Growth Rate Dispersion in Batch Crystallization with Transient Conditions

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Since the concept of growth rate dispersion was first introduced by White and Wright (1971) to explain an increase in the spread of crystal sizes during batch growth of sucrose crystals, mathematical models (Zumstein and Rousseau, 1987; Ramanarayanan *et. al.,* 1984; Randolph and White, 1977) have been developed to describe the effects of growth rate dispersion on the crystal size distribution (CSD) in batch crystallizations. Several studies (Jančić *et. al,* 1984; Tavare and Garside, 1982) have also been conducted demonstrating techniques for estimating growth rate dispersion parameters from batch crystallization experiments. However, both the mathematical models and the parameter estimation techniques have been developed assuming that crystal growth conditions (temperature, supersaturation, etc.) remain constant during crystallization. Constant system conditions are achieved only rarely in industrial operation and are difficult to accomplish in laboratory experiments. The study described here resulted in a model of CSD in a batch crystallizer with transient system conditions. Additionally, methods for estimating growth rate dispersion parameters from experimental data are presented using previously reported experimental data on potassium alum.

The phenomenon of growth rate dispersion is a deviation from the ΔL law (McCabe, 1929); it is a deviation in which crystals in the suspension do not grow at identical rates and/or individual crystals do not grow at constant rates even though the system conditions may remain constant. Moreover, the difference in crystal growth rates in the suspension is not related to the size of the growing crystals, which distinguishes this growth abnormality from size-dependent growth. Zumstein and Rousseau (1987) describe two distinctly different mechanisms that have been proposed to explain the apparent occurrence of various growth rates for crystals within the same environment: random fluctuations in the growth rates of individual crystals, and inherently different mean growth rates among crystals characterized by a distribution of time-averaged growth rates.

Ramanarayanan et. al (1984) demonstrated a method of incorporating the distribution function for crystal growth rates into a mathematical model for batch crystallization. However, Zumstein and Rousseau (1987) presented a single model that incorporates both growth rate dispersion mechanisms utilizing a growth rate diffusivity parameter D_G to represent the magnitude of the random growth rate fluctuations and a distribution function for time-averaged growth rates with mean $\overline{G}$ and variance σ_G^2. This model is based on the general assumption that crystals are introduced into the system with a distribution of time-averaged growth rates and, due to changes in the dislocation networks of the crystals, individual crystal growth rates fluctuate about their time-averaged values during growth. As pointed out by Zumstein and Rousseau, both mechanisms of growth rate dispersion may be present during batch crystallization and could contribute to the increase in variance of the CSD during growth.

Both growth kinetics and growth rate dispersion are affected by changing environmental conditions within an agitated crystallizer. The objective of the present study was to develop a mathematical model for batch crystallization that includes growth rate dispersion in order to predict CSD and estimate growth rate dispersion parameters. The model includes both mechanisms of growth rate dispersion. Crystals are allowed to have a distribution of time-averaged growth rates that all have similar dependencies on crystallizing conditions and, due to the

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changes in the dislocation networks of the crystals, individual crystal growth rates are allowed to fluctuate randomly about their time-averaged values.

Growth Rate Dispersion Model

Variations of supersaturation with time during batch crystallization operations are typical. This results in transient growth conditions. The dependence of crystal growth rate G on supersaturation σ is given by the BCF growth theory as

$$G = A \frac{\epsilon\sigma^2}{\sigma_1'} \tanh \frac{\sigma_1'}{\epsilon\sigma} \tag{1}$$

where A is a constant and σ_1' is system-dependent and inversely proportional to temperature. The parameter ϵ is known as the screw dislocation activity and represents the extent to which a group of dislocations enhance the growth rate of a crystal face. Varying values of ϵ among crystals may account for the different growth rates of crystals in a suspension. More simply, but less fundamentally, growth rate can be approximated by a power-law expression:

$$G = k_G \sigma^n \tag{2}$$

where k_G and n are parameters evaluated by fitting Eq. 2 to growth kinetic data.

In order to develop a model to account for the effect of varying supersaturation on growth rate dispersion, relationships for the influence of supersaturation on both growth rate dispersion mechanisms had to be established. There is evidence that the magnitude of random growth rate fluctuations is dependent on supersaturation (Janse and deJong, 1979; Randolph and White, 1971). Analogous to the approximation in Eq. 2, the dependence of the growth rate diffusivity parameter D_G on supersaturation was assumed to follow a power-law expression:

$$D_G = k_D \sigma^m \tag{3}$$

k_D and m are system-specific parameters that were assumed to be constant over the range of supersaturations considered. A distribution of crystal growth rates can be expressed by assuming that a distribution of growth rate parameters k_G exists for the crystals with mean $\overline{k}_G$ and variance $\sigma_{k_G}^2$. The distribution parameters, $\overline{k}_G$ and $\sigma_{k_G}^2$, are related to the mean and variance of the distribution of crystal growth rates by

$$\overline{G} = \overline{k}_G \sigma^n \tag{4}$$

$$\sigma_G^2 = \sigma_{k_G}^2 \sigma^{2n} \tag{5}$$

It was assumed that the parameter n does not vary among crystals.

By analogy to the derivation of the constant-supersaturation model (Zumstein and Rousseau, 1987), a conditional moment $\overline{m}_j(k_G)$ of the CSD can be defined as the jth moment of the CSD for crystals with growth kinetic constant k_G. $\overline{m}_j(k_G)$ is related to the jth moment of the entire CSD m_j by

$$m_j = \int_0^\infty f(k_G) \overline{m}_j(k_G)\, dk_G \tag{6}$$

where $f(k_G)$ is the distribution function for k_G. Moment transformation of a conditional population balance for a batch crystallizer can be performed to give the following set of conditional moment equations:

$$\frac{d\overline{m}_0(k_G)}{dt} = 0 \tag{7a}$$

$$\frac{d\overline{m}_1(k_G)}{dt} = G\overline{m}_0(k_G) \tag{7b}$$

$$\frac{d\overline{m}_2(k_G)}{dt} = 2G\overline{m}_1(k_G) + 2D_G\overline{m}_0(k_G) \tag{7c}$$

$$\frac{d\overline{m}_j(k_G)}{dt} = jG\overline{m}_{j-1}(k_G) + j(j-1)D_G\overline{m}_{j-2}(k_G) \tag{7d}$$

The solution to this set of ordinary differential equations requires stipulation of the initial conditions of the moments. For a crystal population with initial mean size $\overline{L}_i$ and variance $\sigma_{L_i}^2$, the initial conditions for the first three moments are

$$\overline{m}_0'(k_G) = 1 \tag{8a}$$

$$\overline{m}_1'(k_G) = \overline{L}_i \tag{8b}$$

$$\overline{m}_2'(k_G) = \sigma_{L_i}^2 + \overline{L}_i^2 \tag{8c}$$

Since supersaturation is a function a time, Eqs. 2 and 3 indicate that the G and D_G are also time-dependent. Substituting for G and D_G using Eqs. 2 and 3, respectively, the general solution of the conditional moment equations gives

$$\overline{m}_0(k_G) = 1 \tag{9a}$$

$$\overline{m}_1(k_G) = \overline{L}_i + k_G \int_0^t \sigma^n(s)\, ds \tag{9b}$$

$$\begin{aligned}\overline{m}_2(k_G) &= \sigma_{L_i}^2 + \overline{L}_i^2 + 2k_G\overline{L}_i \int_0^t \sigma^n(s)\, ds \\ &\quad + 2k_G^2 \int_0^t \sigma^n(s) \left[\int_0^s \sigma^n(r)\, dr\right] ds + 2k_D \int_0^t \sigma^m(s)\, ds\end{aligned} \tag{9c}$$

where r and s are dummy variables of integration. Applying Eq. 6 to these results, the moments of the CSD in a batch crystallizer are

$$m_0(t) = 1 \tag{10a}$$

$$m_1(t) = \overline{L}_i + \overline{k}_G \int_0^t \sigma^n(s)\, ds \tag{10b}$$

$$\begin{aligned}m_2(t) &= \sigma_{L_i}^2 + \overline{L}_i^2 + 2\overline{k}_G\, \overline{L}_i \int_0^t \sigma^n(s)\, ds + 2(\overline{k}_G^2 + \sigma_{k_G}^2) \\ &\quad \cdot \int_0^t \sigma^n(s) \left[\int_0^s \sigma^n(r)\, dr\right] ds + 2k_D \int_0^t \sigma^m(s)\, ds\end{aligned} \tag{10c}$$

Finally, moments of the CSD can be used to give the mean $\overline{L}$ and the variance σ_L^2 for the distribution:

$$\overline{L} = \overline{L}_i + \overline{k}_G \int_0^t \sigma^n(s)\, ds \tag{11}$$

$$\sigma_L^2 = \sigma_{L_i}^2 + 2\sigma_{kG}^2 \int_0^t \sigma^n(s)\left[\int_0^s \sigma^n(r)\,dr\right] ds + 2k_D \int_0^t \sigma^m(s)\,ds \quad (12)$$

Explicit solutions for $\bar{L}$ and σ_{L_i} are dependent on the relationship between time and supersaturation during the batch process.

Experimental Procedure

As details of the experimental procedure used in the present study are given elsewhere (Girolami and Rousseau, 1985), they are only summarized here. A jacketed glass vessel with three baffles and a capacity of 200 mL was used as the batch crystallizer. The crystallizer temperature was held constant at 29.4 ± 0.1°C throughout each experiment by circulating coolant through the jacket of the vessel. The crystallizer was equipped with a 200 μm aperture tube to monitor the CSD by a TA-II Coulter Counter. A glass stirring rod was used to provide mechanical agitation.

At various times during a run, samples were withdrawn from the batch crystallizer for measurement of solute concentration and CSD. The solute concentration C was used to determine the relative supersaturation σ, which was defined as

$$\sigma(t) = \frac{C(t) - C_s}{C_s} \quad (13)$$

where C_s is the equilibrium solute concentration in the liquor at the crystallizer temperature. Liquor concentrations were expressed as g alum dodecahydrate/g solution. Figure 1 presents measured desupersaturation of liquor during three representative experiments. CSD measurements during experiments were corrected for background counts and the trailing tail of the distribution also was corrected for contamination of nuclei formed after the initial breeding, so that a smooth curve falling to zero as size decreased was obtained. As a guide, the total number of small crystals was restricted to a constant value for successive transients curves in the same experiment. From each of the measured distributions, the mean crystal size and variance of the distribution were determined from the expressions

$$\bar{L} = \frac{\Sigma N_k L_k}{\Sigma N_k} \quad (14)$$

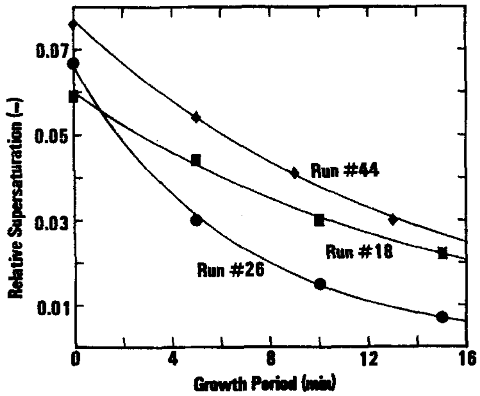

Figure 1. Typical rates of desupersaturation of seeded potassium alum solutions.
—Eq. 16 fitted to data

$$\sigma_L^2 = \frac{\Sigma N_k (L_k - \bar{L})^2}{\Sigma N_k} \quad (15)$$

where N_k is the number of crystals/mL in channel k of mean size L_k. Eleven experiments were conducted covering a range of supersaturations from 0.004 to 0.085.

Results and Discussion

In order to solve Eqs. 11 and 12 explicitly, the time dependence of the supersaturation had to be established. To approximate liquor desupersaturation, the supersaturation measurements for each run were fitted to an exponential decay function:

$$\sigma(t) = a \exp(-bt) \quad (16)$$

where a and b are constants for a particular batch experiment. As shown in Figure 1, the exponential decay seems to describe the desupersaturation of the liquor adequately. Incorporating Eq. 16 into Eqs. 11 and 12, the mean and variance of the CSD predicted by the model follows the expressions

$$\bar{L} = \bar{L}_i + \frac{\bar{k}_G a^n}{bn}[1 - \exp(-bnt)] \quad (17)$$

$$\sigma_L^2 = \sigma_{L_i}^2 + \frac{\sigma_{k_G}^2 a^{2n}}{b^2 n^2}[1 - \exp(-bnt)]^2 + \frac{2k_D a^m}{bm}[1 - \exp(-bmt)] \quad (18)$$

Since the initial crystal population was similar for all experiments, the mean crystal sizes determined from the measurements of the transient CSD were fitted to Eq. 17 to estimate the mean size of the nuclei from initial breeding and the growth kinetic expression parameters of Eq. 4. This gave $\bar{L}_i$ = 7.07 ±0.36 μm, $\bar{k}_G$ = 138.1 ±14.1 μm/min, and n = 1.38 ±0.04 with a correlation coefficient of 0.952. Figure 2 illustrates the fit of Eq. 17 for three typical experimental runs. Girolami and Rousseau (1985) also estimated these parameters from the same experimental data, but they assumed that constant growth conditions existed between measurements and used the average supersaturation over the interval. Their estimates varied slightly from the parameters estimated in the present study; they

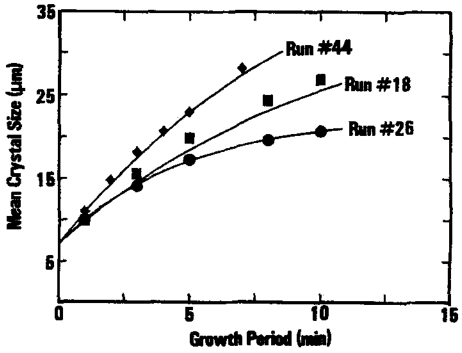

Figure 2. Typical fit of observed mean crystal size during experimental runs to Eq. 17.
$\bar{L}_i$ = 7.07 μm; $\bar{k}_G$ = 138.0 μm/min; n = 1.38

reported values for $\bar{L}_i$ of 5.0 μm, $\bar{k}_G$ of 243 μm/min, and n of 1.56.

Experimental values of the variance of the CSD at various times were fitted to the general expression for growth rate dispersion given by Eq. 18. Regression analysis gave estimates for $\sigma^2_{L_i}$ of 18.2 ±4.6 μm², $\sigma^2_{k_G}$ of 4,649 ±705 μm²/min², k_D of 29.1 ±36.4 μm²/min, and m of 0.98 ±0.33 with a correlation coefficient of 0.951. The error span for the estimates of the random growth rate fluctuation mechanism includes a value of zero for the parameter k_D, which suggests either that this mechanism is insignificant in comparison to the growth rate distribution mechanism or, possibly, that the model does not correctly account for random growth rate fluctuations.

To examine more carefully the magnitude of the two growth rate dispersion mechanisms for the potash alum nuclei from the present study, reduced versions of Eq. 18 were developed for each of the two growth rate dispersion mechanisms. First, it was assumed that only a distribution of k_G values existed among the small crystals and that these values did not fluctuate during growth ($k_D = 0$). The experimental data were again used to estimate the parameters of this model and regression gave values for $\sigma^2_{L_i}$ of 25.2 ±1.9 μm² and for $\sigma^2_{k_G}$ of 5,698 ±186 μm²/min² with a correlation coefficient of 0.945. The correlation coefficient for the fit of the data to this reduced form of Eq. 18 was comparable to that using the complete form of Eq. 18. As shown for three typical runs in Figure 3, this model produced an excellent fit to the experimental data for the individual runs.

If growth rate fluctuations alone account for the observed increase in spread, the second term in Eq. 18 becomes negligible ($\sigma^2_{k_G} = 0$). Regression analysis of the experimental data gave the values of $\sigma^2_{L_i}$ as −6.16 ±3.62 μm², k_D as 432 ±61 μm²/min, and m as 1.34 ±0.06 with a correlation coefficient of 0.908. As shown in Figure 3, the fit for the individual experimental runs demonstrates that random growth rate fluctuations alone fail to describe two important characteristics of the CSD. First, it is impossible for the variance of the CSD to be less than zero, as the fit of the data to this reduced form of Eq. 18 has predicted. Second, in most of the experimental runs, even with the desupersaturation of the liquor, the rate of change in the CSD variance continuously increased. If random growth rate fluctuations were responsible for growth rate dispersion, the magnitude of growth rate fluctuations D_G would have to increase as supersaturation decreased to account for the increase in the rate of change of the CSD variance. This relationship would be contrary to the observations of Janse and deJong (1979) and Randolph and White (1971). Also, BCF growth theory indicates that the magnitude of growth rate dispersion should decrease as supersaturation decreases, so that m in Eq. 3 must be greater than zero. The regression gave a value of m greater than zero, but as shown in Figure 3, the model for growth rate dispersion assuming only random growth rate fluctuations provides a poor fit to the data.

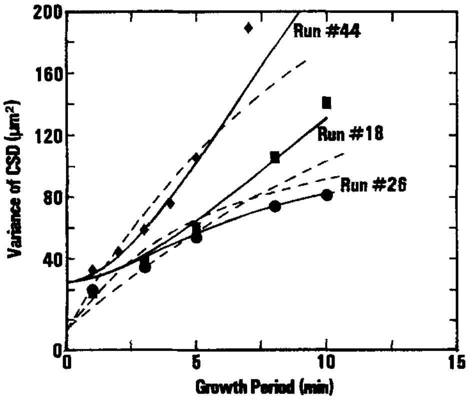

Figure 3. Typical fit for observed variance of a CSD to reduced forms of model, Eq. 18.

—Only a distribution of invariant crystal growth rates $\sigma^2_{L_i} = 25.2$, $\sigma^2_{k_G} = 5{,}698$
– – –Only random growth rate fluctuations; $\sigma^2_{L_i} = -6.16$, $k_D = 432$, $m = 1.34$.

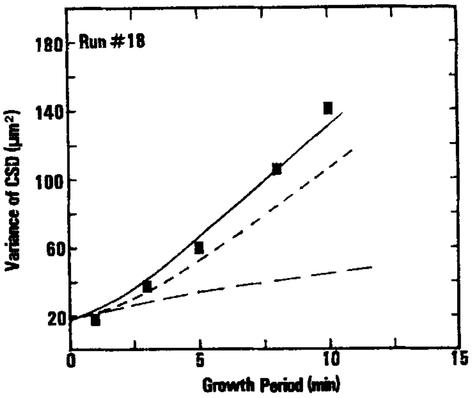

Figure 4. Relative magnitude of two growth rate dispersion mechanisms for a typical run.

—Total predicted increase in variance from Eq. 18; $\sigma^2_{L_i} = 18.2$, $\sigma^2_{k_G} = 4{,}649$, $k_D = 29.1$, $m = 0.98$
– – –Predicted increase due only to distribution of growth rates from Eq. 18; $\sigma^2_{L_i} = 18.2$, $\sigma^2_{k_G} = 4{,}649$
— —Predicted increase due only random growth rate fluctuations from Eq. 18; $\sigma^2_{L_i} = 18.2$, $k_D = 29.1$, $m = 0.98$

From the above observations, it is clear that the growth rate distribution model fits the data much better than the corresponding model based on growth rate fluctuations. The estimate of the variance of the initial size distribution $\sigma^2_{L_i}$ is more reasonable and, as Figure 3 shows, the growth rate distribution model allows the rate of increase for the variance of the crystal size distributions to increase even with the occurrence of liquor desupersaturation. In order to determine if both mechanisms for growth rate dispersion were significant, a partial F-test was used to test the null hypothesis: random growth rate fluctuations are not important given that crystals have a distribution of growth rates. The null hypothesis was rejected at the 95% confidence limit, indicating that addition of the random growth rate fluctuation mechanism to the model does improve the fit to the data. However, as shown in Figure 4, random growth rate fluctuations only account for a small portion of the change in variance for a typical run, so that a distribution of k_G values for the nuclei appears to account for most of the observed growth rate dispersion for the potash alum crystals.

Conclusions

A dual-mechanism model was fitted to experimental data to determine growth rate kinetics and dispersion parameters for potassium alum nuclei resulting from initial breeding. The mean growth rate of the crystals was found to be related to supersaturation by the expression

$$\bar{G}(\mu m/\min) = 138.0\sigma^{1.38} \qquad (19)$$

The experimental data indicated that growth rate dispersion was primarily a consequence of a distribution of crystal growth rates for the nuclei. However, random growth rate fluctuations were also found to be statistically significant. Since the source of growth rate dispersion appears to be the dislocation networks of individual crystals, the magnitude of its influence may vary between different seed populations and the dislocation networks of crystals obtained from initial breeding are expected to be quite different from those of much larger, well-formed crystals used in previous studies.

Notation

A = constant, Eq. 1
a = parameter, Eq. 16
b = parameter, Eq. 16
C = liquor solute concentration
C_s = saturation liquor solute concentration
D_G = growth rate diffusivity parameter
$f(k_G)$ = distribution function of k_G for crystals
$\underline{G}$ = time-averaged crystal growth rate
$\overline{G}$ = mean time-averaged crystal growth rate
k_D = parameter, Eq. 3
$\underline{k}_G$ = growth kinetic constant, Eq. 2
$\overline{k}_G$ = mean growth kinetic constant for all crystals of the CSD
$\underline{L}$ = characteristic one-dimensional crystal size
$\overline{L}$ = number-weighted mean crystal size of population
m = parameter, Eq. 3
m_j = jth moment of population density function
$\overline{m}_j(k_G)$ = jth moment of CSD with growth kinetic constant k_G
N = number of crystals per volume
n = growth kinetic order, Eq. 2
r = dummy variable of integration
s = dummy variable of integration
t = crystallization time

Greek letters

ϵ = screw dislocation activity
σ = relative supersaturation $(C - C_s)/C_s$
σ_1' = parameter, Eq. 1
σ_X^2 = variance of X distribution function

Subscripts

i = nuclei or seed crystals
k = channel k

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