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Short communication

# Effect of cooling mode on product crystal size in seeded batch crystallization of potassium alum

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## Abstract

Potassium alum was crystallized by seeding in a batch crystallizer under controlled and natural cooling modes. Regardless of the cooling mode, the product crystal size distribution (CSD) became bi-modal at low seed concentrations because of enormous secondary nucleation. The mean mass size of the product was smaller for the natural cooling mode compared to that for the controlled cooling mode with more intensive secondary nucleation. On the other hand, at high seed concentrations, the product CSD became uni-modal with the same mean mass size for both cooling modes, where the crystallization was dominated by seed growth. The low supersaturation caused by the growth of enough seeds plays a key role to produce uni-modal size distribution with suppressed nucleation. Adhering of small crystals (secondary nuclei) to growing seed crystals is also considered to be another mechanism for generating uni-modal CSD. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Crystallization; Potassium alum; Crystal size distribution

## 1. Introduction

Batch cooling crystallization is widely used in the production of fine chemicals or pharmaceuticals. In this process, the size of product crystals should be controlled as desired. According to previous studies by Jagadesh et al. [1,2] using a laboratory-scale crystallizer of 12.2 l, large crystals of uni-modal distribution can be produced with virtually no nucleation under natural cooling condition if enough seeds are loaded. The same results were reported by Doki et al. [3] for a large scale (600 l) crystallizer. This cooling mode is very easy to operate. But it has never been believed to be optimal for obtaining large or desired size product crystals of grown seeds [4–7].

The cooling method that has been long believed to be optimal for batch crystallization is the controlled or programmed cooling mode, which was first proposed by Mullin and Nyvlt [8]. Further, Jones and Mullin [9] and Jones [10] suggested a systematic approach to calculate theoretical programmed cooling curves by considering nucleation effects. The controlled cooling is a cooling mode so as to keep the supersaturation at a low level within the so-called metastable zone throughout the batch. In this cooling mode, no small crystals (nuclei) are assumed to be generated by secondary nucleation mechanisms. However, generation of nuclei cannot be avoided completely according to literature data.

In this study, batch crystallization experiments were conducted for both controlled and natural cooling modes over a wide range of seed loadings. The results were compared in terms of product crystal size distributions (CSDs) and the mean mass product size for these two cooling modes. If enough seeds were loaded, no cooling mode effect on CSD was observed with virtually no nucleation, and product crystals were of grown seeds. At low seed concentrations, however, the cooling mode effect was observed; in the controlled cooling mode the product size was larger because of more suppressed secondary nucleation. Mechanisms for generating uni-modal CSDs at enough seed loadings are discussed.

## 2. Experimental

A 12.2-l draft tube jacketed crystallizer made of glass was used, and fitted with a turbine stirrer, a thermocouple, an electrical conductivity cell and a sampling tube. The experimental set-up was the same as in previous papers [1,2].

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**Nomenclature**

| | |
|---|---|
| $C_s$ | seed loading or seed concentration ($=W_s/W_{th}$) (dimensionless) |
| $C_s{}^*$ | critical seed concentration (dimensionless) |
| $\Delta c$ | supersaturation (kg-hydrate per kg free water) |
| $\Delta c_i$ | initial supersaturation (kg-hydrate per kg free water) |
| $L$ | crystal size (μm) |
| $L_s$ | mean mass size of seed crystals (μm) |
| $L_{sp}$ | mean mass size of grown seed crystals (μm) |
| $L_{wp}$ | mean mass size of the product crystals (μm) |
| $t$ | batch time (h) |
| $W_s$ | mass of the seed added (kg of hydrate) |
| $W_{th}$ | theoretical yield calculated from solubility (kg of hydrate) |

### *2.1. Controlled cooling experiments*

An aqueous solution of potassium alum, saturated at 35°C, was cooled from 33.8 to 20°C with an initial supersaturation of $\Delta c_i=5\times10^{-3}$ kg-hydrate per kg free water by pumping cooling water of 20°C through the jacket. The temperature was lowered along with the controlled cooling curve (Eq. (1)). Cooling time or batch time was 3 h. The speed of agitation was maintained at 400 per minute to ensure homogeneous crystal suspension. A known amount of seed crystals of potassium alum was introduced into the solution at the start of a batch. During the run, temperature and electrical conductivity data were collected. These data were fed to a computer through a multi-logging meter. The supersaturation was calculated on-line from these data following the method of Hlozny et al. [11]. At the end of the run, a volume of the suspension was sampled from the crystallizer. Product crystals were separated by filtration under suction, and sieved to obtain CSD after drying with air.

All the seed crystals were prepared by sieving recrystallized crystals. The average size of the seeds used was 41.5, 165 and 328 μm. The average size was calculated from the two adjacent sieve openings. Because of narrow size distribution, this average size can be approximated to the mean mass size. The seeds of 41.5 μm were added without washing, while the other size seeds were introduced after washing with a slightly undersaturated potassium alum solution at room temperature. The seed amount added was changed widely.

A general expression of controlled cooling curve for a seeded system by assuming growth only on the added seeds with negligible nucleation [6] is given as

$$T(t)=T_i-(T_i-T_f)\left(\frac{t}{t_f}\right)^3 \tag{1}$$

where $T(t)$ is the temperature at time $t$, and $T_i$ and $T_f$ are the temperatures at the beginning and the end of a run, respectively. The actual curve in this study was calculated for a batch time of 3 h with $T_i$=33.8°C and $T_f$=20°C.

### *2.2. Natural cooling experiments*

The natural cooling or quenching experiments were performed similar to those for the controlled cooling mode. Aqueous solution of potassium alum, saturated at 35°C, was cooled naturally from above 40 to 20°C by pumping cooling water of a constant temperature of 20°C through the jacket. Temperature decreased exponentially. Seeding was made at a temperature of 33.8°C with the same initial supersaturation of $\Delta c_i=5\times10^{-3}$ kg-hydrate per kg free water. Batch time was 3 h.

## 3. Results and discussion

### *3.1. Effect of cooling mode on CSD*

Fig. 1 shows differential size distributions (mass basis) of the product crystals obtained for the seeds of a mean size of 165 μm under both controlled and natural cooling modes. The distribution varies with seed concentration, which is defined by $C_s=W_s/W_{th}$ as the ratio of the seed amount added ($W_s$) to the theoretical yield ($W_{th}$) calculated from solubility. At a relatively high seed concentration of $C_s$=0.0715, the CSD was uni-modal. The product crystals in this case are considered to be grown seeds with virtually no nucleation, because the normalized product mean mass size ($L_{wp}/L_s$=2.45) was closely in agreement with the calculated size of grown seeds ($L_{sp}/L_s$=2.47) for $C_s$=0.0715 from the following simple mass balance equations [1–3] assuming no

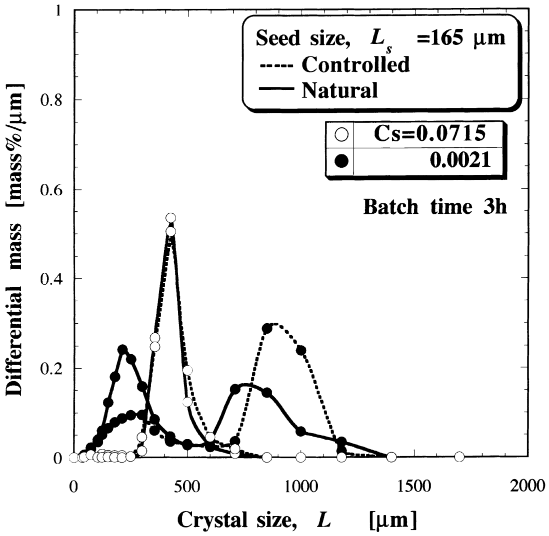


Fig. 1. Effect of seed concentration and cooling mode on product CSD.

change in total crystal numbers (no nucleation, no agglomeration and no breakage) and no change in crystal shape,

$$\frac{L_{\rm sp}}{L_{\rm s}} = \left(\frac{1+C_{\rm s}}{C_{\rm s}}\right)^{1/3} \tag{2}$$

where $L_{\rm sp}$ is the mean mass size of grown seeds and $L_{\rm s}$ the seed mean mass size. However, the CSD became wide-spread and bi-modal as the seed concentration is reduced to a low level of $C_{\rm s}$=0.0021 (see Fig. 1 again). The smaller part of the distribution corresponds to newly generated crystals by secondary nucleation mechanisms, while the larger part can be attributed to grown seed crystals.

The uni-modal distribution at high seed concentrations were completely the same regardless of the cooling mode. But, in the bi-modal distribution, the distribution pattern was different. As seen in Fig. 1, the amount of particles of the smaller part of the distribution is larger for the natural cooling mode than that for the controlled cooling mode. This means that generation of new particles by secondary nucleation mechanisms are suppressed more effectively in the controlled cooling mode as claimed in the literature [4–7].

The same results were obtained from experiments using other size seeds of 41.5 and 328 μm (data not shown).

### 3.2. Effect of cooling mode on product mean mass size $L_{\rm wp}$

The normalized mean mass product size $L_{\rm wp}/L_{\rm s}$ is plotted as a function of seed concentration $C_{\rm s}$ on a seed chart (Fig. 2) for the controlled and natural cooling modes over a wide range of seed concentrations $C_{\rm s}$. In the figure, an ideal growth line (Eq. (2)) is also drawn as a dotted line. The mean mass size can be seen to approach the ideal growth line as the seed concentration is increased regardless of the cooling mode and seed size, and eventually coincides with it above a critical seed concentration $C_{\rm s}$*. This value does not depend on the cooling mode but depends only on the seed size.

In the range of seed concentration below $C_{\rm s}$*, however, the value of the mean mass product size depends on the cooling mode. It becomes smaller for the natural cooling mode as compared to the controlled cooling mode. This is because secondary nucleation was suppressed more effectively in the programmed cooling than in the natural cooling mode in this low seed concentration range, as mentioned earlier.

It must be noted that the product mean mass size for the 41.5 μm seeds at $C_{\rm s} > C_{\rm s}$* is slightly larger than the value of the ideal growth line (Eq. (2)). This means that the number of seeds is not conserved as assumed in Eq. (2). The number of crystals is considered to decrease by agglomeration among seed crystals (not between nuclei and seed crystals) [3].

### 3.3. Transient supersaturation profile

Fig. 3 shows transient supersaturation profiles during crystallization with seeds of 165 μm. The supersaturation has a peak, whose position depends on the cooling mode. It appears earlier for natural cooling mode, while later for controlled cooling mode. The peak position corresponded to the position of the high rate of cooling, i.e., the high generation rate of supersaturation.

The supersaturation peak became lower upon increasing the seed loading. The supersaturation can be said to be created by cooling but consumed by the growth of seeds and nuclei. Therefore, since the consumption rate is increased as the seed amount is increased, the supersaturation peak can be suppressed from the supersaturation balance. Supersaturation profiles for both cooling modes at $C_{\rm s}$=0.0715 (enough seeds) are given in Fig. 3. The low supersaturation profiles led to less secondary nucleation regardless of the cooling

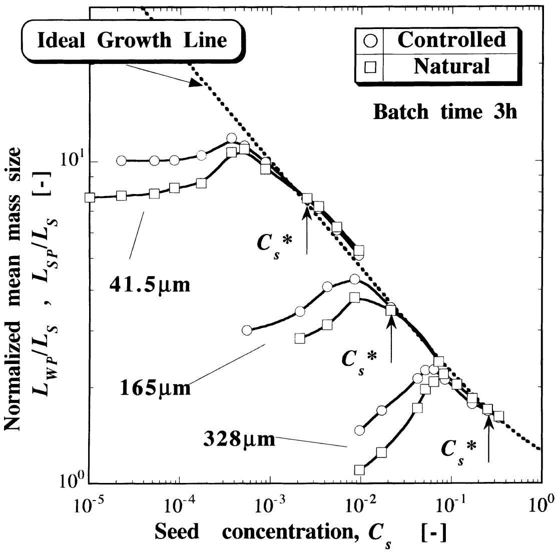


Fig. 2. Comparison of the product mean mass size for two cooling modes on a seed chart.

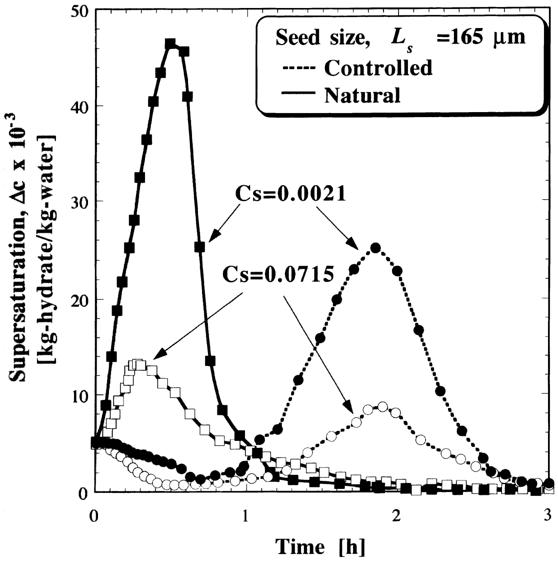
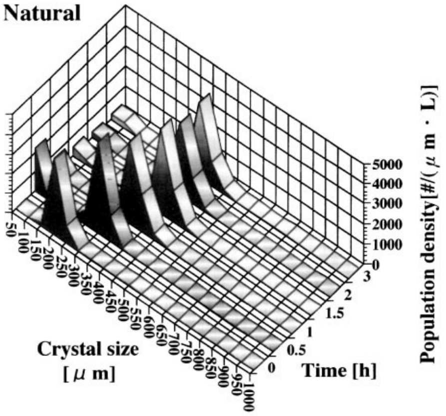


Fig. 3. Transient supersaturation profiles.

**(a) Natural**



**(b) Controlled**

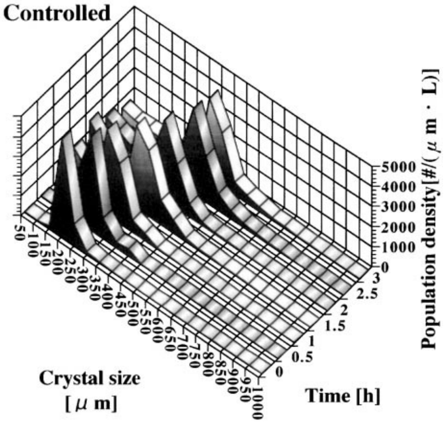


Fig. 4. Developments of crystal population density distribution for (a) natural and (b) controlled cooling modes ($C_s$=0.0715, $L_s$=165 μm).

mode. This is the main mechanism to suppress secondary nucleation.

### 3.4. Development of CSD

As additional experiments, the development of CSD during a batch was measured both for the controlled and natural cooling modes at $C_s$=0.0715 with a seed size of 165 μm. CSDs are shown in Fig. 4 as population density distributions. Crystals larger than 38 μm (the minimum sieve size) were converted from sieve data of particles.

Fig. 4(a) shows the CSD development for natural cooling mode. The larger part of the CSD shifts with time to the direction of large size by seed growth as expected. An interesting point is that a large number of small crystals, seen at 0.5 h, which are generated in the crystallizer, disappear afterward. This is considered to be caused by adhering of small crystals to growing seed crystals. This type of agglomeration was verified by observations with a polarizing microscope. Small crystals were found buried in large seed crystals. This type of adhesion is an additional mechanism to produce uni-modal product distribution.

Fig. 4(b) shows the CSD development for controlled cooling mode under the same seeding condition as in the natural cooling mode. Generation and agglomeration of small particles are also seen.

## 4. Conclusions

1. With enough seed loading above a critical seed concentration, uni-modal product crystals of grown seeds with virtually no nucleation were obtained in seeded batch cooling crystallization, regardless of the cooling mode.
2. At low seed loading below the critical concentration, the bi-modal CSD was obtained both for the controlled and natural cooling modes. The amount of small particles was less for the controlled cooling mode as secondary nucleation was suppressed more effectively in the controlled cooling mode. But, it still occurred extensively.
3. Supersaturation was suppressed during a batch by solute consumption by growing enough seeds. This is the main mechanism to produce uni-modal CSD with suppressed secondary nucleation. Agglomeration of small particles (nuclei) to growing seeds was suggested as an additional mechanism for generating uni-modal CSD.

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