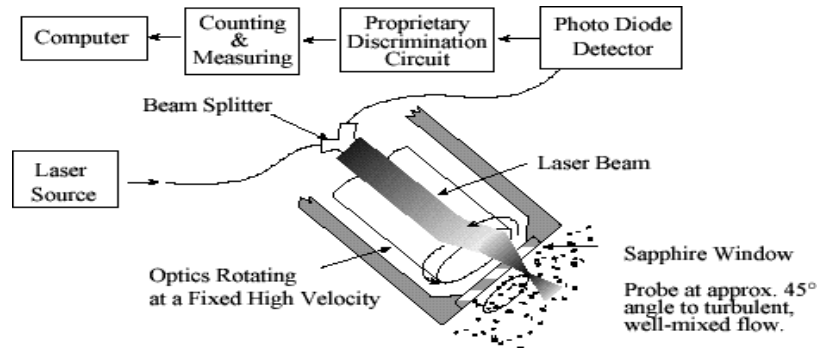


Fig. 8.2: The measuring system in situ of Lasentec FBRM.

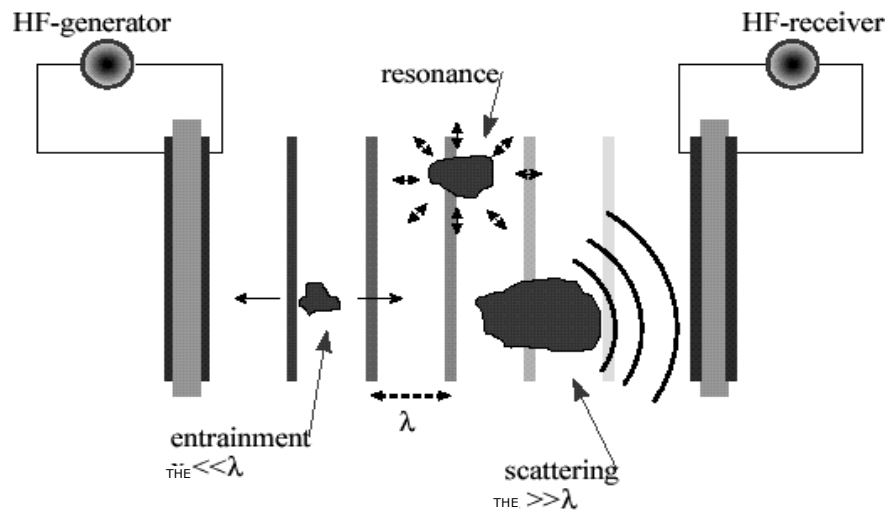


Fig. 8.3: System of operation of one with ultrasound attenuation instrument.

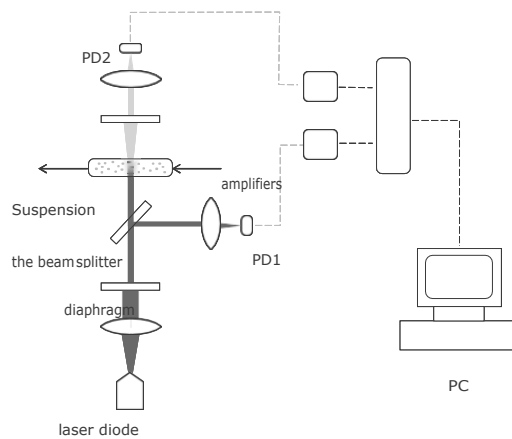


Fig. 8.4: The turbidity of the scheme developed by Bravi and Chianese.

9 INDUSTRIAL CRYSTALLIZERS

The application of industrial crystallization fields ranging from the production of chemicals base, such as potassium sulfate and ammonium chloride, to that of high value-added specialties such as active pharmaceutical ingredients. It appears evident that the production requirements are equally varied, as well as the characteristics of the plant crystallizers. In particular the pharmaceutical industry, given the scarce productivity demands and the high value-added products, relies mainly of batch crystallizers equipped with sophisticated and expensive instrumentation, in which the operating conditions can be adjusted with extreme precision. In this way the crystallizer itself can be used in production of different specialties. By contrast the basic chemical industry typically uses dedicated devices, preferably operating in continuous, in which the cost of the instrumentation must often be content.

A second aspect to keep in mind is that the constructive characteristics of the crystallizers are often related to the companies that build and sell devices: in fact often is identified with the company name not only the manufacturer but also the type of device, as in the case of crystallizers Swenson is Oslo. The plant engineering solutions are often the result of the individual companies.

The picture painted clarifies how difficult it is to talk about industrial crystallizers in general. However, you can define the guidelines that are the basis of different plant engineering solutions.

A need that unites virtually all industrial crystallizers is a need to stir the suspension to prevent deposits and agglomeration of the crystals produced. The mixing system is a critical point in the crystallizers of the design, since it is necessary to avoid excessive crushing of the crystals.

When the suspensions are particularly viscous, a circumstance which occurs frequently in the food industry, are adopted preferably crystallizers with horizontal axis, continuous or discontinuous. In the case of continuous apparatus, the mixing device is often of the screw type and also has the function of moving the suspension inside the appliance. To the suspension is not too viscous crystallizers the vertical axis are by far the most commonly adopted. These devices are equipped almost always conical bottom, to facilitate the emptying of the apparatus (see Fig. 9.1). The agitator is generally of the type with marine screw propeller, to facilitate the axial mixing. Often the axial movement is conveyed by means of a cylinder surrounding the helix, as shown in Fig. 9.2: draft tube); It is also quite common for the adoption of vertical baffles which restrict movement roundabout around the axis.

When the supersaturation is induced by evaporating the solvent or by cooling must equip the crystallizer of an apparatus for heat exchange: the exception, of course, the rare cases in which it is adottala the adiabatic evaporation. Similarly to what takes place for the in mixing reactors, the exchange device may be constituted by an outer jacket, a coil inside the crystallizer or by an external circuit with a heat exchanger, depending on the extent of the exchange

heat that is necessary to realize. In the case in which the indoor coil is adopted, this is shaped as shown in Fig. 9.2, so it will work even from draft tube. When adopted an external heat exchange circuit, the circulation of the suspension can also be exploited to ensure the mixing inside the crystallizer (the crystallizer with forced circulation): in Figs. 9.3 and 9.4 are depicted the heat exchange circuits and blending respectively for crystallisers type and evaporative cooling.

When the external circuit is not used as the mixing device, it is convenient to reduce the presence of crystals, especially large, the current that is recirculated. To this end, it creates an annular settling zone near the wall of the crystallizer from which to make a withdrawal (see Fig. 9.5). In this case the circuit may also have the function of reducing the percentage of fines in the product: in fact, the smallest crystals are carried by the current drawn and can be dissolved in the external circuit.

Finally, in figure 9.6 it is represented a crystallizer in which process a product classification. The device that allows the classification is said elutriation leg: the current that comes from the external circuit through this device from the bottom upwards, allowing only the larger crystals to reach the product withdrawal zone.

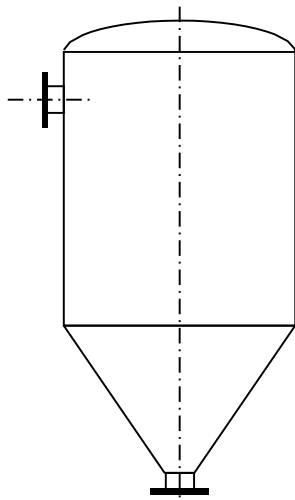


Fig.9.1: Crystallizer with a vertical axis

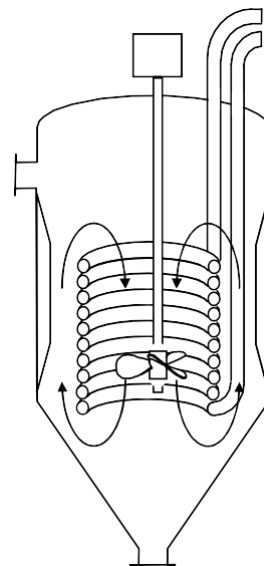


Fig 9.2: Crystallizer with indoor coil functioning by draft tube

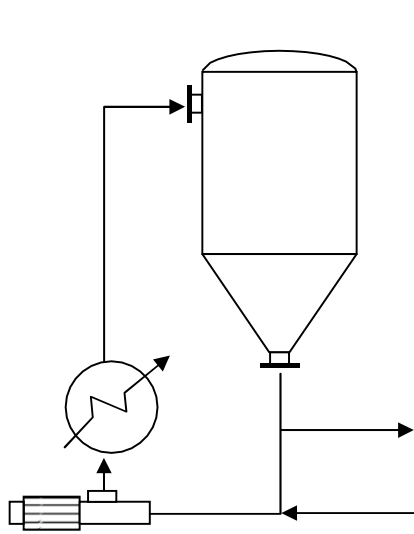


Fig. 9.3: Crystallizer for cooling with forced circulation

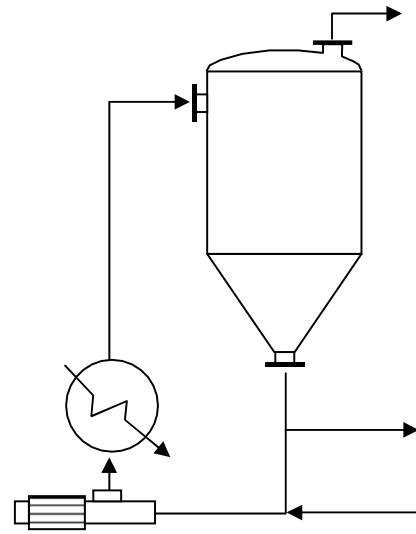


Fig 9.4: Crystallizer by evaporation in forced circulation

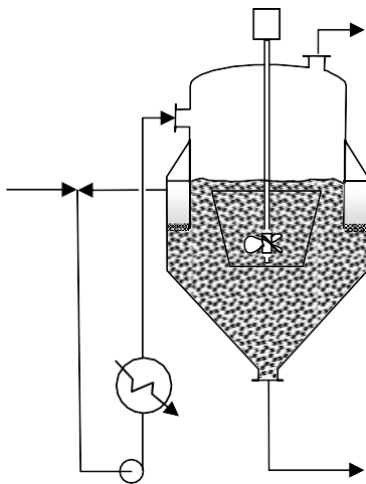


Fig. 9.5: Crystallizer for evaporation type DBT

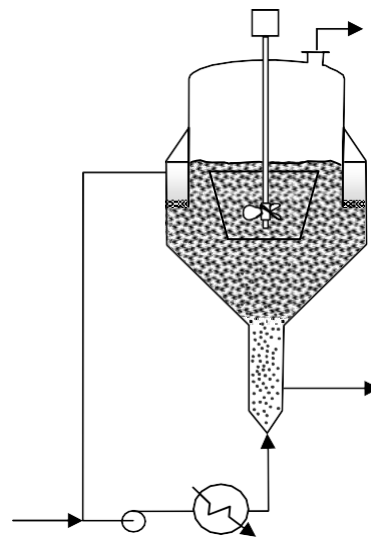
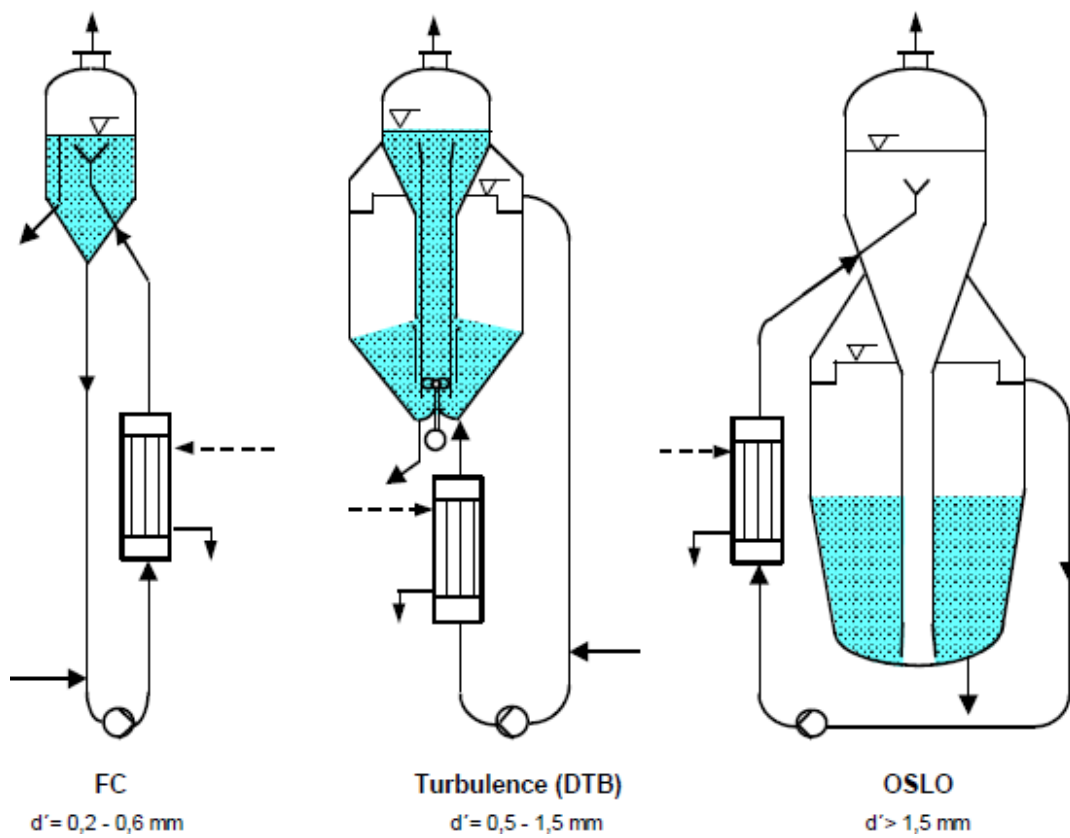


Fig. 9.6: by evaporation crystallizer with elutriation leg



Industrial Crystallizers:
Forced circulation (left), DTB (center) and Oslo
(right)