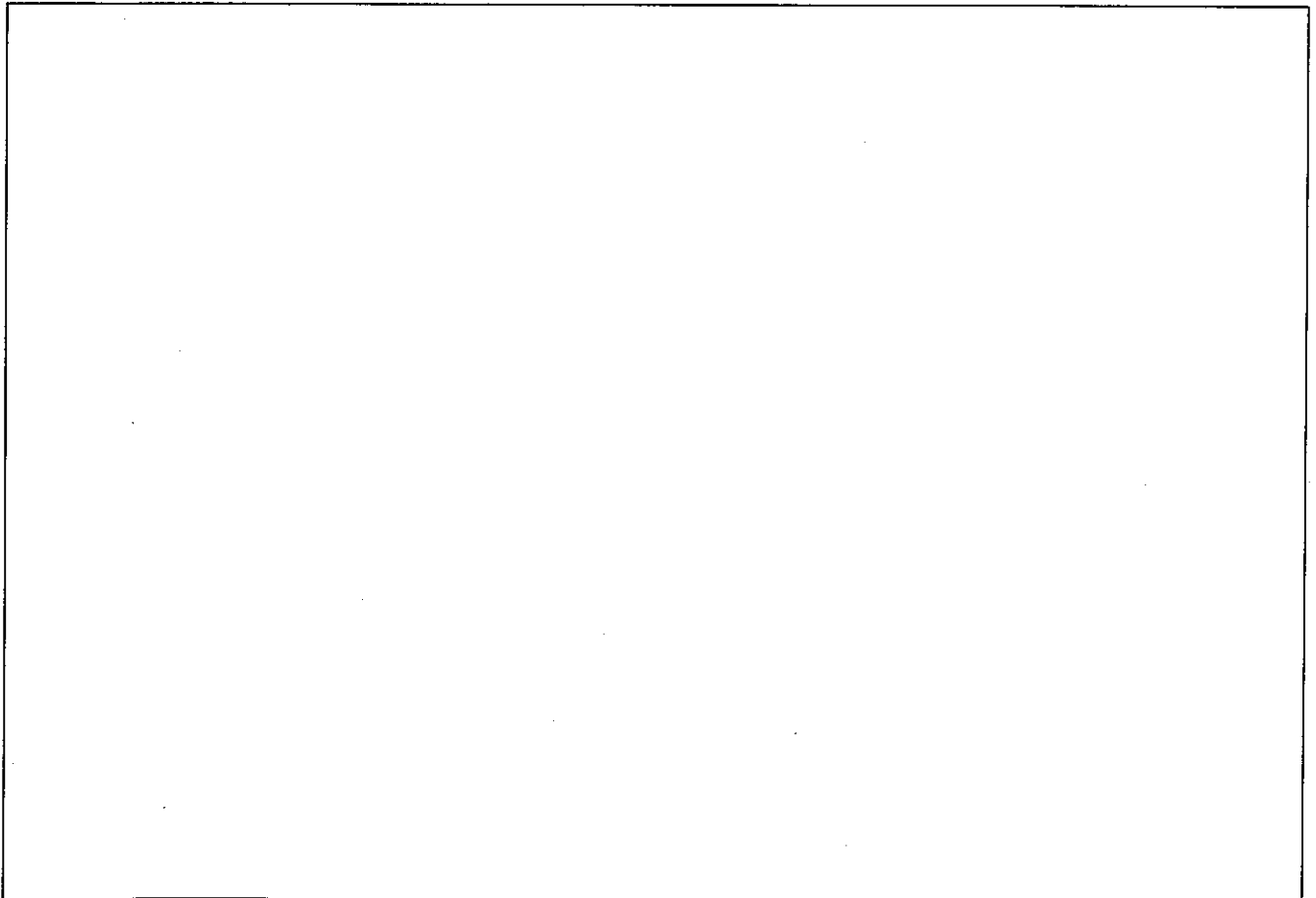


Types of Crystallizers

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Types of crystallizers

Requirements with respect to the quality of the crystallize in industrial crystallization are ordinarily well defined, and a clear choice between various types of crystallizers can be made in order to satisfy these requirements. The present state of the art includes magma types (e.g., agitated-tank crystallizers, forced-circulation and draft-tube-baffle crystallizers) as well as classifying types (e.g., the Oslo crystallizer). The rates of secondary nucleation decrease in the order given above, and the possibilities of influencing the crystal-size distributions increase, making possible the production of coarser crystals.

1. Introduction

Crystallization is one of the oldest unit operations known to mankind. Since the beginning of civilization, cooking salt has been produced by the evaporation of sea water. Even today solar evaporation is still customary in regions with plentiful sunshine. Here, the advantages are the very simple technology and a cost-free supply of energy. On the other hand, a very large surface area is needed, as well as considerable manual labor. The rates of production per unit surface area fall in the range of 3 to 10 g/m²·hr. The purity of the product which can be attained in the production of salt in solar pans is also limited. In the case of salt from a solar brine, the product always consists of aggregates of single crystals which have grown together, this leading to inclusions of mother liquor and higher residual moisture, and thereby higher levels of impurity. Untreated salt from

solar pans can be obtained with purities up to about 98%.

In modern equipment for crystallization, on the other hand, cooking salt can be produced with purities of about 99.9% and with almost any desired crystal-size distribution and crystal form. The specific rate of production in technical crystallizers is several thousand times larger than in solar pans.

The rise of the modern chemical industry and the increasing requirements for the quality and quantity of crystalline products were the triggers for the development of industrial crystallizers.

Today a whole range of crystallizer types is available. The choice of a special type depends significantly on:

- the crystal-size distribution required;
- the physical and other properties of the feed solution and the crystallize;
- the process of crystallization which is selected.

2. Discontinuous crystallizers

Batch crystallizers are used particularly (though by no means exclusively) for small throughputs, the crystallization of sugar being a classic exception. Even today, the largest quantities of sugar are still produced by batch processing.

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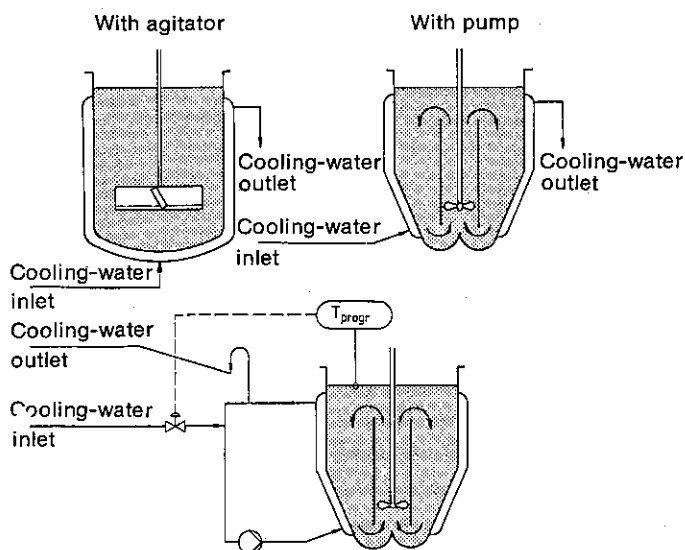


Fig. 1. Batch cooling crystallizers. T_{prog} = program-controlled temperature.

Typical forms of batch crystallizers are shown in Figure 1. The mixing time and the suspension of the crystallize impose special requirements for the design of those types with agitators [1], but draft-tube crystallizers are simpler to design. With the controlled recirculation of the latter case, certain flow patterns over all of the zones of the crystallizer are maintained. The calculation of the heat transfer coefficients is simplified, and the level of supersaturation can be controlled. In crystallizers of the types shown at the top of Figure 1 the cooling water is fed directly to the cooling surfaces. When the cooling water flow is held constant, a drastic temperature drop in the contents of the crystallizer occurs at the beginning. The arrangement in the lower part of Figure 1 is characterized by the temperature-controlled feed of new cooling water into a circulating flow.

The crystallization of adipic acid can be used to illustrate the effect of these different modes of operation on the operating results. The solubility of adipic acid is highly temperature-dependent (Figure 2). In the upper range of temperatures, a small cooling step causes a large difference in concentration. If a saturated solution at 80 °C is cooled with a constant rate of flow of cooling water, a cooling curve such as that shown by the dashed line in Figure 3 is obtained. The rate of cooling is then largest at the beginning because of the large temperature difference, while toward the end of the process the rate of cooling falls off markedly.

The kinetics of crystallization imply that large supersaturations are produced very rapidly at the beginning of the batch, and that these super-

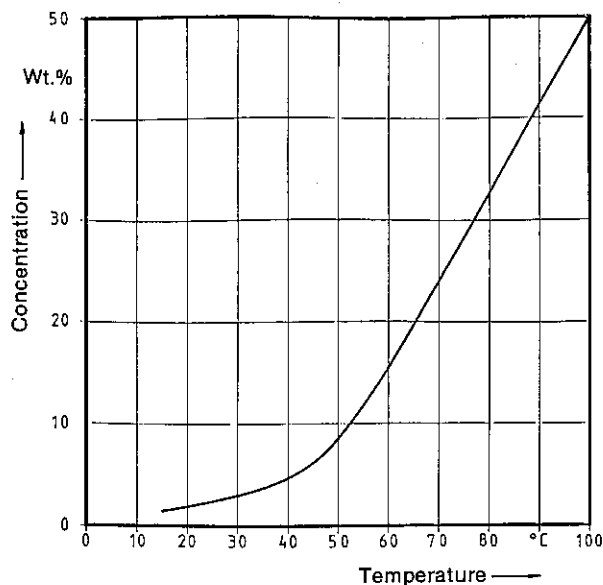


Fig. 2. Solubility of adipic acid in water.

saturations cannot be relieved rapidly by crystal growth because the active, crystal-surface area is still insufficient. The metastable zone is greatly exceeded, and numerous primary nuclei result. On the other hand, toward the end of the process the rate of cooling, and hence the degree of supersaturation, are much smaller than for the prevailing metastable conditions.

To optimize the operating conditions, the rate of cooling must be controlled differently. The correct manner of operation is achieved when the value of the supersaturation at all times during the batch crystallization is maintained at a value below the

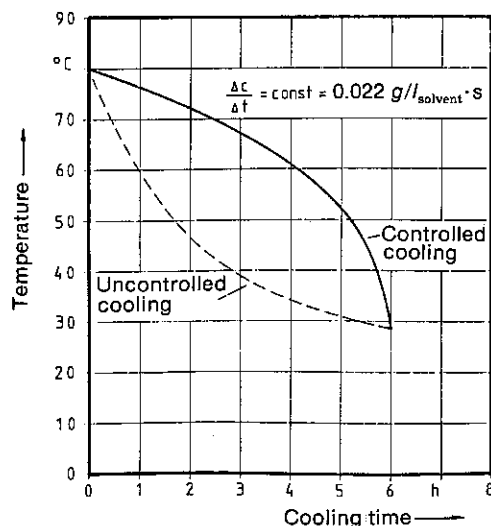


Fig. 3. Temperature profiles in batch, surface-cooling crystallization. $\Delta c/\Delta t$ = supersaturation ratio.

limit of metastable supersaturation. This is the case with the cooling function shown by the solid line in Figure 3. The slow cooling at the beginning is particularly important; the more time taken at the beginning to exceed the metastable limit, the less primary nucleation. Figure 4 shows the paths of the supersaturation ratios $\Delta c/\Delta t$ for controlled and uncontrolled cooling. Operation with uncontrolled cooling results in much too high a supersaturation in the critical start-up phase, and later much too low a supersaturation. The program-controlled cooling, shown in Figure 1, maintains the supersaturation constant over the entire period of time.

3. Continuous crystallizers

3.1. Magma-type crystallizers

By changing to a continuous mode of operation the following features are achieved:

- an increase in the space-time yield;
- a reduction in the requirements for manpower
- a more uniform quality of product

If the rates of production are large enough, continuous crystallizers are usually used. The lower limit for their rational introduction lies between 80 and 400 kg/hr of crystallizate.

Several basic types of continuous crystallizers can be distinguished. These classes typically are characterized by the crystal-size distributions which can be achieved. Increasing demands on the quality of the crystals are making crystallizers more expensive. A multiplicity of crystallizer types can be used for the different processes: cooling crystallization, vacuum-cooling crystallization, evaporation crystallization, and reaction crystal-

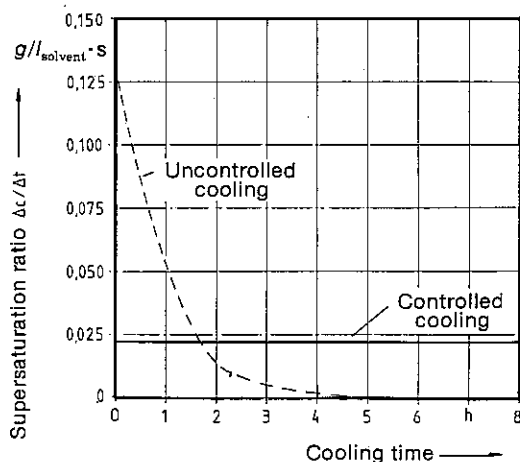


Fig. 4. Supersaturation profiles in batch, surface-cooling crystallization.

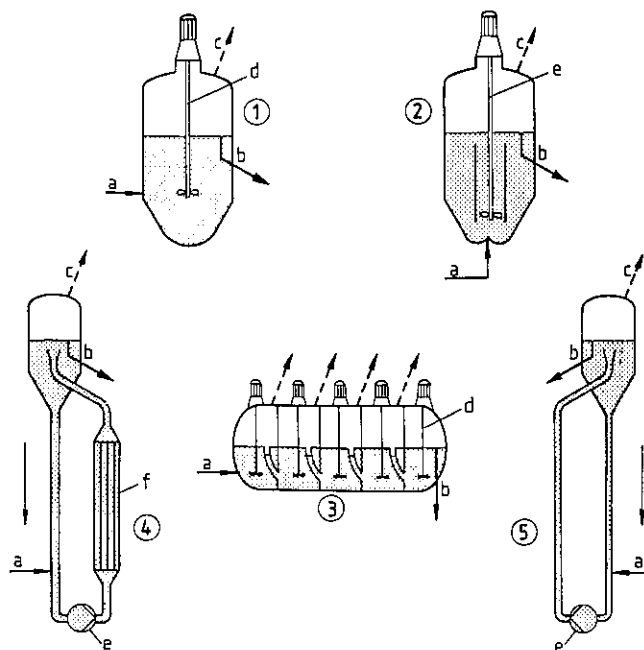


Fig. 5. Magma crystallizers without removal of clarified solution (MSMPR). 1 Agitated-tank crystallizer; 2 Draft-tube crystallizer; 3 Horizontal crystallizer; 4 and 5 Forced-circulation crystallizers; a Solution feed; b Suspension; c Flash vapor; d Agitator; e Recirculating pump; f Heat exchanger.

lization.

Figure 5 shows the simplest types of agitated-tank, draft-tube, and forced-circulation crystallizers. The suspension of crystals is moved by agitators or pumps, and supersaturation is generated within the suspension. The stirred-tank crystallizer (1) is selected for vacuum-cooling crystallization if the crystallizate grows well and has a sufficiently wide metastable zone. Several demands are imposed on the agitator, including suspension of the crystals as homogeneously as possible in the crystallizer and intermixing the feed solution as rapidly as possible. The shear forces which are dissipated from the agitator to the crystals are relatively large, and hence the rate of secondary nucleation is correspondingly high.

The horizontal crystallizer (3), which is used exclusively for vacuum-cooling crystallization, is characterized by several series-connected stages in a single shell. Compared to the single-stage, vertical, agitated-tank crystallizer, a horizontal crystallizer of this type has several advantages:

- (1) Subdividing the total cooling into several stages results in smaller stages. The suspensions can therefore be kept homogeneously mixed with a significantly smaller consumption of energy.
- (2) The mechanical stressing of the crystallizate

is smaller, and larger crystals can be achieved. For some products the homogenization can be carried out by air agitation, which is less likely to damage the particles.

(3) The investment costs for multistage horizontal crystallizers are significantly lower than for the same number of vertical agitated-tank crystallizers.

The draft-tube crystallizer (2) operates with a circulating pump instead of an agitator, and therefore produces a controlled circulation. In contrast to the agitated-tank crystallizer, direct adjustment of the supersaturation is possible. The primary nucleation which arises from exceeding the metastable limit can therefore be prevented more positively. This type is used for crystallizates which grow less rapidly and have smaller metastable zones, and, in the form shown, is used exclusively for vacuum-cooling crystallization.

The forced-circulation crystallizer (4) is comparable in function to the draft-tube crystallizer, but is used preferentially for evaporation-crystallization and surface-cooling crystallization. The controlled conveying of the suspension is carried out by means of an axial pump through an external heat exchanger. This type of crystallizer can also be used for vacuum-cooling crystallization (5). The resulting products are comparable with those from a draft-tube crystallizer when the critical, pump-design data are similar.

With these magma crystallizers, the density of the suspension is fixed directly by the mass flux. Higher densities (e.g., for extending the residence time of the crystals) can be achieved only if clarified solution is removed from the crystallizer as well as from the suspension. Such possibilities

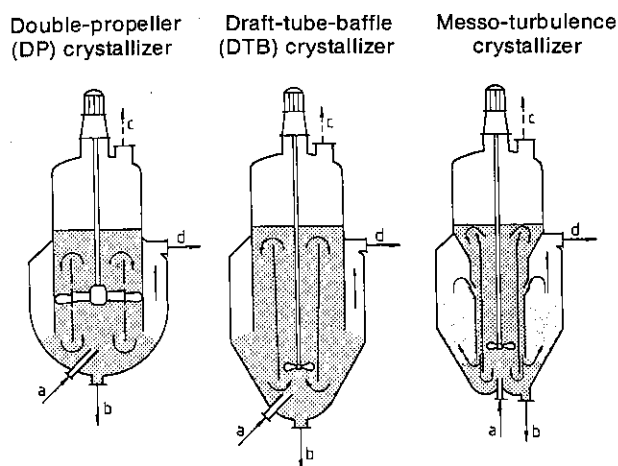


Fig. 6. Magma crystallizers with removal of clarified solution. a Solution feed; b Suspension; c Flash vapor; d Withdrawal of clarified solution.

for the removal of clear mother liquor have been developed in draft-tube crystallizers with clarifying zones (Figure 6). As a result, the residence times of the crystals and solution can be adjusted independently, so that greatly increased residence times for the crystals can be realized, even with economical volumes for the crystallizer. The separation of the crystal slurry and the mother liquor is carried out by sedimentation. Depending on the up-flow velocity selected in the clarifying zone and the particle-size distribution of the suspended crystallizate, the clarified liquor (d) always contains residual quantities of the finest crystals. Although their mass may be completely negligible, the number of very fine crystals removed in this way often exceeds the number of crystals in the extracted stream of suspension (b) [2]. The achievable crystal size, as well as the suspension density, can then be influenced positively by the withdrawal of the liquor. In evaporation-crystallization the withdrawal of the clear liquor is used to supply heat to the system. The solution, after being heated, flows back into the crystallizer (a).

The circulating pumps produce a controlled recirculation of the liquid, as in the types discussed previously, so that an exact adjustment of the supersaturation is possible. They can be designed to provide a specially gentle treatment of the crystallizate. This is achieved by using larger impeller diameters and, hence, lower circumferential velocities.

In the DP-crystallizer [3] the pump impeller is

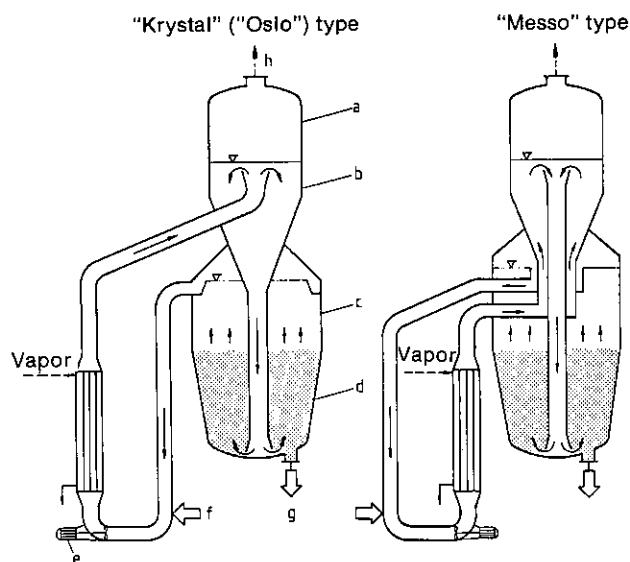


Fig. 7. Fluidized bed crystallizers (CSCPR). a Evaporation space; b Liquid space; c Sedimentation zone; d Fluidized bed; e Recirculating pump; f Solution feed; g Removal of the crystal suspension; h Flash vapor.

subdivided into inner (upwards conveying) and outer (downwards conveying) rotor blades. The outer and inner impeller parts of the pump each produce the same rate of flow. The total pressure drop of the system is divided between the two halves of the impeller, as a result of which lower peripheral velocities are achieved for the impeller.

In the Messo-Turbulence-Crystallizer (Figure 6) the coarser crystallizate, which is particularly sensitive to attrition, collects below the clear zone in a fluidized bed by means of the installation of a secondary circulation loop (see outer central tube with the ejector nozzle). The elimination of the circulating pump avoids disturbance of further growth of these coarser crystals until they are extracted at the point of removal (b). The classification caused by this fluidized bed (only crystallizate of the desired crystal size is removed) can also be achieved in DP- and DTB-crystallizers by the additional installation of a leg for elutriation.

The gentle conveying of the suspension, the removal of the fine crystals, and the separate removal of clarified liquor, as well as the classifying effect, allow the production of medium-coarse to coarse crystallizates. Thus, products such as ammonium sulfate, potassium chloride, or urea are made in this type of crystallizer, with average particle sizes of about 1.5 mm.

3.2. Fluidized bed crystallizers

Still coarser crystallizates can only be produced by another type of crystallizer. To a great extent, crystal size is a function of the rate of nucleation. In industrial crystallizers more than 90% of newly formed particles are the result of secondary nucleation. This secondary nucleation, in turn, is determined by the impact energy dissipated by the circulation pump or the agitating impeller. To achieve larger crystals than are attainable in magma-type crystallizers, the circulation pump for the suspension must be removed. This leads to crystallizers (Figure 7) in which the suspension is carried out in a fluidized bed. All of the crystals present in the crystallizer, except the very fines, are present in this fluidized bed. The recirculated solution is freed of crystallizate by sedimentation, so that only substantially crystal-free solution passes the circulating pump. Thus, secondary nucleation and mechanical attrition from this source disappear.

At present, two forms of this crystallizer type exist. The crystallizers known by the name "Krystal" or "Oslo" are an older design which is not without problems in operating behavior. In the

production of sodium chloride, e.g., encrustations have reached such a thickness in only three days that they exceed their adhesion force to the walls, fall down and block the annulus to the fluidized bed. As a direct consequence, the fluidized bed collapses irreversibly, and the crystallizer must be emptied, washed out, and put back into operation.

The more recent type [4] was developed especially for the crystallization of substances prone to form encrustations, and does not have these problems of the older type. By reversing the flow in the evaporation section, the solution which has been superheated by the heat exchanger (and which is therefore undersaturated) is passed over the cone of the evaporator before the evaporation occurs on reaching the solution surface and supersaturation sets in. The formation of encrustations on the wall surfaces of the evaporation section is thus avoided, and undisturbed operating times of many weeks can be achieved.

The Oslo principle makes possible the continuous production of particularly coarse and uniform crystallizates. Mean particle sizes of some millimeters with few over- or under-sized particles can be reliably attained with this design. Such operating results naturally influence the investment costs.

Figure 8 shows the specific rates of production of Oslo-type crystallizers. These are governed by the sinking velocities of the smallest crystals to be separated in the clarifying zone (i.e., by the upflow velocity of the solution to be circulated by pumping) and by the permissible supersaturation. The larger the permissible (metastable) supersatura-

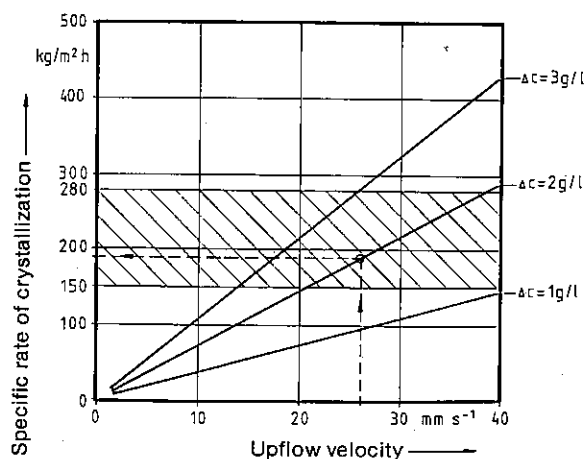


Fig. 8. Specific rates of crystallization in fluidized-bed crystallizers. Example KCl: a specific rate of crystallization of an Oslo crystallizer of 190 kg/m²·hr leads to a crystal diameter of $d' \approx 2$ mm; in a turbulence crystallizer with 500 kg/m²·hr, $d' \approx 1$ mm.

tion and the larger the sinking velocity of the particles to be separated, the greater becomes the specific rate of production of crystallizate. The usual rates for Oslo crystallizers lie between 150 and 280 kg/m²·hr. Below 150 kg/m²·hr the crystallizer becomes uneconomically large. The upper limit of 280 kg/m²·hr is usually fixed by the physical properties of the materials.

These specific rates of crystallizate produce large diameters in Oslo crystallizers. For example, for the production of 10 tons of KCl per hour, a diameter of 8.4 m is needed for an Oslo crystallizer using a specific rate of crystallizate of 190 kg/m²·hr; for a magma crystallizer (with removal of clarified solution), a diameter of only 5 m is required, based on a rate of 500 kg/m²·hr. The application of an Oslo crystallizer is therefore only to be considered when the higher investment costs can be balanced by a higher market for the coarser product.

4. Main design aspects

A controlled recirculation is a common feature in all continuous crystallizers (except the agitated-tank crystallizer). This controlled conveying of the suspension has to satisfy two requirements in industrial crystallizers:

- (1) to suspend the crystals;
- (2) to create a preselected level of supersaturation.

In industrial crystallizers the rate of recirculation is governed exclusively by the boundary conditions for the crystallization kinetics. It is always larger than that strictly necessary to satisfy the criterion of suspension [1]. Even in a small industrial crystallizer (for illustration, a 5-m³ draft-tube crystallizer is shown in Figure 9) the fluid velocities and Reynolds numbers for a suitable construction of the crystallizer bottom lie far above the critical values.

As sketched in Figure 10, controlled conveying produces a cyclic pattern of supersaturation. The highest supersaturation occurs at the location where supersaturation is produced. In the example of Figure 10, this is the evaporation surface in a vacuum-cooling crystallizer (point 1). The supersaturation which is produced is then relieved in the suspended crystallizate according to an exponential relationship:

$$\frac{d(\Delta c)}{dt} = -k_g A \Delta c^m \quad (1)$$

Here, $d(\Delta c)/dt$ denotes the removal of supersatura-

tion per unit time; k_g is the proportionality constant for crystal growth; A is the surface area of the crystallizate; Δc is the supersaturation; and m is the supersaturation exponent of the crystal growth.

The level of supersaturation decreases steadily during a recirculation cycle. The smallest supersaturation in a recirculation cycle occurs shortly before the liquid surface is reached again. Point 2 in the diagram shows the residual supersaturation which remains at this location. The larger the rate of recirculation at a given production rate of crystals, the more the supersaturation produced at the liquid surface distributed over a larger quantity of the solution, and, hence, the lower the degree of supersaturation. The level of the supersaturation Δc generated afresh per recirculation cycle is therefore given by the ratio of the rate of production \dot{P} of the crystallizer and the rate of recirculation \dot{V} :

$$\Delta c = \dot{P}/\dot{V} \quad (2)$$

The addition of the residual supersaturation to this supersaturation gives the maximum supersaturation occurring in the crystallizer. This quantity must be smaller than the value at the boundary of the metastable zone.

For practical purposes of design, the size of the metastable zone (Δc_{met}) of the solution being dealt with is determined experimentally, and about one half of this value is used in calculating, to a first approximation, the rate of recirculation in the crystallizer:

$$\Delta c = 0.5 \Delta c_{met}, \quad \dot{V} = \dot{P}/(0.5 \Delta c_{met}). \quad (3), (4)$$

In this way, the possibility of the metastable limit being exceeded and, hence, of primary nucleation occurring are safely excluded, as long as:

- the density of the suspension is sufficiently high;
- the cycle time is long enough, *i.e.*, the residual supersaturation is small.

With primary nucleation prevented, secondary nucleation becomes the deciding parameter for the design of industrial crystallizers. The main cause of secondary nucleation in a magma crystallizer is the circulating pump. Recent research results have established the frequency of secondary nucleation B° as a function of the pumping power ϵ dissipated per unit mass [5,6]:

$$B^\circ \sim \epsilon^r m_T^l G^l, \quad (5)$$

which leads to the mean particle size

$$\bar{x} \sim \epsilon^{-x} m_T^y \tau^z \quad (6)$$

Here, B° denotes the rate of nucleation, \bar{x} the mean particle size, m_T the crystallize mass per unit volume, G the linear rate of growth, and τ the residence time: r, l, i, x, y and z are experimentally determined exponents. The smaller the input of energy, the larger the crystallization size which can be achieved. With $\epsilon = \text{constant}$, some system-specific crystal-size distribution can be ascribed to each system. However, depending on the design of the recirculating pump for a given specific input of energy, the rate of recirculation \dot{V} (governed by the permissible supersaturation, Equation (4)) and the delivery head H (governed by the pressure drop of the system) are fixed. Hence, the energy requirement N for the recirculating pump and the specific input of energy ϵ are also fixed:

$$N = \frac{\dot{V} \rho g H}{\eta}, \quad \epsilon = \frac{\dot{V} \rho g H}{\eta} \frac{1}{V_{\text{cryst}} Q} \quad (7), (8)$$

Here, ρ denotes the density of the suspension or solution, g the acceleration due to gravity, H the delivery head, η the efficiency, and V_{cryst} the filled volume of the crystallizer. In designing the recirculating pump, the impeller diameter D and the number of revolutions n of the impeller per unit

time can be varied at constant power N :

$$N \sim n^3 D^5 \quad \text{or} \quad \epsilon \sim n^3 D^5 \frac{1}{V_{\text{cryst}} \rho} \quad (9), (10)$$

As a result, the peripheral velocity and, hence, the secondary rate of nucleation B° can be altered at a constant rate of dissipated energy ϵ . Industrial-scale experience indicates that

$$\dot{V} = \text{const} \rightarrow \epsilon = \text{const} \begin{cases} n_{\text{large}} D_{\text{small}} - B_{\text{high}} - \bar{x}_{\text{small}} \\ n_{\text{small}} D_{\text{large}} - B_{\text{small}} - \bar{x}_{\text{large}} \end{cases}$$

“Pumps” with larger impeller diameters (*i.e.*, lower peripheral velocities and lower secondary nucleation) are used in draft-tube crystallizers when a coarse crystallize is to be produced.

5. Summary

The design concepts herein allow the crystal-size distribution in batch crystallizers to be controllable and reproducible. For higher rates of production, continuously operated crystallizers are usually applied. Crystals up to about 1.5 mm can be produced in magma-type crystallizers, while bigger crystals require fluidized-bed (Oslo-type) crystallizers.

In the design of magma-type crystallizers special attention must be paid to the design of the circulating pump. The selection of an adequate pump size helps to reduce the secondary rate of nucleation.

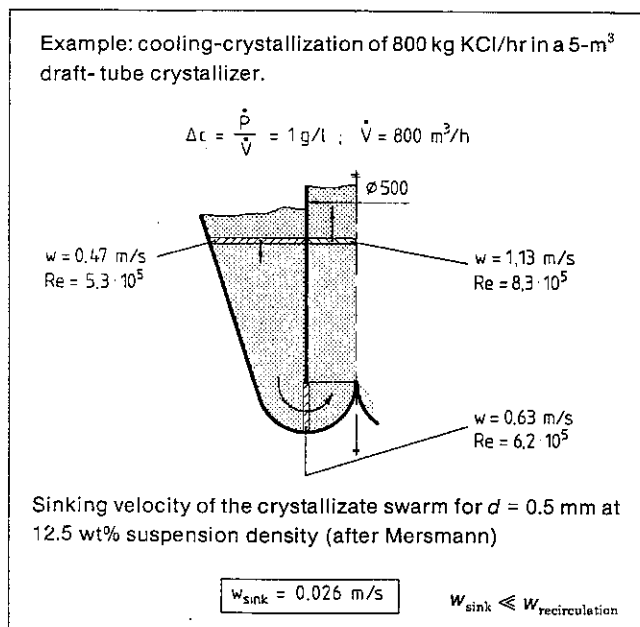


Fig. 9. Velocity distributions at the bottom of a crystallizer.

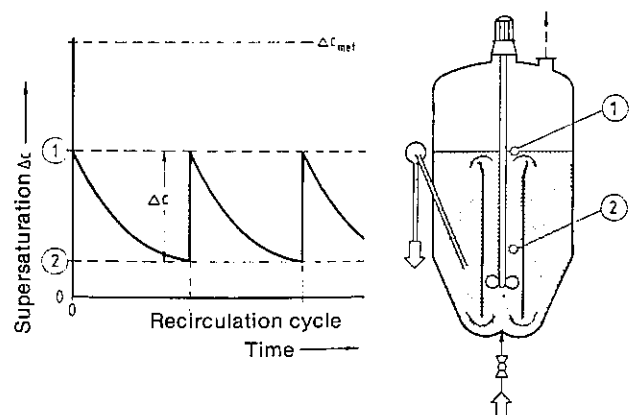


Fig. 10. Supersaturation cycles in an industrial crystallizer.

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