Scaleup Experiments on Seeded Batch Cooling Crystallization of Potassium Alum

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Potassium alum was crystallized by natural cooling in two well-mixed laboratory-scale (12.2 L) and pilot-scale (600 L) crystallizers. When unimodal product crystals of grown seeds were used, no scaleup effect on product crystal-size distribution (CSD) was observed if enough seeds were loaded over a critical seed concentration. Cooling rate, crystal yield (crystal suspension density), and stirring condition do not seriously affect the product CSD under such a seeding condition. Low supersaturation peak caused by the growth of enough seeds, the short period of nucleation, and the agglomeration of nuclei to the growing seed crystals are considered to be mechanisms working to produce unimodal product crystals of grown seeds. Simple design calculations are demonstrated to determine the amount of seed with the help of a critical seed concentration, which can be determined easily from laboratory-scale experiments. Crystallizer volume was calculated simply from a mass balance.

Introduction

Batch cooling crystallization is widely used in the production of fine chemicals or pharmaceuticals. For purposes of purification or separation, large-size product crystals of monodispersed or unimodal distribution are wanted to improve downstream processing efficiency and total separation economics. For the purpose of production of crystalline particles, the size of product should be controlled as desired. Two methods have been developed so far for optimal batch cooling crystallization: controlled cooling method and fines destruction technique.

The controlled cooling method was first proposed by Mullin and Nyvlt (1971) as a cooling mode so as to keep the supersaturation during cooling at a low level within the so-called metastable zone. This method seems to come from an idea of Griffiths (1925) that seeding effect does not work effectively unless cooling rate is controlled to be low. In this cooling mode, no small crystals (nuclei) are assumed to be generated by secondary nucleation mechanisms. Further, Jones and Mullin (1974) and Jones (1974) suggested a systematic approach to calculate theoretical cooling curves by considering nucleation effects. However, generation of nuclei could not be avoided completely. The other method, the fines destruction technique, is a method to dissolve fine crystals generated in a crystallizer in a circulation loop, where a heating unit is equipped (Jones and Chianese, 1987). The fines destruction method was combined by Rohani et al. (1990) to a feedback control scheme.

Natural cooling mode is a method to cool the crystallizer contents by circulating a constant-temperature coolant through jacket or cooling coils with no temperature control. This cooling policy is very easy to operate and no additional temperature control unit is required (low investment cost). This cooling policy, however, has never been believed to be appropriate for optimal operation of batch crystallizer, that is, for obtaining large-size or desired-size product crystals of grown seeds, because of enormous nucleation (Nyvlt, 1976; Mullin, 1993; Moore, 1994; Dunuwila and Berglund, 1997). However, according to a previous study by Jagadesh et al. (1996), using a laboratory-scale well-mixed crystallizer of 12.2 L equipped with a draft tube and a turbine stirrer, large monodispersed crystals can be produced even under natural cooling conditions if enough seeds are loaded at the beginning of the run.

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Seeding has been known for a long time to stabilize the batch crystallization process with suppressed nucleation, but quantitative information is limited. No one can determine how many and what size of seeds should be introduced into a crystallizer to produce product crystals of a desired size. No methodology has been developed. Therefore, seeding in industry does not seem to be used under optimal conditions.

In this study, seeded batch-cooling crystallization experiments were conducted with natural cooling mode by using a pilot-scale well-mixed large crystallizer (600 L) equipped with an anchor stirrer. The results are compared with those of laboratory-scale experiments using a well-mixed crystallizer of 12.2 L equipped with a geometrically similar anchor stirrer. No scale-up effect was observed in terms of product crystal-size distributions (CSDs) if enough seeds are loaded, that is, more than a critical seed concentration. The product crystals were grown seeds. Simple design calculation is shown, which is based on a mass-balance equation correlating crystal size and seed concentration with no nucleation. Additionally, the effect of some other operational conditions on the performance of batch crystallization was examined with the laboratory-scale 12.2 L crystallizer.

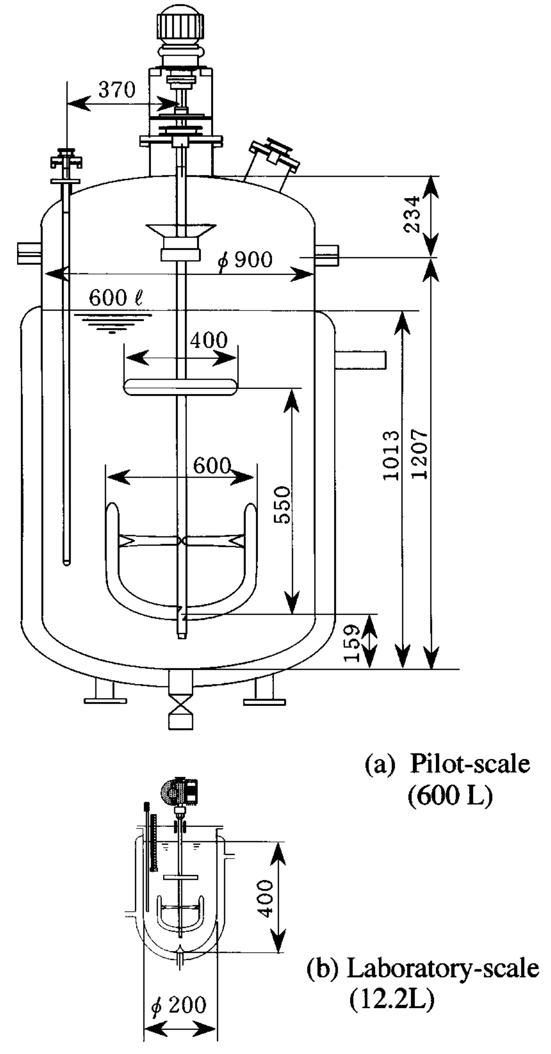


Figure 1. Crystallizers used (a) pilot-scale and (b) laboratory-scale.

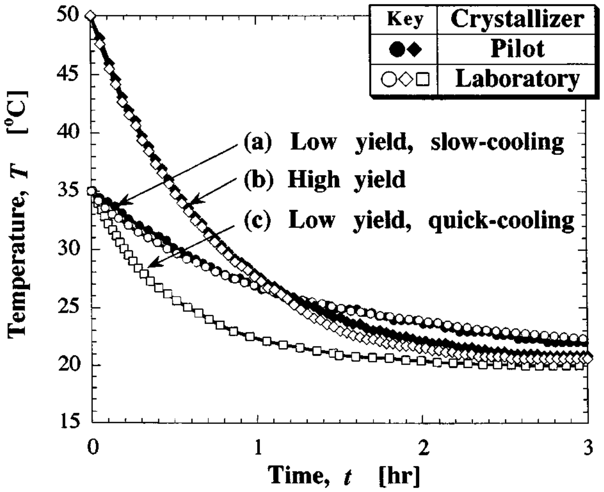


Figure 2. Temperature profiles examined for natural cooling crystallization.

Experimental Studies

Pilot-scale experiments

The pilot-scale experiments were performed in the Iwate Factory of Daiichi Pure Chemicals, Co. Ltd. The pilot-scale jacketed crystallizer (600 L) used in this study is shown in Figure 1. It is made of stainless steel (SUS304), and is equipped with a stainless-steel anchor stirrer (SUS304) and a temperature sensor. No stationary baffles are included. Stirrer speed was fixed at 88 min^{-1} (tip speed: 2.76 m/s) to ensure well-mixed crystal suspension.

Typically, an aqueous solution of potassium alum, saturated at 35°C, was cooled naturally from above 50°C to 22°C by pumping cooling water of constant temperature (19.5°C) through the jacket. The cooling time, the time period needed for the temperature to drop from the saturated temperature (35°C) to 22°C was 3 h (see a temperature profile in Figure 2a, low yield, slow cooling). A known amount of seed crystals (potassium alum crystals) was introduced into the solution during cooling at 34°C, a temperature of 1°C lower than the saturation temperature. At the end of the run, a volume of the suspension was drawn from the bottom of the crystallizer. Product crystals were separated by filtration under suction, and sieved to obtain the crystal-size distribution after being air-dried.

Experiments were also performed with a solution of high initial concentration (saturation temperature of 50°C) to discuss the effect of crystal yield or final crystal suspension density. In this case, the solution was cooled from above 58°C to 20.8°C. The temperature profile is shown in Figure 2 (line (b), high yield). Seeding was made during cooling at a temperature 1°C lower than the saturation temperature.

Seed crystals of two different mean mass sizes were examined. Seeds of 41.5 μm were prepared by sieving ground commercial crystals. Seeds of 315 μm were nonsieved unimodal products from an earlier batch using 41.5 μm seeds (see the dotted CSD lines for seeds in Figures 3a and 3b. These seeds were used without washing, because the 41.5 μm seeds were too small to wash and there were too many of the 315 μm seeds. Seed concentration was changed widely as a major operational variable.

Laboratory-scale experiments

The laboratory-scale experiments were performed by using a well-mixed 12.2 L crystallizer with no baffles, and equipped with a geometrically similar anchor stirrer. It is shown in Figure 1 together with the pilot-scale crystallizer. To critically assess the scale-up effect of the product crystal size, the experimental conditions of the laboratory experiments were basically the same as those of the pilot-scale experiments: tip speed of the anchor stirrer was 2.76 m/s (388 m^{-1}), at which speed crystals were well suspended, and the temperature profile was also the same (see lines (a) low yield, slow cooling, and (b) high yield in Figure 2).

The solution was cooled naturally from above 50°C to 22°C for the solution of a saturation temperature of 35°C, and the seed crystals were introduced during cooling just at the time when the solution temperature reached the saturation temperature. Other experiments were also performed with the solution of high concentration at a saturation temperature of 50°C. The solution in this case was cooled naturally from above 58°C to 20.8°C, and seed crystals were also added at the saturation temperature (50°C). These two temperature profiles were completely the same as those of the pilot-scale experiments. Batch time was also the same (3 h) as in the pilot-scale experiments.

The mean mass size of the seeds used was 41.5, 165, and 315 μm. The 165 μm seeds were sieved commercial crystals. The other two groups of seeds were prepared the same as those of the pilot-scale experiments. They were sieved ground commercial crystals (41.5 μm) and nonsieved products from an earlier laboratory-scale batch (315 μm). The 41.5 μm seeds were added without washing, while the seeds of other sizes were introduced after washing with undersaturated potassium alum solution. Seed concentration was changed widely.

Additional Experiments. Some additional experiments were conducted using the 12.2 L crystallizer for dry seeds of 315 μm to examine the effects of other operational variables on the performance of seeded batch-cooling crystallization. Quick-cooling experiments (line (c) low yield, quick cooling in Figure 2) were conducted at the normal stirrer speed of 388 min^{-1}. Under the slow-cooling condition (line (a) in Figure 2), the effect of stirrer speed was examined with the anchor stirrer. Experiments with a turbine stirrer (400 min^{-1}) were also conducted the same as those of Jagadesh et al. (1996) with 41.5, 165, and 315 μm seeds (cooling curve (a) in Figure 2).

Results and Discussion

Effect of seed concentration on CSD

Pilot-Scale Crystallizer Case of Large-Size Seeds, $Ls = 315$ μm. Figure 3a shows differential size distributions (mass basis) of the product crystals obtained in the pilot study with a seed size of 315 μm. The distribution varies of seed concentration, C_s, which is defined by $C_s = W_s/W_{th}$ as the ratio of the amount of seed added (W_s) to the maximum theoretical yield (W_{th}) calculated from solubility. At a relatively high seed concentration of $C_s = 0.25$, the CSD was unimodal. The product crystals in this case are considered to be grown seeds with virtually no nucleation, because the normalized product mean mass size ($L_{wp}/L_s = 535.5$ μm/315.0 μm $= 1.70$) was in close agreement with the calculated size of grown seeds ($L_{sp}/L_s = 1.71$) for $C_s = 0.25$ from the following simple mass-balance equation, assuming no nucleation:

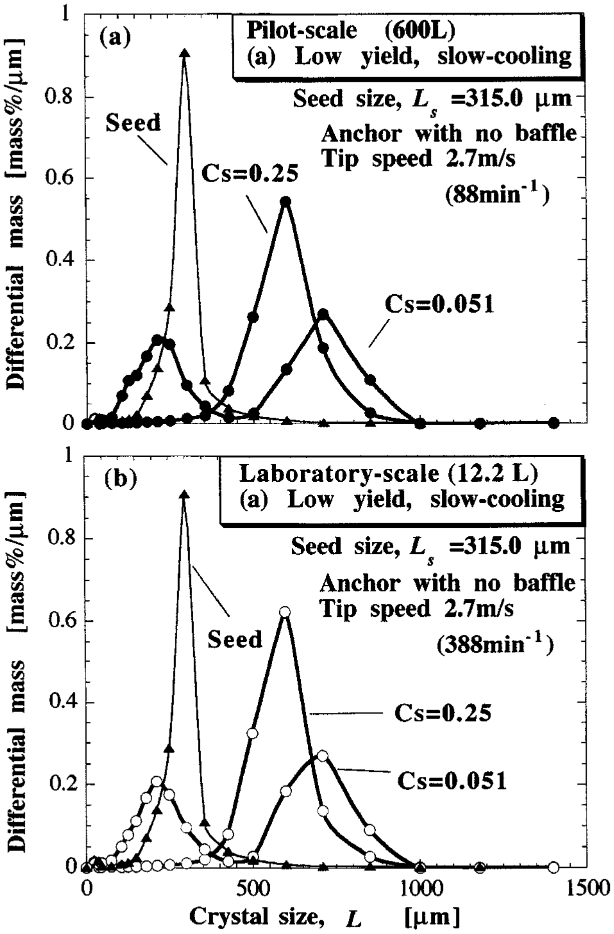


Figure 3. Effect of seed concentration on the CSD of products obtained from (a) pilot-scale and (b) laboratory-scale crystallizers (large seeds).

$$\frac{L_{sp}}{L_s} = \left(\frac{1 + C_s}{C_s} \right)^{1/3}, \tag{1}$$

where L_{sp} is the mean mass size of grown seeds; L_s is the mean mass size of the original seeds; and L_{wp} is the mean mass size of product crystals. [*Note:* The mean mass size $L_{3,0}$ of particles is defined by

$$L_{3,0} = \left(\int_0^\infty nL^3\, dL \Big/ \int_0^\infty n\, dL \right)^{1/3} = \left(\frac{m_3}{m_0} \right)^{1/3} = \left(\frac{W}{\rho k_v N} \right)^{1/3}, \tag{2}$$

where n is the population density; L is the characteristic size of the particles; m_i is the ith moment of the particle-size distribution; W is the total particle weight; N is the total number of particles; ρ is the density of a particle; and k_v is the volume shape factor.]

However, product CSD became widespread and bimodal, as the seed concentration is reduced to a low value of $C_s = 0.051$. The smaller part of the distribution is considered to be newly generated crystals by the secondary nucleation mechanisms, while the larger part can be classified as grown seed crystals.

Laboratory-Scale Crystallizer. The CSDs in Figure 3a were compared with laboratory CSDs (Figure 3b) obtained under the same seed concentrations for the anchor stirrer operating at the same tip speed of 2.76 m/s (388 min^{-1}). The temperature profile was also the same as that of pilot-scale experiments (line (a) in Figure 2). At a high seed concentration of $C_s = 0.25$, CSD became unimodal, while at a low seed concentration of $C_s = 0.051$, CSD became widespread and bimodal. These CSD characteristics were the same as those of pilot-scale experiments. The mean mass size of the product at $C_s = 0.25$ was 532 μm, and hence $L_{wp}/L_s = 1.69$, which is almost the same as that of the pilot study ($L_{wp}/L_s = 1.70$). It is concluded that the product crystals are grown seeds. Thus, no scale-up effect can be seen in terms of CSD if enough seeds are loaded. Scaleup effect will be discussed in detail later.

Case of Small-Size Seeds, $Ls = 41.5\ \mu m$. Figure 4 shows differential size distributions (mass basis) of the product crystals obtained in the pilot study with a small seed size of 41.5 μm. At a high seed concentration of $C_s = 0.00337$, the size distribution was unimodal. On the other hand, as the seed concentration was reduced to a low value of $C_s = 0.00051$, the product CSD became widespread and bimodal. The product crystals in the former case are considered to be grown seeds with no nucleation. Thus, the CSD characteristics were the same as those of large size seeds ($L_s = 315$ μm), that is, the same seed concentration effect was observed. In the laboratory-scale study (data not shown here), the same unimodal distribution was observed as obtained in the pilot study at a high seed concentration of $C_s = 0.00337$, while at a low value of $C_s = 0.00051$ a slightly different but widespread and bimodal distribution were obtained. Thus a slight scaleup effect was observed only at a low seed concentration.

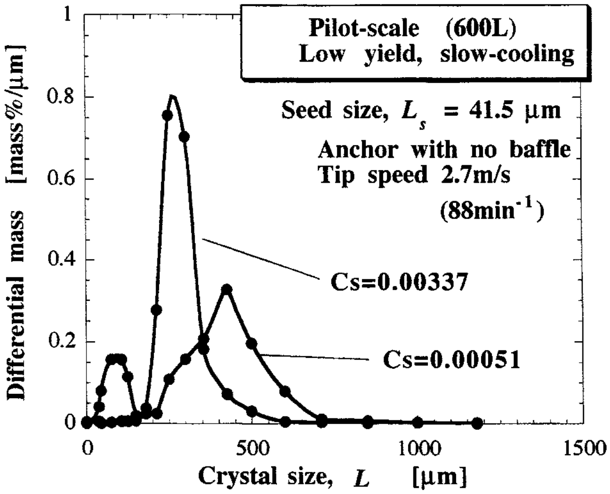


Figure 4. Effect of seed concentration on the CSD of products obtained from pilot-scale crystallizer (small seeds).

It must be mentioned that the absolute value of seed concentration C_s was much reduced in the case of 41.5 μm seeds compared to that in the case of 315 μm seeds. This can be attributed to the large surface area offered by small seed crystals.

The normalized product mean mass size ($L_{wp}/L_s = 302$ μm/41.5 μm $= 7.28$) at a high seed concentration of $C_s = 0.00337$ was not completely in agreement with the grown seed size ($L_{sp}/L_s = 6.68$) calculated from the simple mass balance (Eq. 1). This fact of $L_{wp} > L_{sp}$ clearly indicates that the number of seed crystals has decreased during crystallization. (*Note:* In the derivation of Eq. 1, the number of seed crystals is assumed to be conserved.) This decrease in number is considered to be caused by agglomeration among seed crystals. However, this agglomeration effect is not serious from a practical point of view, because it does not occur intensively and can be avoided by selection of a large seed size if necessary.

Effect of crystal yield or final suspension density on CSD

The preceding discussion was on the experiments of relatively low initial solution concentration (saturation temperature: 35°C). The crystal yield or final suspension density was 97.5 kg/m^3 (5.54 vol %), which is not so high. The final suspension density should be as high as possible in industrial operation.

Figures 5a and 5b show the CSDs obtained from high crystal yield experiments using the solution of high initial concentration (saturation temperature = 50°C). The final suspension density was 245 kg/m^3 (13.9 vol %). As observed in the low crystal yield experiments (Figure 3), the same unimodal CSDs were obtained both for the pilot- and laboratory-scale experiments with enough seed loading of $C_s = 0.25$. No suspension density effect was seen on the scaleup characteristics. At a low seed concentration of $C_s = 0.051$, however, slightly different CSDs were obtained, depending on the crystallizer scale.

The same CSD behavior was observed for the 41.5 μm seeds in high crystal yield experiments as that for the 315 μm seeds. It can be expected, even for other systems, that no suspension density effect will appear on the scaleup characteristics (if enough seeds are loaded).

Scale-up effect on mean product size

The results shown in Figures 3–5 are summarized as follows. The CSD was bimodal at a low seed concentration, while it was unimodal at sufficient seed loading. At a low seed loading, the CSD became slightly different, depending on the crystallizer scale. However, at high seed concentration, the CSD coincides perfectly regardless of crystallizer scale, and the product can be assigned to grown seeds with no nucleation.

This coincidence with no nucleation (that is, an evidence of no scale-up effect) is very important for the design and operation of a batch cooling crystallizer. If a condition for the perfect coincidence for a given material system is known, an

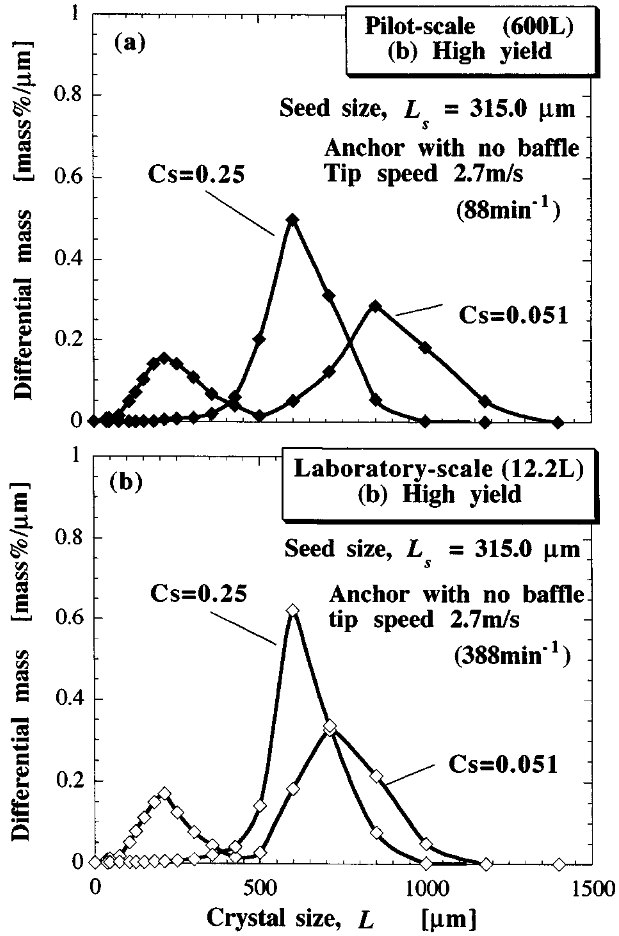


Figure 5. CSD of products obtained under the condition of high crystal yield or high suspension density from (a) pilot-scale and (b) laboratory-scale crystallizers (large seeds).

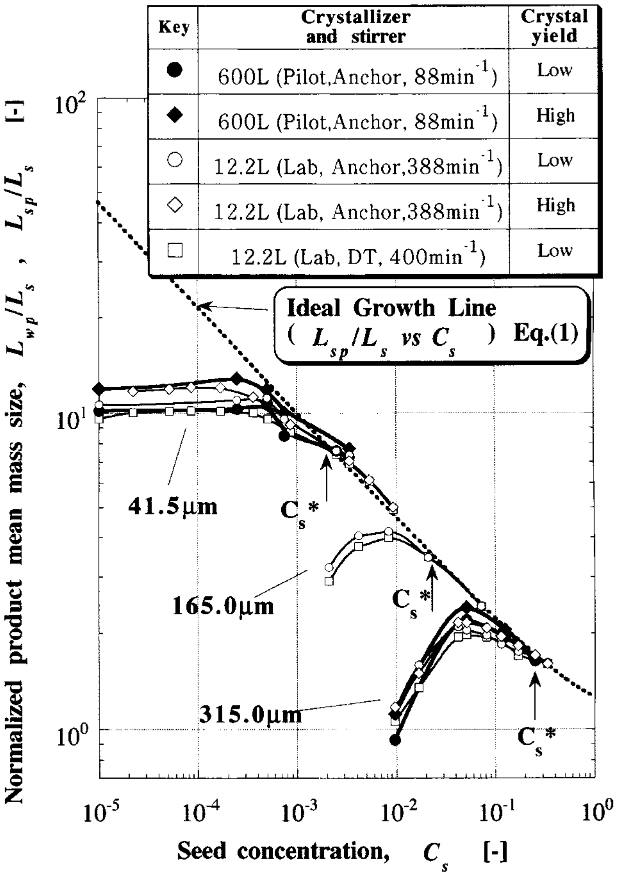


Figure 6. Seed chart correlating normalized product mean mass size and seed concentration with seed size as a parameter.

industrial-scale crystallizer can be designed easily with the use of the mass balance equation (Eq. 1). For an actual industrial crystallizer, an optimal seeding policy also can be determined. To find such a condition for a given system, a seed chart (Jagadesh et al., 1996) can be used conveniently.

Seed Chart. In a seed chart (Figure 6), the normalized product mean mass size of product crystals is plotted as a function of seed concentration with seed size as a parameter. All the data obtained in this study for both the pilot- and laboratory-scale crystallizers are shown in Figure 6. In the figure, the ideal growth line, calculated from Eq. 1 assuming no nucleation, is denoted by a dotted line. Figure 6 shows that the mean size approaches the ideal growth line as the seed concentration is increased, and it eventually coincides over a critical seed concentration C_s^* (see arrows in Figure 6). However, the value of C_s^* does not depend on the crystallizer scale. Therefore, it can be found easily from laboratory-scale batch crystallization experiments. $C_s > C_s^*$ could be a condition for the perfect coincidence. With the help of C_s^* a simple design calculation is given later in the subsection on scaleup design calculation.

In the range of seed concentration less than C_s^*, however, the product mean mass size deviates less from the ideal growth line because of nucleation. Deviated points correspond to bimodal CSDs in Figures 3–5. The degree of deviation in the seed chart was different for laboratory-scale and pilot-scale experiments, probably due to different nucleation characteristics.

As mentioned earlier, the product mean mass size for the 41.5 μm seeds became slightly larger than the size of seeds grown at $C_s > C_s^*$, because of agglomeration among seed crystals (not between seeds and nuclei). This type of agglomeration and the agglomeration between the seeds and nuclei has a reverse effect on the deviation just mentioned. The latter type of agglomeration is discussed below in the section about proposed mechanisms.

Scaleup design calculation

If a critical seed loading is determined for a given seed size on a seed chart using data obtained from a laboratory-scale batch crystallizer, the number of seeds to be added to produce product of a desired mean size can be determined with Eq. 1. For instance, for the desired product of L_{wp} ($= L_{sp}$) $= 300$ μm, the seed loading required is calculated to be $C_s = 0.00265$ (0.265 mass %) for a seed size of 41.5 μm. This loading is acceptable, since it is much larger than the critical C_s^* ($= 0.2$ mass %; see Figure 6) for the 41.5 μm seeds. Further, the crystallizer volume V [m^3] can be estimated for a desired crystal yield W expected for one batch with the help of initial and final solution concentrations by the following equation:

$$V = \frac{W\left[1 - C_2(R-1)\right]}{R(C_1 - C_2)\rho_l} \tag{3}$$

where ρ_l is the density of initial solvents; C_1 is the initial solution concentration (kg anhydrous salt/kg solvent); C_2 is the last solution concentration (kg anhydrous salt/kg solvent), which is equal to the solubility at the final temperature if no supersaturation remains; and R is the ratio of molar masses of hydrate and anhydrous salt. Additionally, the crystal yield W needed to meet a desired production rate also can be determined by using the batch time, which can be obtained simultaneously from laboratory-scale batch experiments performed to determine the critical seed concentration.

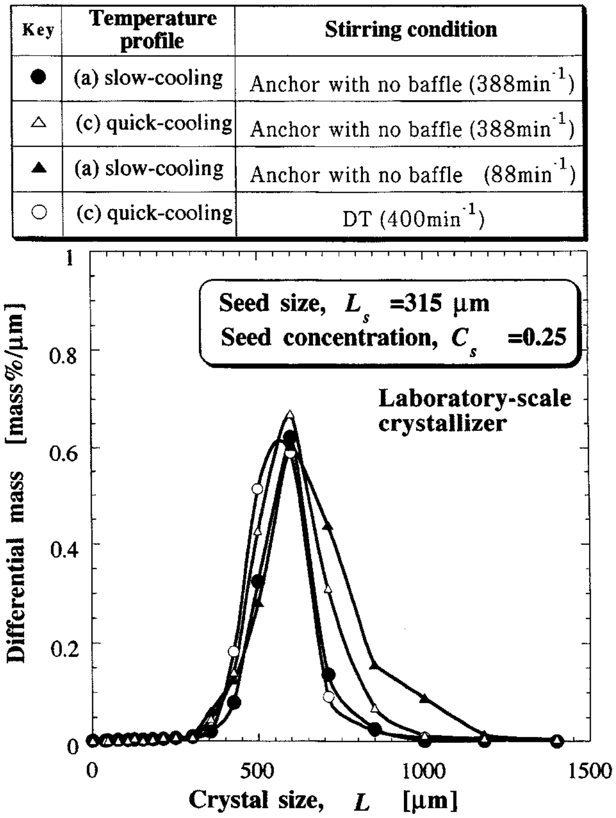
Effects of other operational variables on CSD

When a crystallizer is cooled naturally by circulating coolant through the jacket or cooling coils, the temperature drops more slowly in a large-scale crystallizer than in a laboratory-scale crystallizer, because of the different volume–surface ratio. Laboratory-scale experiments are usually cooled rapidly. (*Note:* In this scale-up study, the cooling rate was made the same (line (a) in Figure 2) intentionally by adjusting the flow rate of cooling water.) Therefore, the effect of the cooling rate was examined.

Figure 7 shows a CSD obtained in the quick-cooling (see temperature profile (c) in Figure 2) experiments at $C_s = 0.25$ ($> C_s^*$) for the 315 μm seeds, together with CSDs obtained under other conditions. This CSD (△) became slightly wider with the same mean size as that of the previous CSD (●) of the slow cooling rate adjusted to that of the pilot study (see line (a) in Figure 2). Only a little change was observed.

The stirring condition was also tested. A CSD at a low stirring speed of 88 min^{-1} (▲) with the anchor stirrer became slightly broadened to the right (see Figure 7). Under this condition, grown crystals were not suspended homogeneously. Larger crystals were seen to move only in the lower part of the crystallizer. Because of this inhomogeneity, agglomeration is thought to proceed extensively and that the CSD eventually was widened. A CSD obtained at an agitation speed of 400 min^{-1} with a turbine stirrer with a draft tube (○) was the same as the previous CSD (●). This condition of 400 min^{-1} with a draft tube is the same as that given in Jagadesh et al. (1996). It must be noted that, in a previous seed chart (Figure 6), the mean product size under this condition was also overplotted. This agrees with other data at high seed concentrations above C_s^*. For the sake of clarity, data of Jagadesh et al. (1996) are not plotted in Figure 6, although those data are in close agreement with those of the corresponding data in this study.

To summarize this subsection: (1) the temperature profile has little effect on the CSD, and (2) the stirring condition also has little effect, unless the crystals are suspended homogeneously.



Key	Temperature profile	Stirring condition
●	(a) slow-cooling	Anchor with no baffle (388min^{-1})
△	(c) quick-cooling	Anchor with no baffle (388min^{-1})
▲	(a) slow-cooling	Anchor with no baffle (88min^{-1})
○	(c) quick-cooling	DT (400min^{-1})

Figure 7. Effects of stirring condition and temperature profile on CSD under the condition of enough seeding.

Proposed mechanisms

All the preceding discussions were made on the basis of the experimental data obtained in this study. There was no speculation. However, this may have caused readers to wonder, since the results do not agree with the common belief (Nyvlt, 1976; Mullin, 1993; Moore, 1994; Dunuwila and Berglund, 1997) that natural cooling, which proceeds very rapidly at the beginning of a run, causes enormous nucleation and eventually yields widespread product CSD. Therefore, some additional experiments were conducted using natural cooling and the laboratory crystallizer for the seeds of 315-μm. The stirrer speed was kept at 388 min^{-1}. The potassium alum solution, whose saturation temperature was 35°C, was used.

Figure 8 shows (Figure 8a) transient supersaturation, and (Figure 8b) the transient number of crystals present in the crystallizer. The number of crystals was converted from sieve data (≥ 38.0 μm). At a low seed concentration, the transient supersaturation profile has a higher peak (see the dotted line in Figure 8a) because of the lower deposition rate of solute on the smaller surface of the seeds, and hence many nuclei were produced (see the dotted line in Figure 8b). However, at a high seed concentration, the transient supersaturation profile has a lower supersaturation peak, and hence, fewer nuclei were produced. These results are not surprising.

The important thing is that, at the high seed loading (solid line), the number of crystals continued to increase only before the supersaturation peak, while at the lower seed concentration it continued just after the peak (dotted line). In either case, the number of particles was found to increase for only a short period during the early part of natural cooling.

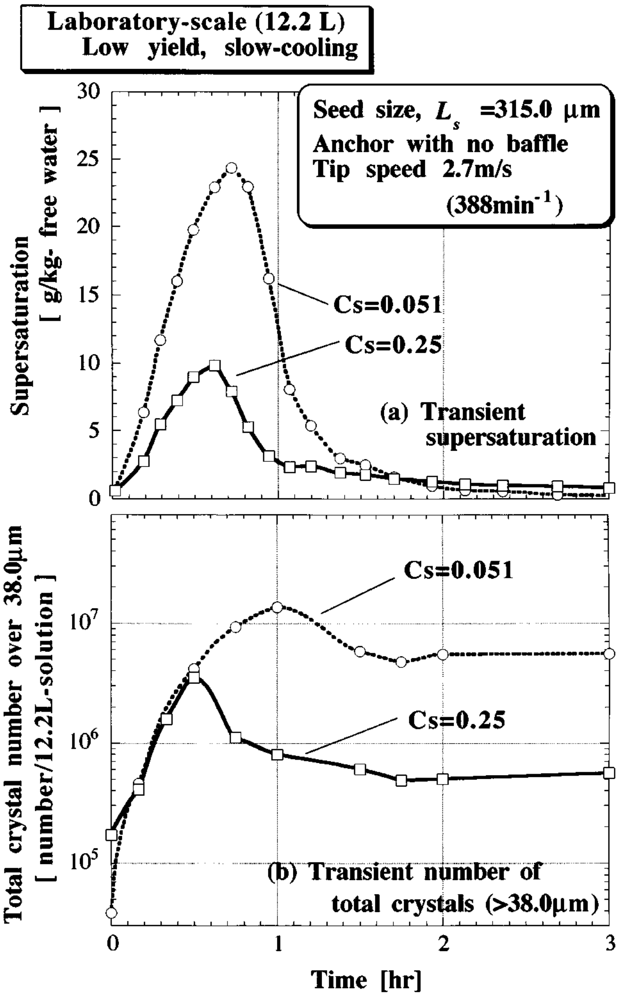


Figure 8. (a) Transient supersaturation and (b) transient number of crystals present in the crystallizer.

During the long period of relatively low supersaturation after the peak, no increase in the particles was observed. The short period of nucleation is one way of suppressing the number of particles during the batch. This is not surprising, because the secondary nucleation rate is an increasing function of supersaturation, so the number of particles could increase only during the short period before and after the supersaturation peak.

Another important point is the fact that the number of crystals decreased after the peak. We can conclude that this decrease is caused by the agglomeration of nuclei to the growing seed crystals. This conclusion that small crystals were present in product crystals was supported by observation using a polarizing microscope. Agglomeration among the seeds was not observed for the 315 μm seeds. It is interesting to note that in the case of $C_s = 0.25$ ($> C_s^*$), the decrease in number after the peak was comparable with the increase in number by nucleation before the peak. Therefore, there was no significant net increase in number of crystals, that is, virtually no nucleation occurred.

In summary: there are three mechanisms working to produce unimodal crystal products in seeded batch cooling crystallization with natural cooling mode: (1) low supersaturation peak; (2) a short period of nucleation; and (3) agglomeration of nuclei to the seed crystals.

Conclusions

1. With enough seed loading over a critical seed concentration under well-mixed conditions, unimodal product crystals of grown seeds were obtained in seeded batch cooling crystallization using natural cooling.
2. No scaleup effect on CSD was observed if enough seeds were loaded over the critical seed concentration under well-mixed conditions. It can be determined easily from laboratory-scale experiments for design purposes.
3. Simple design calculations using Eq. 1 are shown to determine the amount of seed, with the help of critical seed concentration.
4. Cooling rate, crystal yield, and stirring conditions do not have serious effects on the CSD product if enough seeds are loaded under well-mixed conditions.
5. The three mechanisms of (1) low supersaturation peak, (2) short period of nucleation, and (3) agglomeration of nuclei to the seed crystals are shown to work to produce unimodal product crystals.

Acknowledgments

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