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51 Industrial Crystallization

Seppo Palosaari, Marjatta Louhi-Kultanen, and Zuoliang Sha

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51.1 INTRODUCTION TO CRYSTALLIZATION

Crystallization from solution is known to produce particles of high purity and of an approximately uniform size. The major fields of application are in the chemical, pharmaceutical, and food industries. However, in some cases, difficulties in separation and drying of the crystals turn into the obstacles of an otherwise ideal method.

This chapter is an overview of industrial crystallization from the point of view of facilitating the downstream processes for product-quality improve-

ment. Some aspects of process considerations, equipment as well as the advantages and limitations of the technique are also discussed.

Over the past decades, many handbooks on crystallization have been published, such as Mullin's *Crystallization* [1], Randolph and Larson's *Theory of Particulate Processes* [2], the *Crystallization Technology Handbook* edited by Mersmann [3], the *Handbook of Industrial Crystallization* edited by Myerson [4], Tavare's *Industrial Crystallization* [5], Davey and Garside's *From Molecules to Crystallizers* [6], and Sönnel and Garside's *Precipitation: Basic Principles and Industrial Applications* [7]. Each of these works

contains an introduction to the fundamentals of crystallization.

The easy dewatering and drying of crystals requires that the crystals be of a uniform and sufficiently large size. This is, therefore, the major theme of this chapter.

51.1.1 SOLUBILITY AND SUPERSATURATION

The amount of solute required to obtain a saturated solution under given conditions is called the solubility. The variation of solubility according to temperature, pH level, pressure, and the presence of other chemicals is the basis for the design of a crystallization process. Moreover, a phase diagram provides useful data for designing the crystallization process for a multicomponent system.

The traditional approximation is to consider supersaturation as the driving force behind crystallization and precipitation. In fact, the true driving force is the chemical potential. In reaction crystallization, in particular, this approach is important. However, we will use the simplified concept of supersaturation in the following discussion. Supersaturation is defined as the difference between the actual and equilibrium, and is expressed as follows:

$$\Delta c = c - c^* \quad (51.1)$$

$$S = \frac{c}{c^*} \quad \text{the supersaturation ratio, } S > 1 \quad (51.2)$$

$$\sigma = \frac{c - c^*}{c^*} \quad \text{relative supersaturation} \quad (51.3)$$

Supersaturation can be brought about in various ways, some of which are listed below:

1. By the evaporation of the solvent
2. From a change in the temperature of the solution
3. By a chemical reaction
4. Through the addition of an antisolvent or supercritical CO₂, which decreases the solubility of the solute
5. With the use of high pressure up to 8000 bars

Supersaturation is the main parameter in determining the rate of crystal growth and nucleation. In order to control the properties of a crystalline product, it is essential that the supersaturation level be controlled by desupersaturation rate, i.e., by the release of supersaturation which is mainly determined by the crystal growth rate and the available crystal surface area. Furthermore, the level of supersaturation is the main parameter that determines the agglomeration, shape, and purity of the crystals.

51.1.2 METASTABILITY

In the metastable zone the concentration is higher than in saturation but below the one where spontaneous nucleation occurs. Therefore, the crystal growth is mainly occurring in the metastable zone. Figure 51.1 schematically shows the solubility and supersaturation diagram. Primary nucleation takes place when the solution does not contain any crystals. Primary nucleation can be divided into homogeneous nucleation, in the absence of other substances, and heterogeneous nucleation, in the presence of other substances. Secondary nucleation is defined as the generation of nuclei with the presence of crystals. Then the nuclei are crystal fragments or added seed crystals, which grow under supersaturated conditions. The width of the metastable zone influences the nucleation mechanism and may depend on the operating conditions such as the mixing conditions, solution composition, dust, dirt, and cooling rate. In secondary nucleation, where crystallization starts in the presence of crystals and the existing crystals catalyze nucleation, the crystal surface, shape, and size of the seeds may also be important factors for nucleation kinetics. The metastable zone is, in this case, more narrow, i.e., new nuclei form easier.

In general, in order to obtain a narrow crystal size distribution (CSD), undesired nucleation should be avoided. In batch crystallization, the use of an optimal quantity of seed crystals of an optimal size may be the way to obtain a narrow CSD. According to Kohl et al. [8], the metastable zone of organic compound systems can be quite wide. Therefore, pri-

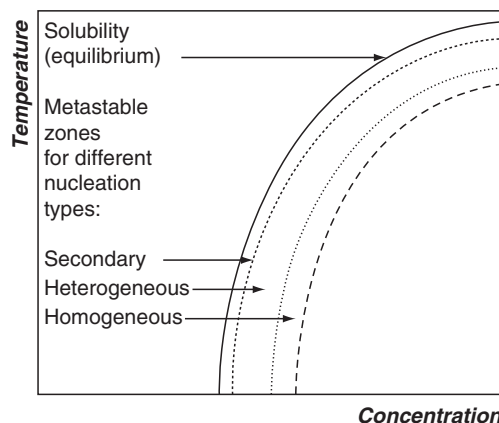


FIGURE 51.1 A schematic presentation of the metastable zone in primary and secondary nucleation. The width of the metastable zone, which is the concentration difference between saturated and operational concentration, shows the maximum degree of supersaturation where spontaneous nucleation starts.

mary crystallization occurs only at a very high level of supersaturation.

51.1.3 MEAN CRYSTAL SIZE AND CRYSTAL SIZE DISTRIBUTION

Normally, a crystalline product does not consist of single-size crystals, but consists of a wide distribution of sizes instead. The CSD or other statistical parameters, such as the mean crystal size, are used for describing the crystalline product. There are several mathematical models that can be used for describing the CSD produced by industrial crystallizers. The particle size distribution of the product can be determined by particle size analyzers.

The prediction of CSDs is still quite difficult; hence, data on crystallization kinetics are required, which means that the rate of nucleation should be known. The rate of nucleation can usually be obtained only to a sufficient accuracy by using empirical methods.

Generally, the “particle size” is used to denote the mean size of the crystals. However, several other terms have been used, such as the median size and the dominant size of crystals, as discussed in Allen’s book [9] where particle characterization is discussed in detail.

Particle size and the particle size distribution are important characteristics for dewatering and drying. For example, the smaller the size of the crystals, the more difficult the dewatering and drying. The effect of a wide distribution of crystal sizes is the same. Especially in precipitation, where agglomerates are formed, the porosity and roughness of the crystal surface may also affect dewatering and drying.

The population balance equation is the central equation with respect to CSD. A simple population balance is introduced by Equation 51.6. In a population balance, each crystal size is treated separately, and the growth rate in terms of an increase in the diameter of a crystal in each size class is calculated by the mass balance.

Besides agglomeration and attrition, the rates of nucleation and growth are the main kinetic parameters that determine the size distribution. These parameters, which are required in crystallizer design and simulation, can be determined on the basis of the population balance equations. Section 51.2 discusses the methods for controlling the particle size and particle size distribution.

51.1.4 CRYSTAL SHAPE

Crystalline material is usually nonspherical, except for agglomerates and larger crystals that have been

partly ground around the edges due to longer residence times under conditions where collisions occur between crystals, the agitator, and the crystallizer wall. Organic compounds, such as pharmaceutical compounds, usually have a needle-shaped crystal morphology.

The control of crystal morphology is a very complex process. This may be accomplished by the choice of an appropriate solvent system or by adding a chemical into the solution. Two methods may be used. Firstly, the experimental method can provide reliable results, but requires an excessive amount of work and extensive experience in order to be used for the testing of various solvents and additives. Secondly, computerized molecular modeling can be used in the search for suitable solvents and additives. Molecular modeling is neither very useful nor straightforward in addressing the solvent-selection problems. Molecular modeling may provide some insights, although it is still rather difficult and time-consuming to understand the whole problem of the solvent–crystal interface. There are various commercial computer applications for molecular modeling. For example, Accelrys Software Inc. [10] supplies commercial applications, named Cerius² and Materials Studio, for the modeling of the crystalline and molecular structures of organic compounds.

Programs such as C²-Polymorphs, C²-Morphology, and C²-Crystal Builder are included in Cerius². Cerius² is able to predict how impurities, tailor-made additives, the crystal growth rate, or changes in the solvent affect the structure of the forming crystal. Two prediction techniques based on the Bravais–Friedel–Donnay–Harker method and the attachment energy model are available in Cerius² that enables one to model both organic and inorganic crystals from the atomic crystal structure. It should be pointed out that the prediction of the morphology of inorganic compound systems is more complicated than that of organic compounds due to the difficulty in predicting the electrochemical phenomena in electrolyte solutions. HABIT95 is another commercial application [11]. HABIT95 predicts the external crystal structure based on the knowledge of the internal structure.

Winn and Doherty [12] have developed a new technique for predicting the shape of solution-grown organic crystals. This technique was used for predicting the crystal shape of adipic acid grown from water, biphenyl from toluene, and ibuprofen from polar and nonpolar solvents. As a general rule, the crystal shape can be described as follows: the greater the surface density of molecules on a face, the stronger the lateral interactions between the molecules and the more stable and slow the crystal growth. Furthermore, HABIT95 is based on the calculation of the

interaction energy within organic crystals solely from the knowledge of the internal crystal structure. The influence of the solution and supersaturation on crystal growth is more difficult to predict, especially for solution growth. Winn and Doherty [12] have also developed a method that requires the knowledge of readily available, pure-component properties, such as the crystal structure and internal energy of the solid, and the pure-component surface free energy of the solvent.

51.1.5 CRYSTAL PURITY

Crystallization is a unit operation where the solid product, i.e., the crystal lattice, is highly pure. More than 64% of the organic binary compound systems, where crystallization has been used as a purification or concentration method, are eutectic. In eutectic binary compound systems, only one compound in a certain solution composition forms the solid material, except at the eutectic point at which both components crystallize. As a general rule for purification by crystallization, the slower the crystal growth rate, the purer the crystal. A part of the smallest crystal fraction, i.e., fragments formed by attrition, may have a higher concentration of impurities due to the higher crystal growth rate. The reason can be explained by the "healing effect." Tiny crystals, which are fragments of larger crystals and, therefore, of an irregular shape, tend to initially obtain a more regular morphology at a relatively high growth rate. If agglomeration takes place, the secondary crystals may contain inclusions of the mother liquor, which decreases the purity of the crystalline product. An impure product is usually caused by traces of mother liquor adhered on the crystal surface in the crystal cake. This makes filtration and crystal-cake washing so important for final purity.

A better understanding of the behavior of a solution during crystallization requires a knowledge of the chemistry of the solution that may contain numerous other solutes or solvents in addition to the crystallizing compound. Firstly, these other compounds may influence the crystal growth or nucleation rate, which are the kinetic parameters that dominate suspension crystallization. Secondly, the other compounds may greatly change the solubility of the crystallizing substance to an extent that the supersaturation level in the process changes or it becomes possible for one or more compounds to salt out the main product at a certain concentration level. Thirdly, the other compounds may lead to an impure product due to inclusions that contain the mother liquor or to adhesion onto the crystal surface. Furthermore, other compounds may influence the mass transfer phenomena

of the crystallizing substance, which leads to the need for a better understanding of multicomponent diffusion [13]. Other components may adsorb onto a certain facet of the crystal surface, thereby affecting the crystal growth rate and the final crystal shape.

In the pharmaceutical industry, in addition to chemical purity, it is essential that the product has a desired polymorphic and pseudopolymorphic form. A chemical may have several crystal structures; the chemical compositions of these polymorphs are identical. This phenomenon is called polymorphism. A different lattice usually causes changes in crystal morphology. The chemical nature may be about the same from one polymorph to another, whereas the physical properties may differ greatly. Density, heat capacity, melting point, thermal conductivity, and optical activity are examples of these properties, according to Myerson [4, pp. 36–38]. The various melting points and the difference in dissolution rates from one polymorph to another are the main factors that have to be taken into account in the pharmaceutical industry. The forming of polymorphs depends on the crystal growth conditions, which are mainly affected by temperature, pressure, impurity content, growth rate, etc. During the crystallization process, the polymorph that forms first is often crystallized under metastable conditions. This metastable polymorph often transforms into a stable polymorphic form, which is known as polymorphic transition. It is essential to avoid the formation of an undesired polymorph or the desired polymorph should be prevented from transforming into another undesired polymorphic form. This is not easy because a small change in temperature may cause a polymorphic transition, which can occur quite often in suspensions. However, some materials may change into a polymorphic form in the dry, powder form. Seeding with the desired polymorph is especially important, according to Ulrich [14], when the conditions are close to the transition point. Two polymorphs can remain stable close to or at the transition point. Mullin [1] has introduced the principle of how to measure the solubilities for metastable and stable polymorphs. He has also shown how the transformations of various polymorphs can be studied at various temperatures and pressures. The reversible transformation from one polymorph to another is called enantiotropy, whereas the irreversible transformation is known as monotropy. Pseudopolymorphism occurs when a solvent enters the crystal lattice and forms, for instance, a hydrate product in aqueous solutions and a solvate in other solvents, as presented by Ulrich [14]. The bonds forming between the solvent and the solute in the lattice are of a physical nature; they are not chemically bound.

51.2 CONTROL OF CRYSTAL SIZE DISTRIBUTION AND CRYSTAL SHAPE

This section discusses the methods for controlling the CSD and crystal shape for different batch and continuous processes.

51.2.1 CONTROL STRATEGY OF SUPERSATURATION IN BATCH PROCESSES

Several techniques, such as the programmed-cooling rate in cooling crystallization and seeding technology, have been developed for controlling the particle size in batch-cooling crystallization processes. The principle of these methods is to influence the nucleation rate.

Nucleation depends on the total surface area of the crystals. If the total crystal surface area is relatively small in relation to the degree of supersaturation, nuclei, i.e., small crystals, will be formed after the initiation of crystallization. However, if the crystal surface area is sufficiently large, the level of supersaturation will be reduced through the growth of existing crystals.

Traditionally, batch crystallization is driven by the natural cooling of the mother liquor. Natural cooling can be best understood as a process where the crystallizer is left to cool down by natural convection of heat into the surrounding air. A faster variation of essentially the same method is to have a jacketed tank, where the jacket is thermostated to the end temperature of the process as desired by the user. In both cases, the temperature initially falls rapidly, after which it then slowly approaches the wall temperature of the tank. One problem of natural cooling is incrustation, i.e., a crystal layer forms on the cooling surface. However, the major disadvantage of natural cooling is that, for some solution systems, it becomes difficult to reliably run the process due to a high level of supersaturation in the initial period. If the total crystal surface area of the seed crystals is insufficient, a large number of very small crystals will be generated. In some systems, the growth rate of small crystals is slower than that of large crystals, and small crystals grow at a slow rate for decreasing temperatures. Next, supersaturation increases again and more tiny crystals are formed; the final crystal size is small due to the large number of nuclei that are generated in the process. In order to increase the particle size, the cooling rate of the solution can be programmed as follows.

At the first stage, when nucleation starts, the cooling rate should be slower. The second stage is faster when the existing crystals grow. According to Mullin [1, p. 355], an adequate cooling profile

for a general application, when seeding is used, is shown below:

$$T = T_0 - (T_0 - T_f)(t/\tau)^3 \quad (51.4)$$

Mayrhofer and Nývlt [15] derived the following expression for the optimal temperature profile of a batch crystallizer for both seeded and unseeded processes:

$$\frac{T_0 - T}{T_0 - T_f} = \left[1 - K\left(1 - \frac{t}{\tau}\right)\right] \left(\frac{t}{\tau}\right)^3 \quad (51.5)$$

The slope of solubility as a function of temperature is assumed to be constant in this derivation.

On an industrial scale, the maximum cooling rate is often limited by the heat-transfer capacity of the equipment, which means that the theoretical cooling program cannot be followed during the final stage of the batch. A high suspension density may cause high secondary nucleation and, thus, decrease the crystal size of the product.

Industrial experience shows that the above method may produce larger crystals than by natural cooling. The obtainable size depends on the system, though an increase in crystal size due to programmed cooling can be expected. Obviously, programmed cooling should first be tested with bench-scale equipment before investing in a programmed-cooling system.

According to Mersmann [16], the supersaturation in cooling crystallization is usually small, i.e., relative supersaturation, σ , is less than 0.1 and the relative solubility expressed by the ratio of solubility (kg/m^3) and crystal density is usually higher than 0.01. As a result, primary nucleation does not take place and the nuclei are formed only as attrition fragments. If a coarse product is desired, the attrition rate should be low and the crystal growth rate at the maximum allowable level with respect to crystal purity, all of which depends mainly on the mean residence time of the slurry.

51.2.2 SEEDING

Seeding is commonly used as a control technique, especially in batch crystallization processes. The nucleation rate depends on the total surface area of the crystals. If the total crystal surface is relatively small in relation to the level of supersaturation, small crystals or crystals of undesired shapes may be formed in the early stage of crystallization. Otherwise, if the crystal surface area is sufficient, supersaturation will cause the existing crystals to grow.

Heffels and Kind [17] have reviewed the general principles of seeding in a batch and continuous solution crystallization as well as in melt crystallization. They have provided practical ideas on how to carry out seeding with various crystallization systems. For instance, in practice, 0.1 to 0.3 times the final size and 0.1 to 3% of the final mass of the seed area are good choices for the seed size and mass, respectively. Usually, seed crystals of 20 to 50 μm are appropriate for the production of final crystals of 500 to 1000 μm . However, for a final product size of less than 100 μm , a seed size of 1 to 10 μm is more appropriate. For biotechnological and pharmaceutical processes, e.g., the production of insulin, the seeds should be 1 to 2 μm in size and obtained by freeze-drying. Seed sizes below 10 μm are not recommended because it is difficult to create a mass with a narrow CSD for such small crystals. Furthermore, small crystals tend to dissolve due to the Ostwald ripening effect and the crystal growth rates of tiny crystals are lower than that of larger ones. In addition, tiny crystals may form agglomerates and stick onto other crystals. Therefore, the introduction of crystalline dust must be avoided. The seed crystals should be washed or slightly dissolved to remove adherent crystalline dust, especially when dry crystals are used as the seeds. The addition of dry seeds may cause the seed crystals to float or agglomerate if they remain floating on the surface. It has been observed that ground seed crystals grow faster than seed crystals that have a smooth surface, though the reason is not clear. Therefore, milled seeds are used in the sucrose industry, for instance. Seeding with impure seed crystals may decrease the crystal purity and the used seeds should, therefore, be sufficiently pure. With compound systems of stereo chiral isomers, optical isomers or enantiomers, for instance, the type of seed crystal usually dictates the crystalline product that is formed. In this way, seeding affects the selectivity of crystallization.

The addition of the seed slurry can be done at different stages: onto the liquid surface (the crystals tend to agglomerate if they are not dispersed); near the stirrer, where the liquid is well mixed; or by one of the feed streams in a bypass or loop in the crystallizer. The best way is to add seeds to the solution beneath the liquid level or to add them to a feed stream at the beginning of the batch or, in case of a semibatch system, continuously. In reactive batch crystallization, the nucleation rate can be decreased by the dilution of the feed streams or by the addition of fine crystals into one of the feed solutions or the reactor. The surface area and growth rate should be large enough to quickly reduce the supersaturation. The recirculation of the crystal suspension creates an

effect similar to seeding in the growth regions of the reactor. In some cases, large particles are produced by agglomeration, which is triggered by electrostatic forces. These forces can be measured with a zeta potentiometer. The simplest method to prepare the seed crystals is with the use of the final product of the previous production batch. In addition, the milling and dispersion of the seeds in inert solvents or saturated solutions are the generally used methods.

In some processes, the residual suspension droplets at the stirrer and wall are able to capture enough crystals from the previous batch, and these crystals function as seeds for the next batch. Some researchers have postulated that the growth of nuclei in secondary nucleation dominates the final CSD. However, there are reports that show that seeding does not significantly increase the crystal size. Heffels and Kind have, nevertheless, shown that seeding improves the quality of the crystalline product in many cases and has a clear advantage.

Kohl et al. [8] studied seeding in batch crystallization. The system studied was an aqueous β -cyclodextrin solution that had a wide metastable zone. They determined a critical size for the seed crystals in this system. When the size of the seeds used was larger than the critical size, secondary nucleation took place.

Furthermore, Jagadesh et al. [18,19] have studied seeded batch-cooling crystallization without temperature control for aqueous potassium alum, and potassium sulphate solutions. In their approach, the solution was cooled according to a natural profile. They succeeded in attaining a monodispersed and relatively narrow CSD by controlling the level of supersaturation in such a way that the existing seed crystals grew and no nucleation occurred. This controlling method was based on the use of small, ground, seed crystals of diameter below 50 μm . The required mass of the seeds was less than 1% of the total crystal mass in the product. Hence, the main idea was to add small-sized seeds in order for no new nuclei to be formed during the batch process. However, for some compound systems, secondary nucleation cannot always be fully avoided at usual suspension densities.

51.2.3 PRECIPITATION

Precipitation technology is not yet very advanced, and many industrial companies experience problems with small crystals that cannot be separated easily. Furthermore, for some purposes, it is necessary to produce very small crystals (e.g., pigments, paper-coating materials, and paper fillers) and, therefore, solid-liquid separation becomes inevitably difficult. In the paper industry, submicron-sized paper-coating agents may be produced in a process in connection to

the paper mill so that the suspension is transported as slurry and no filtration is required. If the filtration of small crystals is needed, the problem is the need to be handled by filtration specialists.

Precipitation is an operation known for producing small crystals that are difficult to filter and dry. Batch precipitation is usually carried out in the form of a semibatch process, i.e., one or two reactants are continuously added to the reactor. The control of the particle size distribution in a precipitation process is very complicated because of the high level of supersaturation generated by the fast reaction. According to Mersmann [16], the important factors for sparingly soluble systems in isothermal precipitation are:

- The concentration of reactants
- The rate of the chemical reaction
- The intensity of macro- and micromixing
- The dilution of solution
- Agglomeration

If nanometer-scale crystals are required, a tiny crystal size can be obtained by applying very high primary nucleation rates, which require extremely strong supersaturations. Such high levels of supersaturation can be achieved through

1. The high concentration of reactants
2. The avoidance of agglomeration (using surfactants, pH control, etc.)
3. Rapid quenching or diluting in order to halt growth (a combination of a T-mixer and a stirred vessel, Figure 51.2)

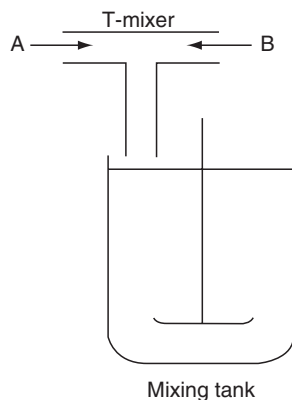


FIGURE 51.2 The operation of a T-mixer and a stirred vessel. The reactants are mixed in a T-mixer where the chemical reaction takes place. The suspension is then introduced into the vessel operating at a relatively low level of supersaturation.

4. No dilution (T-mixer) in order to produce many nuclei
5. The rapid local micromixing and poor macro-mixing of the reactants
6. Products with high concentrations and low solubilities
7. Rapid micromixing at the feed point of the reactants for a fast chemical reaction

On the other hand, if a coarse product is required, supersaturation must be kept at a low level through

1. The use of low-concentration reactants (perhaps by dilution)
2. Good macromixing in the entire precipitator
3. Seeding by recycling the slurry at high rates in order to reduce local supersaturation peaks while keeping primary nucleation at a minimum and promoting crystal growth

Kind [20] has discussed the basic factors that affect reactive crystallization. The first crystals that appear are micrometer or even nanometer in size range. Interfacial forces govern the behavior of suspended particles in these size ranges, as a result of which the fine particles are affected by colloidal interaction. Therefore, the final product particles are often secondary, formed by the aggregation of small primary particles. The final product morphology results from the action of aggregation, the rheological behavior of the suspensions, and the shear rates present in the precipitator. The primary processes are mixing on the macro, micro, and molecular scale, as well as the reaction, nucleation, and growth of the particles. The formation of primary crystals depends mainly on the mixing conditions. If mixing does not control reactive crystallization, the crystallization reaction can be best controlled by initial supersaturation. Under ideal mixing conditions, the final primary particles in the nanometer size range are rapidly formed within a few milliseconds and remain unchanged, except in the case of long-term ripening and aging. Aggregation, aging, and ripening are secondary processes. At moderate shear rates, the secondary particles can be found in the size range of 5 to 20 μm . It is relatively difficult to scale-up precipitation. Generally, the design of precipitation processes still requires experience from the behavior of each system.

51.2.4 CONTINUOUS PROCESSES

Continuous crystallizers are used for the separation of large quantities of fertilizers, salts, and sugars. The common feature of crystallization is the existence of a

driving force for crystallization, i.e., supersaturation. The method by which supersaturation is generated and the various factors affecting its local and average values have a strong influence on all the properties of the crystallized material. It may be noted that the local and average values of supersaturation affect the growth, nucleation, and aggregation rates, which in turn determine the population density and CSD. The CSD, on the other hand, determines the specific surface area and magma density, which strongly affect the growth and aggregation rates, the rate of secondary nucleation, and the solute mass balance in a feedback fashion. Irrespective of the mechanism of the generation of supersaturation, impurities exert a strong effect on the width of the metastable zone. Impurities also influence crystallization kinetics, crystal purity, crystal morphology, and the aggregation rate. Optimum supersaturation, at which the existing crystal growth is at the maximum rate permitted (i.e., the desired particle shape is obtained without mother-liquor inclusions) and at which a certain crystal number is not exceeded, must be determined experimentally.

The objectives in the operation of a crystallization process are to meet the product specification, i.e., a narrow CSD, maximum crystal purity, high yield, and an acceptable crystal morphology. Moreover, the manufacturer's requirements for economic and trouble-free operation should be met. The CSD and crystal morphology are important parameters for downstream operations of crystallization such as filtration and drying.

Any attempt to control a crystallization process to meet the above-mentioned product specifications should be directed toward generating and maintaining a mild and homogenous supersaturation in the bulk of the magma at local and average levels. This favors the growth rate and prevents spontaneous nucleation. In industrial crystallizers, this objective is achieved by improving the design of the crystallizers as well as by controlling some of the easily measurable process variables, such as temperature, pressure, solution level, and flow rates. Such an approach is not sensitive to frequently occurring disturbances such as variations in the feed composition, feed temperature, impurities, and differences in the extent to which mixing is carried out in the tank. Normally, continuous crystallization is carried out in a mixing tank. Internal or external circulation is used to reduce the level of supersaturation.

When the crystallizer is well mixed and operated continuously at steady state, with no attrition and breakage of the crystals at a size-independent crystal growth rate, the simplest population balance equation is

$$G \frac{\partial n}{\partial L} + \frac{n}{\tau} = 0 \quad (51.6)$$

The equation describes how, during the retention time, the crystals move to a higher-size class because of growth. The derivation of the above equation is simple and can be found in textbooks. The particle size distribution is obtained from the above equation and is shown below:

$$n = n_0 \exp\left(-\frac{L}{G\tau}\right) \quad (51.7)$$

The median crystal size, L_{50} , which occurs at a cumulative mass undersize of 0.5, can be evaluated by the following equation:

$$L_{50} = 3.67G\tau \quad (51.8)$$

The maximum of the mass distribution density or the dominant size, L_d , can be calculated using the following equation:

$$L_d = 3G\tau \quad (51.9)$$

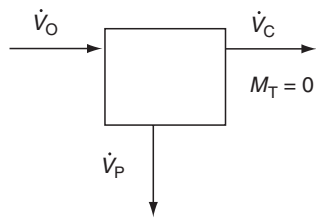
This is a very useful equation for the design of a crystallizer and can be used to obtain a rough estimation of the particle size in industrial processes.

Generally speaking, the median crystal size of a crystalline product can be increased through a decrease in the number of nuclei or an increase in the growth period of the crystals present in a crystallizer operated at an optimum level of supersaturation. Of these, the most practical way to alter the particle size distribution in a continuous crystallization process is to adjust the residence time of the crystals.

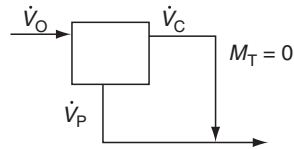
In the following discussion, we give a brief explanation of some of the principles used in controlling the crystal size, roughly following the treatment of the subject by Mersmann [3].

51.2.4.1 Clear-Liquor Advance Operation

A clear-liquor advance operation is one in which the overflow liquid is continuously removed from the tank. The overflow is not actually clear but contains small crystals that have not settled in the overflow section. This method is a simple way of controlling the CSD, because the residence times of the clear mother-liquor overflow and crystal are different. The flows are separated and the excess nuclei are removed with the overflow. The nuclei in the overflow can be used, for example, in the following crystallization unit. The larger the clear-liquor flow for a given feed flow, the longer the residence time of the crystals in the product stream.



(a)



(b)

FIGURE 51.3 Clear-liquor advance operation.

The operation of the clear-liquor advance is shown in Figure 51.3a and Figure 51.3b. The system in Figure 51.3b can also be called a double draw-off crystallizer. The liquor may be recycled separately resulting in the product stream having a high suspension density. For operation with double draw-off, as the production rate is the same as in the mixed-solution–mixed product removal (MSMPR) crystallizer for a given desupersaturation, the suspension density in the unified stream is also equal to the suspension density of the MSMPR crystallizer. In such a case, the nucleation rate of the crystals can be expressed as

$$n_0 = \frac{B_0}{G} = k_n G^{i-1} M_T^1 \quad (51.10)$$

The dominant crystal size, L_d , is proportional to the product of the crystal growth rate, G , and the residence time of the crystals

$$\frac{L_{d2}}{L_{d1}} = \left(\frac{\dot{V}_p + \dot{V}_c}{\dot{V}_p} \right)^{(i-1)/(i+3)} \quad (51.11)$$

The above expression shows that when the flow rate of the clear liquor increases, the dominant particle size also increases.

51.2.4.2 Destruction of Fines with Solute Recycling

The operation of the fines-destruction process is similar to that of clear-liquor advance; as shown in Figure 51.4, the difference is that when the clear liquor is used, the small particles return back to the product flow, thus increasing the proportion of small crystals.

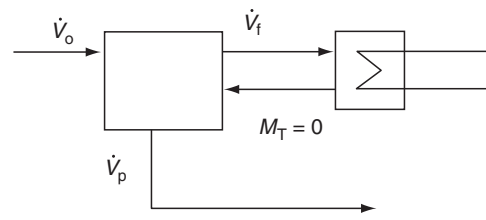


FIGURE 51.4 Fines-destruction crystallization process.

For the fines-destruction operation, very small fines can be withdrawn, and the suspension density of the overflow is very small. The number of crystals in the crystallizer decreases as a result of eliminating the small-sized particles. This operation is very useful in increasing the size of crystals in a system that has a high rate of nucleation. This method does, however, lead to a wide particle size distribution.

The advanced stream is classified at a size of L_f and all the particles with $L < L_f$ are eliminated in the dissolver. The fines are removed at a size that is negligibly small compared to that of the product-size crystals. In this case, the size-improvement ratio, L_{d2}/L_{d1} , is given by

$$\frac{L_{d2}}{L_{d1}} = \left(\frac{1}{\beta} \right)^{1/(i+3)} \quad (51.12)$$

According to this equation, size improvement is appreciable if the kinetic exponent, i , is small and the fraction β of the surviving nuclei is also small.

The efficiency of fines destruction depends on the undersaturation in the destruction system and the residence time that must exceed the dissolution time of the nuclei.

51.2.4.3 Classified Product Removal

The operating system for classified product removal is shown in Figure 51.5. The operation of classified

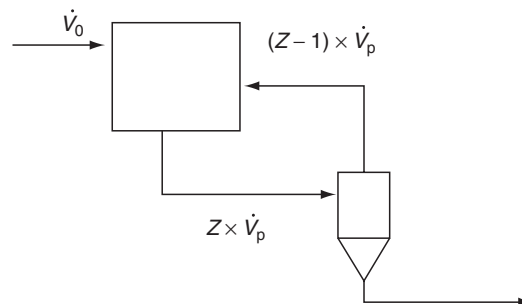


FIGURE 51.5 The classified product-removal crystallization process.

removal can be achieved by a classification device, which may be a hydrocyclone, a classifier, a wet screen, a fluidized bed (FB), or a separating centrifuge. By using a suitable classification device, only the particles of a size larger than that required can be withdrawn from the product; the crystals, the size of which is smaller than the required size, will return to the crystallizer for further growth. In this way, the CSD will become narrower, though the mean size of the crystals will decrease. The drawback of this method is that classified product removal may cause instability in the process and even force the process to be discontinued due to the excessive increase in the amount of small crystals. Therefore, in practice, classified product removal alone is not used in industrial crystallization.

In large-scale industrial crystallization processes, the most commonly used classification device is a hydrocyclone. The advantages of the hydrocyclone are its high capacity within a small equipment volume and an easily adjustable cutting size by the control of the feed-flow rate and the ratio of the up-flow to the down-flow. The fluid bed or elutriation leg is another method often used for classification in crystallization processes. With the elutriation leg, the feed or clear solution is fed from the bottom of the elutriation leg. The up-flow velocity is set based on the settling velocity of the cutting size of the particle. The crystals, the size of which is smaller than the cutting size are sent back to the crystallizer for further growth. The crystals, which are larger than the cutting size, are drawn out of the crystallizer as the product. In principle, the classifier and the separating centrifuge can both be used as classification devices. However, as it is not easy to control the actual cutting size, it is rare to use these devices as classifiers in industrial crystallization processes. These devices are mostly used in separating the solid from the solution. In the elutriation leg, described earlier, this means preventing the small crystals from entering the next separation stage. In the centrifuge, the crystals are simply separated from the crystal slurry. In some processes, the separated solution includes many small-sized crystals. If the solution is sent back to the crystallizer, the separator may be considered to be a classification device. It can be further said that the wet screen is seldom used as a classification device in industrial crystallization processes because the easy blockage of the screen will cause operation problems.

51.2.4.4 Classified Product Removal with Fines Destruction

A crystallizer equipped with the devices for product classification and fines destruction can efficiently

improve the particle size and particle size distribution. With the fines destruction, a portion of the small particles can be eliminated in such a way that the number of crystals in the crystallizer can be controlled within the required range. When this method is complemented with classified product removal, the size of the crystals in the product is controlled; on the other hand, an undesired increase in the amount of small crystals is prevented. With this method, it is possible to obtain crystals of a uniform and large size.

51.2.4.5 Role of Mixing Intensity in Continuous Suspension Crystallization

Industrial crystallization is normally carried out in a mixing tank. Many parameters are affected by the mixing conditions during crystallization. Firstly, mixing affects the temperature or concentration distribution in the mixing tank in such a way that the driving force for crystallization is related to the mixing degree in the tank. If mixing is not complete, there may be a very high local level of supersaturation, which will cause the crystallization process to become uncontrolled. In addition, it is impossible to reach the required product size, morphology, and purity. Secondly, the mixing intensity affects the mass transfer rate between the solid and the solution, and variations in crystal growth rate occur. It is well known that the secondary nucleation rate is strongly affected by the mixing intensity because of the crystal collisions with the impeller, between the crystals, and of the crystals against the wall. The effect of mixing on crystallization kinetics will directly affect the particle size distribution usually in an undesirable way.

Besides the mixing effect on the basic process of crystallization, another important effect of mixing on continuous crystallization is the residence time of the solution and the solid. As shown by Sha and Palo-saari [21] and Sha [22], as the particles of different sizes have different flow patterns in the crystallizer, the particle size distribution is different at different locations. The particle size distribution in the product line depends heavily on the mixing intensity and on the location from which the product is withdrawn.

51.2.5 SIMULATION OF CRYSTALLIZERS

The calculations required for predicting the operating conditions are complicated. It is necessary to have, or write, a computer simulation program. The simplest part of such a calculation is to elaborate the energy and mass balances of the system. The solubility and enthalpy data are also required. The calculation produces the amount of crystals produced in a specific

time unit, and the energy required is usually steam that is fed into the heat exchanger if the system is continuous. This calculation does not produce the crystal size and CSD, which would both be useful in the design of the equipment. Although, in practice, a large part of design work is based on the use of previous experience in crystallization of the same or similar materials, there is, nevertheless, the need for design methods that can predict the particle size.

One method is to solve the population balance equation (Equation 51.6) and to take into account the empirical expression for the nucleation rate (Equation 51.10), which is modified in such a way that the expression includes the impeller tip speed raised to an experimental power. In addition, the experimental value, pertinent to each chemical, is required for the power of the crystal growth rate in the nucleation rate. Besides, the effect of suspension density on the nucleation rate needs to be known. Furthermore, an industrial suspension crystallizer does not operate in the fully mixed state, so a simplified model, such as Equation 51.6, requires still another experimental coefficient that modifies the CSD and depends on the mixing conditions and the equipment type. If the necessary experimental data are available, the method enables the prediction of CSD and the production rate as dependent on the dimensions of the tank and on the operating conditions. One such method is that developed by Toyokura [23] and discussed and modified by Palosaari et al. [24]. However, this method deals with the crystallization tank in average and does not distinguish what happens at various locations in the tank. The more fundamental and potentially far more accurate simulation of the process can be obtained by the application of the computational fluid dynamics (CFD). It will be discussed in the following section.

51.2.6 ROLE OF COMPUTATIONAL FLUID DYNAMICS IN THE RESEARCH OF CRYSTALLIZATION

The accurate simulation of suspension crystallization presumes that the parameters that influence a crystallization process, such as the suspension density and supersaturation, are known for each location in the tank. One method of obtaining this information is the application of CFD, which is the basic tool for the study of fluid dynamics and has been applied in many areas. Recently, CFD techniques have been developed to a level that allows complex flow situations to be modeled to a reasonable degree of detail and accuracy. The application of CFD in chemical engineering processes has been reported in some fields [25–27]. Many methods have been developed for the

simulation of stirred tanks [28–30]. These studies offer a good background for the study of crystallization.

Garside [31] provided an extensive review of crystallization from solution in which he emphasized the pivotal role of fluid mechanics in the kinetics and resulting CSD. As summarized by Rielly and Marquis [32], crystallizer fluid dynamics act at a variety of scales and, to a certain extent, have some local influence on each of these kinetic steps, such as the growth and reaction rates, aggregation, breakage, supersaturation, nucleation, and residence-time distribution of the particles. On a macroscale in the order of the crystallizer dimensions, the fluid mechanics of the mean flow affect the spatial distribution of the fluid and solid phases, imposing a degree of backmixing that determines the solid and liquid residence-time distributions. Mesoscale fluid mechanics in the order of the impeller blade width affect the local liquid-concentration distributions of the feed reagents, interaction of the crystals with the impeller (crystal abrasion on impact with the impeller leads to secondary nucleation), and heat-transfer rates from crystallizer internals. At an even smaller scale in the order of the size of turbulent eddies or individual crystals, microscale fluid mechanics affect the mass transfer rates, the rates of turbulent collisions between the particles, and the micromixing of chemical reagents. The fluid mechanics of the suspension flow at these various scales affect the precipitation rates, distribution of supersaturation, nucleation rates, growth, as well as the numerous kinetic processes by which crystals of a given size are born and die. Even processes such as nucleation, which are more directly related to local supersaturation, are indirectly related to suspension fluid mechanics; supersaturation is determined by local micromixing and the reaction and mass transfer rates.

As described above, many phenomena of crystallization are related to the fluid dynamics of the crystallizer and can be studied with the use of CFD. The basic transport phenomena in the crystallization process, which include momentum, heat and mass transfer, can be easily solved using CFD. The mass transfer between the particle and the solution is the main process that describes crystal growth. Zöller et al. [33] have studied single crystal growth under the flow of solution. The nucleation rate was considered directly proportional to the energy of the moving particle, the movement of which can be obtained from CFD. In this way, the nucleation rate can be studied. Ten Cate et al. [34] suggested a model for the study of individual crystals in the flow, through which the collision frequency and energy can be obtained. The collision data obtained in this way can be used in the models that predict the rate of secondary

nucleation and attrition. The nucleation study using CFD is still at an initial stage; researchers are still looking for the best model for simulation of the nucleation of crystallization, although not much work has been published as yet. Expressions describing the mass transfer rate can be used together with the cooling and chemical reaction rates in order to obtain the concentration distribution in the solution. Then the local supersaturation in the crystallizer can be calculated with improved accuracy for the nucleation and growth rate. Falk and Schaer [35] present a probability density function (PDF) method for the calculation of evolution of the particle size distribution in precipitation reactors. This method contains a micromixing model based on a Lagrangian frame where chemical reactions are treated without modeling and which requires minimal computational resources. The micromixing model considered the concentrates on the interaction and exchange between the fluid and the mean-sized crystals and takes into account nucleation, growth, and aggregation. With this method, it is possible to obtain, for any point in the flow, the reactant concentration and supersaturation fields and the particle size distribution field, using simple moment methods. The agglomeration phenomena can also be described in the CFD environment. Hollander et al. [36] used a lattice Boltzmann scheme to simulate the turbulent flow field and a Monte Carlo algorithm to solve the particle size distribution and studied the dependence of the agglomeration rate constant on the shear rate and on turbulent transport. They concluded that the turbulent transport of particles is an important factor in the overall agglomeration rate.

Apart from the crystallization kinetics, the mixing state of the suspension in a crystallizer has a strong effect on the crystallization process. For the precipitation system, the particle size distribution in the reactor depends on the kinetics of the crystallization process, although it is also strongly influenced by mixing of the different chemical species, including solid particles. This kind of study has been carried out by many researchers [35,37–41]. The different fluid dynamics between the solid and the solution and between the different-sized crystals is the crucial information for the description of the crystallization process, especially in the case of a continuous crystallizer [21] where the concentration fields of different-sized particles are studied using multiphase flow. Here, the effect of the particle size distribution at each point in the flow on the crystallization process is studied. Studies, which have been carried out on crystallization using CFD such as those mentioned earlier, will bring new insights to the understanding of the crystallization processes.

Another objective in the study of the application of CFD in crystallization is to simulate the particle size distribution in crystallization. In order to solve this problem, the simulation should take into account the population balance. The internal coordinates of the population balance make it difficult to utilize it in the CFD environment. In addition, different-sized particles have different hydrodynamics, which causes further complications. Wei and Garside [42] used the assumption of MSMR and the moments of population balance to avoid the above difficulties in the simulation of precipitation. In the CFX commercial application, the MUSIC model offers a method for solving the population balance equation in CFD and defines the flow velocity of different-sized particles on the basis of the ratio of the velocity to a reference-sized particle. The velocity of this reference-sized particle is then simulated using the multiphase-flow model. In this way, the problem of the different hydrodynamics of different-sized particles is solved. However, the accuracy of this model is not sufficient for it to be directly used for bubble-sized distribution only. More work is required before this model can be applied to crystallization.

For the simulation of all the crystallization processes, a detailed approach, as well as certain geometry-independent kinetic models, should be able to take the geometry of the crystallizer into account. Kramer et al. [43–44] propose the division of the crystallizer into a number of well-defined regions in which supersaturation, the rate of energy dissipation, the solid concentration, and CSD are more or less uniformly distributed. With such an approach, the kinetic parameters for these models can be obtained from laboratory-scale experiments or can be estimated from simulation technology, whereas industrial-scale model simulations are able to predict the performance of a full-scale crystallization process. In order to simulate continuous crystallization in an imperfectly mixed suspension, Sha et al. [45] assumed different-sized particles to be distributed differently in the crystallizer. They proposed a population model that takes into account the relationship of particle size distributions, the product-removal location, and different points inside the crystallizer. The particle size distribution in the product can be obtained using kinetic models that can be obtained from experiments or using simulation technology. With this method, it is possible to study the effect of the geometry of the crystallizer, the mixing intensity, and the location of product removal on a continuous crystallization process.

Another task of applying CFD to crystallization is to study the geometry of the crystallizer. It can offer detailed information on the influence of the shape of

the crystallizer and impeller in producing the required mixing conditions of crystallization. Furthermore, the scale-up of crystallization will be a useful task for the study in the CFD environment. It is well known that the scale of the crystallizer affects the crystallization. This is mainly caused by the hydrodynamic differences for different scales of crystallizer. It is a very important subject with respect to the design of the crystallizer. Experimental studies on this subject require large financial resources. CFD simulation, on the other hand, supplies a possibility to investigate crystallization processes for different scales of crystallizer. Zauner and Jones [46] present a model in which the micromixing and mesomixing are combined with a population balance to study the effect of the mixing on the particle size distribution in the precipitation process. Satisfied results were obtained. Wei and Garside [42] studied the power-input effect on the precipitation process for different scales of precipitator with the moment transport population balance equation model. Because the basic model of simulation of crystallization with the tool of CFD is still under development, the scale-up subject cannot produce good results yet.

51.3 INDUSTRIAL CRYSTALLIZERS

Nowadays, a large number of industrial crystallizers are in use. In this section, we will discuss only a few of the basic and most presentative constructions in order to complement the principles explained earlier.

In cooling crystallization, supersaturation is obtained by undercooling the solution that is supersaturated by the evaporation of the solvent in evaporative crystallization. The relatively large average sizes of the end product can be obtained through both cooling and evaporative crystallization.

The criteria for the selection of an evaporative or cooling crystallizer depend on the slope of the solubility curve. If the slope of the solubility curve of a fairly soluble substance, i.e. ($\Delta c^*/\Delta t$), is relatively

low, evaporative crystallization is more preferable; but for a high-solubility slope, such as that of hydrated salts, cooling crystallization is a better alternative. In some compound systems, due to the high solubility of the solute, the final solute concentration of the residue remains too high, even at low temperatures. Evaporative crystallization should be employed in order to obtain as low a final solute concentration in the process solution as possible. This is the case when the main purpose of the crystallization process is to utilize solutes from the process water in order to obtain low-concentration waste solutions.

The operational costs of evaporative crystallization in countries where the cost of energy is low are lower than those of cooling crystallization.

Commercial crystallization processes are usually run in jacketed and baffled mixing tanks equipped with a draft tube, i.e., a draft-tube baffled (DTB) crystallizer. There are also forced-circulation (FC) processes where the solution is pumped through an external heat exchanger. In cooling crystallization, the pumped solution is cooled in the heat exchanger and heated in evaporative crystallization. An evaporative crystallizer is equipped with a vacuum system, which contains either a vacuum pump or an air ejector. Usually, the evaporative crystallization process consists of several stages. Table 51.1 shows the approximate operational conditions of FC, DTB, and FB-type crystallizers. A DTB, FC, and FB crystallizer, which is also an Oslo crystallizer, are schematically shown in Figure 51.7 through Figure 51.9. This equipment will be described in more detail in Section 51.3.2.

Commercial suspension crystallizers are manufactured, among others, by Swenson and GEA Messo GmbH. Wirges [47] cites the following companies as suppliers of solution crystallization processes: CT Umwelttechnik, HPD Evatherm AG, Chematur Eco-planning Oy, Ebner CO KG, Balcke-Dürr GmbH, and Gea Kestner SAS.

TABLE 51.1
The Approximate Operation Conditions of Crystallizers When $\rho^*/\rho_c > 0.01$.

Type	Suspension Density (kg/m ³)	Volume Ratio of Crystals to Suspension (m ³ /m ³)	Residence Time (h)	Specific Power Input (W/(kg Suspension))	$\Delta\rho/\rho_c$	L_{50} (mm)
Forced-circulation (FC)	200–300	0.1–0.15	1–2	0.2–0.5	10^{-4} – 10^{-2}	0.2–0.5
Draft-tube baffled (DTB)	200–400	0.1–0.2	3–4	0.1–0.5	10^{-4} – 10^{-2}	0.5–1.2
Fluidized-bed (FB)	400–600	0.2–0.3	2–4	0.01–0.5	10^{-4} – 10^{-2}	1–5(–10)

Note: ρ^* is the density of the saturated solution and ρ_c is the density of the crystal, i.e., solid density.

Source: Mersmann, A., Ed., *Crystallization Technology Handbook*, Marcel Dekker, New York, 1995, p. 219.

51.3.1 BATCH CRYSTALLIZATION

Usually, batch crystallization is used when a relatively low production capacity is required, e.g., below 50 t of product per day. When batch crystallization is equipped with the proper temperature control and seeding system, the crystallization conditions can be adjusted in such a way that the residence times of the crystals, of various sizes, can be kept about the same. Therefore, the CSD can be narrower in batch crystallization than in continuous crystallization, which is one of the significant differences between batch and continuous crystallization without fine removal or a classification method for the product. In practice, industrial continuous crystallization processes contain fines-removal or classification units, such as hydrocyclones, in order to produce crystals of a narrow CSD.

Jacketed tanks with propeller agitation are widely used for batch crystallization. The agitator is selected by the use of the same principles as in ordinary liquid blending when high pumping rate and low turbulence are required. This condition minimizes excessive secondary nucleation. For cooling crystallization, the programmed-cooling method, presented in Section 51.2.2, produces larger crystals than that by natural cooling. For natural cooling, the temperature first falls rapidly and then more slowly. In some cases, a batch process is equipped with a fines-destruction unit in order to increase the average crystal size or enable a more reliable downstream process, i.e., filtration, where operation conditions may be disturbed by small crystals. In fines destruction, a side flow

from the tank, after a crystal classifier, is directed to pass through a heat exchanger where the smallest crystals dissolve before the flow returns to the tank. Seeding, as was explained in Section 51.2.4, is commonly used.

Figure 51.6 shows a schematic figure of a jacketed, batchwise, multipurpose reactor with baffles, which is used in batch crystallization. For fine chemicals, the tank is usually glass-lined. Various kinds of impellers and propellers can be used as stirrers. From the perspective of the mixing basis and homogenous supersaturation conditions, it should be pointed out here that in this kind of mixing tank, equipped with a single impeller, good mixing takes place only close to the bottom, especially with large-sized crystals. Figure 51.6b shows the control system for programmed cooling, as discussed in Section 51.2.1.

51.3.2 CONTINUOUS CRYSTALLIZATION

Figure 51.7 through Figure 51.9 show some of the most common types of continuous crystallizers for large-scale production. They usually operate under vacuum conditions in order to reduce the evaporation temperature, and heat energy is provided by a heat exchanger. Of these, the FC crystallizer is shown in Figure 51.7. Although it is both reliable and easy to use, it does not have any devices that would allow the CSD to be influenced. It is basically an evaporator that is used as a crystallizer. Figure 51.8 shows a DTB crystallizer, which has become very popular over the years. Its useful features include the draft tube, which

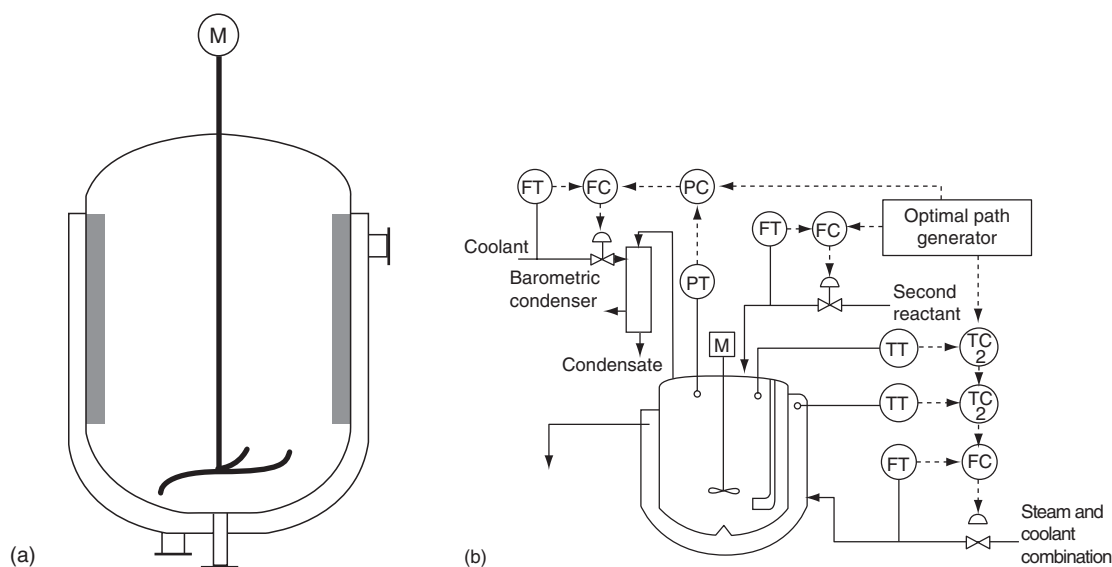


FIGURE 51.6 A schematic figure of a simple batch crystallizer (a) and one with a programmed-cooling system (b). (Reprinted from Mersmann, A., Ed., *Crystallization Technology Handbook*, Marcel Dekker, New York, 1995. With permission.)

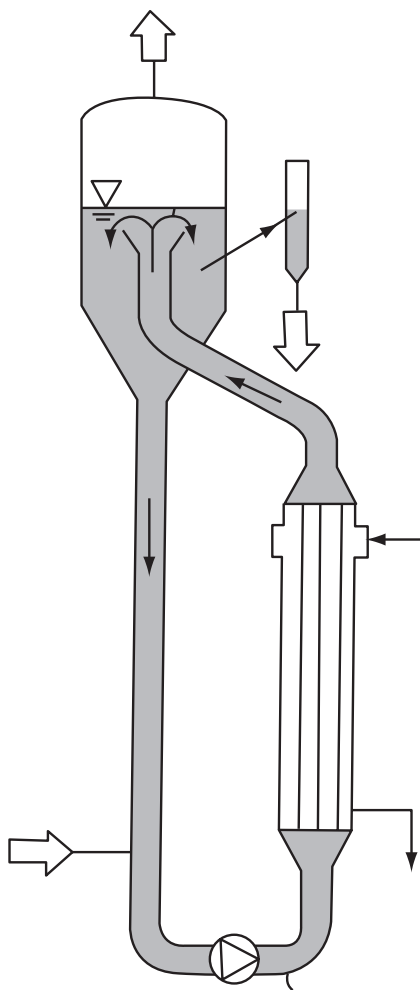


FIGURE 51.7 A forced-circulation (FC) crystallizer. (Reprinted from Mersmann, A., Ed., *Crystallization Technology Handbook*, Marcel Dekker, New York, 1995. With permission.)

improves circulation of the crystal magma, and a settling zone, which selects the small crystals to the circulation flow for partial destruction in the heat exchanger. In this way, the heat exchanger also functions as a fines dissolver, which helps to increase the mean crystal size in the product. The process of fines destruction was discussed earlier in [Section 51.2.5](#).

In the FB crystallizer ([Figure 51.9](#)), the heated mother liquor first goes to the evaporator section where supersaturation takes place. The supersaturated solution then directly enters into the fluid bed of product crystals where the desupersaturation occurs and the crystals grow. This equipment is known for its capacity to produce large crystals of a reasonably narrow CSD. Nevertheless, FB crystallizers are not as commonly used as would be expected on the basis of the advantages of the large product size. The disadvantage of FB crystallization is, for some

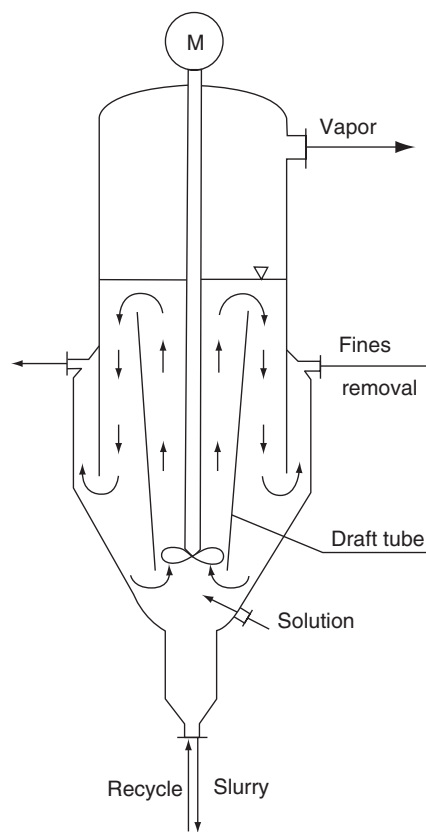


FIGURE 51.8 A draft-tube baffled (DTB) crystallizer. (Reprinted from Mersmann, A., Ed., *Crystallization Technology Handbook*, Marcel Dekker, New York, 1995. With permission.)

chemicals, the unreliability of its operation owing to the fact that unusually high crystal densities may develop in the fluid bed in the bottom end of the crystallizer tank because of which the slurry-withdrawal line tends to get blocked. Operational instability has been reported for some chemicals. When correctly operated with some chemicals, however, the FB crystallizer can produce large crystals of a narrow CSD.

[Table 51.2](#) shows some examples of operating data of large-scale crystallizers. Only some characteristic information of the more comprehensive data given by Mersmann [3] is presented here.

51.3.3 THE SELECTION OF A CRYSTALLIZER

To a certain extent, industrial crystallization is still more an art than science, which can be seen in the selection of a crystallizer. Often existing crystallization methods that have been previously proven successful for certain materials are used for these same materials in new plants, instead of new untried crystallizers. If exotic and unusual crystallization

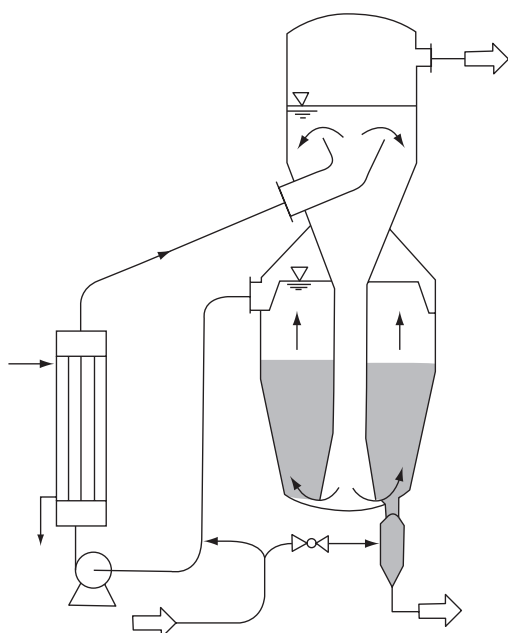


FIGURE 51.9 A fluidized-bed (FB) crystallizer (an “Oslo crystallizer”). (Reprinted from Mersmann, A., Ed., *Crystallization Technology Handbook*, Marcel Dekker, New York, 1995. With permission.)

processes are not taken into account, the thumb rule is that an agitated tank shown in Figure 51.6 is used in batch processes for the production of fine chemicals, whereas one of the types shown in Figure 51.7 through Figure 51.9 is normally selected for continuous processes.

51.4 FILTRATION OF CRYSTAL SUSPENSIONS

Suspension crystallization processes are the most common in industry. After crystallization, the crystalline product is usually separated from the solution

TABLE 51.2
Data of Continuous Industrial Suspension Crystallizers

	Citric Acid	KCl	Na ₂ SO ₄
Production rate (kg/h)	560	7200	10100
Residence time (s)	8380	8100	4040
Volume (m ³)	12	1050	2800
Medium size (mm)	0.41	1.1	0.30
Suspension density (kg/m ³)	132	15	151
Crystallizer type	FC	DTB	FC

Source: Mersmann, A., Ed., *Crystallization Technology Handbook*, Marcel Dekker, New York, 1995, p. 614.

by filtration. The separation of crystals from the mother liquor has an important influence on the whole process. The reader is referred to some basic handbooks on filtration, such as *Solid-Liquid Separation* as edited by Svarovsky [48] and those by Wakeman and Tarleton [49], and Rushton et al. [50].

For easy separation of crystals from a solution, it is important that the crystals are sufficiently large. This can be shown by the Kozeny–Carman equation derived for laminar flow through an incompressible bed of particles, which describes the pressure drop in the bed. The pressure drop relates inversely to the square of the quadratic particle size and directly to the dynamic viscosity of the fluid. The influence of the particle size and solution viscosity on the pressure required in filtration can be estimated as follows. If the viscosity increases tenfold, the pressure drop also increases tenfold. If, on the other hand, the particle diameter drops to 10% of its original value, the pressure drop increases by 100-fold.

However, there are cases when the mother liquor has a relatively high viscosity due to high concentration of dissolved solute, the filtration of crystals from the mother liquor may require higher pressures as the driving force. This occurs quite often in the sugar industry where solutions have a high dynamic viscosity up to 100 MPa (cP). In such cases, the pressure drop in the bed, as compared with water, is 100-fold.

For the above reasons, the aim of suspension crystallization is usually to produce sufficiently large crystals. However, for example, in some applications, such as in the pharmaceutical industry and the production of pigments, paper fillers, and paper-coating substances, crystals of rather small sizes are required. For this reason, the selection of the filter medium plays a key role in order to obtain a sufficient filtration capacity and as low a mother-liquor volume in the crystal cake as possible. Besides cake washing, the fouling of the filter medium is a factor that affects the filtration of small particles. The most commonly used filter media are made of synthetic fibres, such as nylon, polyester, polypropylene, polyethylene, or fluorocarbon [50]. In some fine particle applications, it has been observed that, by adjusting the pH level, it is possible to control the formation of agglomerates or aggregates on the basis of changes in the surface charge at the particle surface surrounded by a double layer. Prior to filtration, the pH level is adjusted in such a way that the solution attains its isoelectric point and the repulsive forces are at their minimum. After filtration, the pH level is adjusted in order for secondary particles to decompose. Flocculation agents and filter aids, such as diatomite and perlite, are commonly used to facilitate the filtration of

fine particles. This subject is discussed in detail in *Solid-Liquid Separation* [48].

The obtained CSD affects the required filtration time. Furthermore, it influences on the final moisture content of the filtered cake, which means with higher moisture content higher energy in thermal drying is required. The width of CSD and the crystal shape are important for the filterability of the crystalline product. If the product contains a lot of tiny crystals, filtration becomes more difficult due to increased specific surface of the crystal cake. Disk-shaped crystals decrease the permeability of the cake due to their high tortuosity and low void ratio. Furthermore, the elasticity of crystals, which is typical for organic compounds, may cause an increase in the compressibility of the crystal cake, thus decreasing the permeability of solid cake at higher filtration pressures.

Häkkinen et al. [51] investigated the filterability of sulfathiazole crystals obtained by crystallization from one-solvent and two-solvent solutions. Their results showed that the choice of the mother-liquor composition affected the obtained resistance of crystal cake. Lowering the cake resistance in a system usually decreases the moisture content of the cake that in turn facilitates the drying process. Organic compounds may also form amorphous solid particles that usually lead to low permeability of the solid bed due to the compression of the filter cake.

Crystal purity depends mainly on filtration efficiency and crystal washing. For instance, when the mother liquor contains high levels of impurities, the level of purity after filtration is affected by the moisture content of the crystal cake, i.e., the amount of mother liquor left in the crystal cake. The washing of the crystals may require high volumes of washing solution. The use of large volumes of washing solution does not dissolve sparingly soluble crystals, i.e., washing does not decrease the yield. Contrary to precipitates, when compounds that have a high level of solubility are used, washing may dissolve the crystals. If the impurity has a relatively low melting point, it can be partially melted by heating the crystal cake and then separating the impurity from the crystal cake by the force of gravity, an airflow, or with the use of a pressure chamber. This technique is called sweating.

One of the most commonly used solid-liquid separation methods in crystallization processes is centrifugal filtration, such as continuous pusher and batchwise peeler centrifuges shown schematically in [Figure 51.10](#). A manufacturer of centrifuges used in crystallization processes is KMPT AG [52]. In addition, Nutsche filters, frame pressure filters, and belt filters have also been used. Most of these filters have a possibility of cake washing which is important for the final purity as discussed earlier.

It may be difficult to choose the right filtration equipment for a crystallization process. The selection of filtration equipment involves balancing the process specifications and objectives with the capabilities and characteristics of the various equipment alternatives. Wakeman and Tarleton [49] provide guidelines for the selection of filtration equipment. Important process-related factors are the slurry character, production throughput, process conditions, performance requirements, and permitted construction materials. The important equipment-related factors are the type of cycle (batch or continuous), driving force, production rates of the largest and smallest units, separation sharpness, washing capability, dependability, feasible construction materials, and cost. No absolute selection techniques are available for obtaining the best choice, as so many factors are involved. Nevertheless, there are some general guidelines for the engineer who faces the selection of filtration equipment. Furthermore, a commercial software package, p^C-SELECT, based on expert systems is available for filter selection, developed by Wakeman and Tarleton [49]. The relative performance characteristics of different filtration equipment under vacuum and pressure are shown in [Table 51.3](#) with the solid concentrations of feed higher than 10 vol%. The crystal volume related to the total suspension volume in industrial crystallizers is frequently 20 vol%. In vacuum filtration, the maximum pressure difference over the cake is below 1 bar, whereas in pressure filtration the maximum driving force of conventional filters can be up to tens of bars. The indices are given for the dryness of the solid product, the effectiveness of solid washing, the quality of the liquid product, and the tendency of the equipment to cause crystal breakage. In addition, [Table 51.3](#) shows the basic feed properties that the equipment can generally handle. Once an initial selection of equipment has been made, the list of the equipment can be sensibly ranked using [Table 51.3](#). [Table 51.3](#) shows that centrifugal filtration results in the highest product dryness. On the other hand, average particle sizes are relatively large and the centrifuging may increase crystal attrition. Vacuum and pressure leaf filters give less-dry cakes than centrifuges, but leaf filters are gentler on the crystalline product and cake washing is more efficient.

51.5 CRYSTAL DRYING

Under otherwise similar drying conditions, the drying rate depends on the surface area of the wet crystals and the air used in drying. This means that small crystals dry quickly in airflow, such as that produced by a pneumatic dryer. Instead, the drying of a solid bed of

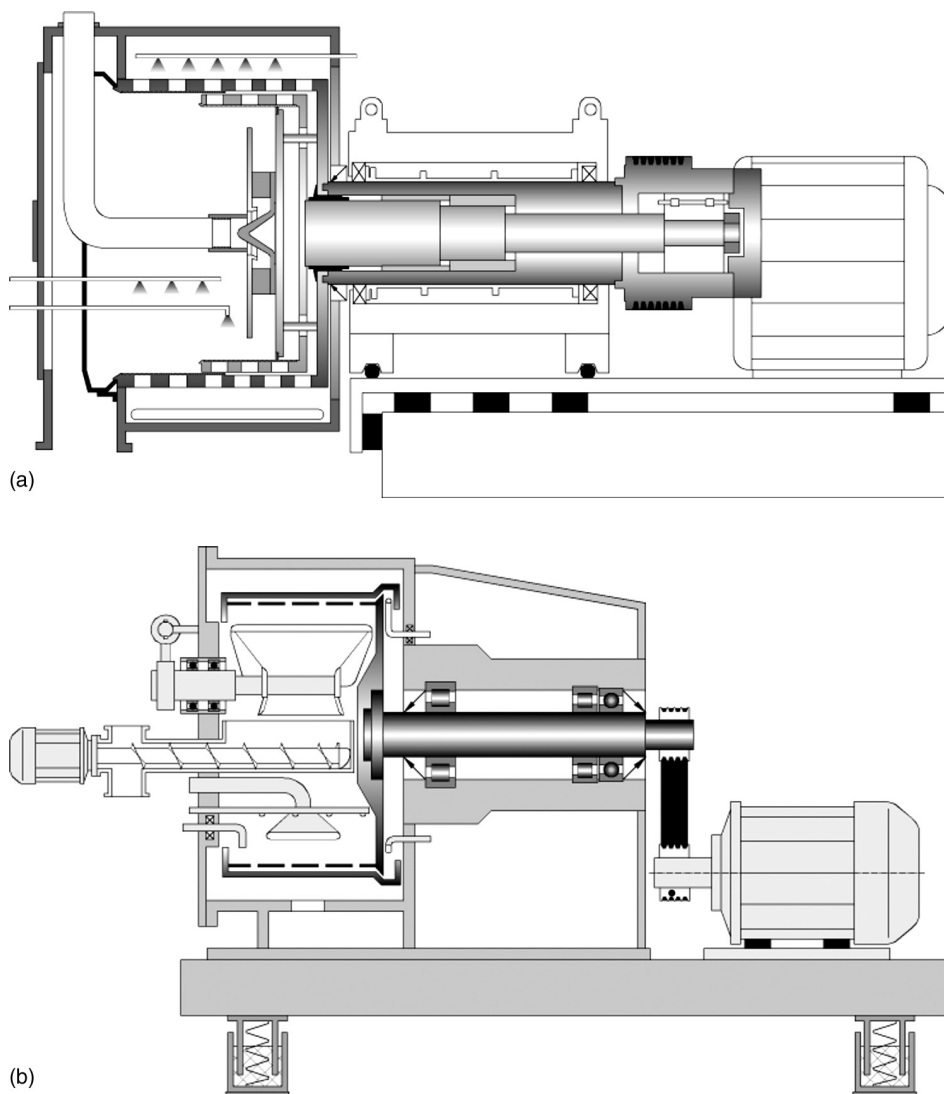


FIGURE 51.10 A pusher centrifuge (a) and a peeler centrifuge (b). (Reprinted from KMPT AG, Internet <http://www.kmpt.com>. With permission.)

crystals tends to be less satisfactory because of the long drying time required and due to agglomeration caused by the contact of the wet crystals. On the other hand, a bed of small crystals cannot be filtered easily but, instead, tends to block the filter. From the viewpoint of drying, it would be best that the crystals be large, within the range of about 1 mm or above. After the filtration stage, the amount of mother liquor in the crystals is low. The large crystal size also improves purity because the same thickness of the attached mother liquor on the surface, which contains impurities, results in a lower level of impurities in large crystals. If the mother liquor remains on the surface of the crystals, it solidifies, with the impurities that it contains, on the surface of the crystal. It should

be mentioned here that crystal sizes above approximately 1 mm tend to be harmful. For crystals larger than 1 mm, it may be difficult to maintain the steady state in a continuous process, due to the decreased overall crystal surface required for releasing supersaturation. Furthermore, large crystals may break in the centrifuge.

The aim of the earlier discussion was to explain how crystals of a desired size could be produced. Furthermore, the CSD should be as narrow as possible for easy drying. In principle, the drying of crystals can be carried out in the same way as that of any particulate material. However, there are some cases when the crystalline structure itself poses problems in drying. We will briefly discuss these cases.

TABLE 51.3
Relative Performance Characteristics of Different Filtration Equipments

Types of Equipment	Performance Indices				Feed Solid Properties	
	Solid Product Dryness	Washing	Liquid Product Quality	Crystal Breakage	Particle Size (µm)	Solids in Feed (vol%)
<i>Filtering centrifuges</i>						
Basket (pendulum)	9	6	5	6	10–1,000	2–10
Basket (peeler)	9	6	5	5	2–1,000	2–30
Cone screen (slip discharge)	7	5	4	4	80–10,000	10–40
Cone screen (vibrating, oscillating, or tumbling)	8	5	4	3	100–10,000	10–40
Cone screen (worm screen)	9	5	4	4	60–5,000	10–40
Pusher (single-stage)	9	7	4	4	40–7,000	4–40
Pusher (multistage)	9	8	4	4	40–7,000	4–40
Baffle	9	5	5	4	100–7,000	4–40
<i>Vacuum filters</i>						
Single leaf (tilting pan)	7	9	7	8	20–80,000	3–40
Multielement leaf	5	5	7	8	1–100	3–30
Horizontal belt or rotary tilting pan	7	9	7	8	20–80,000	3–40
Rotary table	7	8	7	8	20–80,000	3–40
Rotary drum (bottom fed)						
-Knife discharge	6	7	7	8	1–200	3–30
-Roller discharge	6	7	7	8	1–50	3–30
-String discharge	6	7	7	8	1–70	3–30
Rotary drum (top fed)	5	2	7	8	1–600	3–30
Rotary drum (internal fed)	5	—	7	8	10–600	3–30
Rotary disk (cloth covered)	4	—	6	8	1–700	3–30
Rotary disk (ceramic)	4	—	9	8	1–700	3–30
<i>Pressure filters and Presses</i>						
Single leaf (pressure Nutsche)	6	8	8	8	1–200	0.005–30
Filter press	6	8	8	8	1–100	0.005–30
<i>Variable volume pressure filters and presses</i>						
Diaphragm filter press	8	8	8	7	1–200	0.1–25
Tube press	8	4	7	7	1–200	0.1–25
Expression press	6	—	6	5	1–200	5–50
<i>Continuous pressure filters</i>						
Belt press	8	7	7	7	1–200	0.1–25
Vertical filter press	6	6	7	7	1–100	0.01–30
Vertical diaphragm filter press	8	8	8	7	1–200	0.1–25
Tower press	6	—	7	7	1–300	0.1–25
Rotary pressure drum	6	6	7	7	1–100	3–30
Rotary pressure disk (cloth covered)	5	—	6	8	1–100	3–30
Rotary pressure disk (ceramic)	7	—	9	8	1–100	3–30

Allocation 0 to 9 with larger numbers indicating better performance, A “—” performance indicates either equipment is not effective or not suitable for a particular duty.

Source: Wakeman, R.J. and Tarleton, E.S., *Filtration, Equipment Selection, Modelling and Process Simulation*, Elsevier Science, Kidlington, U.K., 1999.

Most crystals are so soft that the corners of the crystalline particles tend to get rounded if collisions occur between the crystals during drying and, as a result, the quality of the product suffers. In addition, dust may be a problem. For example, a traditional rotary

dryer is not suitable for most crystals. Surprisingly, both fluid-bed dryers and pneumatic dryers are relatively gentle, perhaps, because of the shorter residence time.

Then, there is the problem of crystal water. These are often salt hydrates, i.e., inorganic crystals with

different numbers of water molecules attached to each molecule of the basic molecule. Drying may remove crystal water, which leads to quality problems in the product. Furthermore, crystallization at high temperatures may cause the agglomeration and solidification of the product during storage.

51.6 NEW ADVANCES

To conclude the present review, we will mention some trends in the research and development into the technology that may be of importance in the present context in the future. Due to constraints of space, we have to omit most of the important works presently being carried out on various aspects of crystallization, and will only mention those works that may lead to a particle size distribution and particle shapes which facilitate the filtration and drying stages in the process.

The traditional study of suspension crystallization has been carried out using the MSMPR crystallization model. It has been found that uniform mixing in a commercial-size crystallizer, as required by the MSMPR model, is impossible to achieve. Therefore, the understanding of industrial crystallization is hampered by the use of the MSMPR model. Also, it is difficult to experimentally study the effects of mixing on crystallization, as described earlier in Section 51.2.5. Therefore, the CFD presents the means for local simulation in the tank. Furthermore, CFD simulation enables the tank to be designed so that the shape and the positioning of the impellers and the liquid velocity create the optimal level of supersaturation and mass transfer rate in all locations. This is likely to result in a narrowing of the particle size distribution.

Then, there is work with the objective of altering the particle shape, usually from a plate- or needlelike shape into a more rounded shape such as that of a cube or octahedron. The starting point here is the concept of polymorphism discussed earlier in Section 51.1.5. A material may have different crystal structures, and it is useful to find ways of generating the ideal structure. One way to do this is to use different solvents, as mentioned by Davey and Garside [6]. They also discuss the new and promising field of tailor-made additives, which alter the crystal shape during the growth process. In addition, Finnie et al. [53] reported that the level of supersaturation selected different polymorphs for growth, i.e., the level of supersaturation can be used to control the crystal shape. This idea was taken further by Ma and Braatz [54] who showed

that different cooling profiles in batch crystallization, discussed earlier in Section 51.2.1, produced different crystal shapes. Although the above are early results, they, however, show that there may be ways to control the crystallization processes in order to achieve the most desirable product shapes.

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NOMENCLATURE

B	nucleation rate per unit volume, $1/(s\ m^3)$
c	concentration, mol/m^3
G	crystal growth rate, m/s
K	parameter, $K = (1 + 4N_s/B\tau)^{-1}$, ranging from 0 (no nucleation) to 1 (unseeded batch), dimensionless
k_n	kinetic empirical constant, different units interchangeably
L	crystal size, m
M_T	suspension density, kg/m^3
n	population density, number of crystals in a unit volume at each size class, $1/\text{m}^4$
N_s	number of seed crystals per unit volume of solvent, $1/\text{m}^3$
S	supersaturation ratio, dimensionless
t	time, s
\dot{V}	flow rate, m^3/s

Greek Symbols

β	fraction of nuclei that survive in the fines-destruction system, dimensionless
σ	relative supersaturation, dimensionless
τ	overall batch time, residence time, s

Subscripts

*	equilibrium, saturated
0	beginning, feed
1	without fines destruction
2	with fines destruction
50	cumulative mass undersize of 0.5
c	clear-liquor advance
d	dominant
f	final, fines
p	product

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