CRYSTALLIZATION KINETICS REVEALED FROM EXPERIMENTAL DATA ANALYZED BY THE TWO-STEP GROWTH MODEL

CLIFFORD Y. TAI
Department of Chemical Engineering, National Taiwan University,
Taipei, Taiwan

Key Words: Crystallization, Two Step Model, Interfacial Supersaturation, Crystal growth Rate, Secondary Nucleation Rate

The two-step crystal growth model has been employed to analyze the crystal growth rate data and much useful kinetic information is revealed. This report summarizes the important findings existing in the literature. Firstly, experimental methods are suggested to determine the parameters in the two-step model and the factors which influence the mass-transfer and surface-reaction coefficients are identified. Then the controlling step of a crystal growth process is judged from the effectiveness factor. Finally, the secondary nucleation rate data are correlated with the interfacial supersaturation, which is a variable appearing in the two-step model. Therefore, the crystal growth rate and secondary nucleation rate are closely related. As a conclusion, crystal growth and secondary nucleation may be considered as coupled phenomenon.

Introduction

The two-step growth model takes account of the mass-transfer and surface-reaction resistances in series and neglects all other resistances in a crystal growth process, which may be expressed mathematically by the following equations:

\[ R_g = K_d (\sigma - \sigma_i) \]  \hspace{1cm} \text{diffusion transport (1)}

and

\[ R_g = K_r \sigma \]  \hspace{1cm} \text{surface reaction (2)}

where \( \sigma \) is the over-all supersaturation, \( (C - C^*)/C^* \), and \( \sigma_i \) is the interfacial supersaturation, \( (C_i - C^*)/C^* \).

A schematic representation of the two-step model is sketched in Fig. 1, in which \( C_i - C^* \) is used to represent the driving force for surface reaction step; it does not mean a concentration profile existing in the adsorption layer (Tai, et al., 1992b).

The importance of the two-step model has long been recognized by Berthoud (1912) and Mullin and Gaska (1969). Due to the uncertainty of \( r \) and unknown of \( \sigma_i \), the model was not widely adopted to express crystal growth rate; instead, an over-all growth-rate expression was widely accepted for design purpose.

\[ R_g = K_g \sigma^n \]  \hspace{1cm} \text{dependence of } K_g \text{ and } n \text{ on the operating conditions is complicated. Thus, estimation of crystal growth rate is not reliable outside the operating conditions or in the scale-up of crystallizers.}

Recent attempts have been made to determine the individual rate constants, \( K_d \) and \( K_r \), and the surface reaction order, \( r \), in the two-step model. The individual rate constants could be correlated with system and operating variables. This enable us to predict crystal growth rate at different operating conditions with more confidence. Besides, some unanswered questions and conflicting results of secondary nucleation rate reported in the literature have been explained by using the interfacial supersaturation, which is a variable appearing in the two-

* Received on August 9, 1996.
step growth model. This review will attempt to summarize the advances in our understanding of the two-step growth model.

Before reviewing the subject of two-step crystal growth model, it should be understood that the linear growth rate of individual crystallographic face of a crystal is different, and hence the interfacial supersaturation may change from face to face. If the crystal growth rate is estimated by the increase of crystal weight, the interfacial supersaturation so obtained is in a sense of average value, unless a crystal possesses the same faces, such as potassium alum crystal. This is why potassium alum is the most studied system. However, in a single crystal study by measuring the linear advance of a crystal face, this problem does not exist.

1. Estimation of Model Parameters—\( K_d, K_r, \) and \( r \)

When crystal growth is regarded as a two-step process, the surface-reaction order is usually unknown, and the two resistances, mass-transfer and surface-reaction resistances, to crystal growth are generally difficult to separate. In early days attempts have been made to determine these model parameters under certain assumptions at appropriate operating conditions. For example, a limiting growth rate is reached at high solution velocities at which the mass-transfer resistance is eliminated (Clontz et al., 1972; Mullin and Garside, 1967), or the crystal growth becomes diffusion control at high temperatures (Rumford and Bain, 1960). However, Garside et al. (1975) pointed out that the validity of limiting rates is suspicious. Occasionally, \( K_d \) is replaced by mass-transfer coefficient of crystal dissolution obtained under similar hydrodynamic conditions, thus \( K_r \) and \( r \) are estimated from Eq. (2) (Garside et al., 1974; Phillips and Epstein, 1974). This assumption is proven to be correct later; however, errors involved in the estimation of \( K_d \) is unavoidable especially for smaller crystals because the edges of seed crystal become rounded in a dissolution experiment (Tai et al., 1987).

A model developed by Garside et al. (1975) is based on the assumption that \( K_d \alpha U^{1/2} \), where \( U \) is the relative velocity between crystal and solution. The resultant equation is given below:

\[
R_g U^{-1/2} = K_d \alpha - (K_p K_r^{-1/r}) R_g^{1/r}
\]

where \( K_p \) is a proportionality. Different values of \( r \) were chosen on a trial and error basis to obtain a linear plot of Eq. (4). Using this procedure, they were able to determine \( K_r \), but left \( K_d \) and \( r \) uncertain. This is because values of \( r \) between 1.5 and 3 all give near-linear plots and the calculated values of \( K_r \) differ by 3% only.

Karpinski "standardized" \( r=2 \) for several systems, including copper sulfate, potassium alum, magnesium sulfate, and sodium thiosulfate (Budz et al., 1984; Karpinski, 1985), to determine the individual rate constants from the following equation, which is derived by combining Eqs. (1) and (2):

\[
\sigma R_g^{-1/2} = K_d^{-1} R_g^{1/2} + K_r^{-1/2}
\]

Thus some interesting growth behaviors concerning mass-transfer and surface-reaction processes were revealed. For example, surface reaction rates exhibited a maximum when cation admixture was present in potassium alum and magnesium sulfate systems (Karpinski, 1985), and the activation energy of diffusion step changed at 318 K for potassium alum crystal (Budz et al., 1985), indicating a change in diffusion mechanism above 318 K.

In principle, estimation of \( r \), \( K_d \) and \( K_r \) can be done by using statistical methods (Tai and Lin, 1987). Eliminating \( \alpha \), Eqs. (1) and (2) are combined to give,

\[
\sigma = p_1 R_g + p_2 R_g^{p_3}
\]

where \( p_1 = K_d^{-1} \), \( p_2 = K_r^{-1/r} \), \( p_3 = r^{-1} \). There are two ways of solving Eq. (6) for the three parameters. The first one is to use a non-linear regression method for estimating the three parameters simultaneously; an alternative is to assume values of \( r \) then followed by a standard least square analysis to find a minimum error for a certain value of \( r \). Tai and Lin (1987) and Tai and Pan (1985) have failed to do so because no convergence for the former method and no minimum error for the latter method were achieved. Tai and Lin (1987) continued their effort to analyze growth rate data of magnesium sulfate using Eq. (7), which is obtained by rearranging Eq. (4).

\[
R_g \sigma^{-1} U^{-1/2} = K_p - K_p K_r^{-1/r} (R_g^{1/2} \sigma^{-1})
\]

Assigning values to \( r \) from 0.5 to 2.0, they were able to find the best fit of growth rate data at \( r=1 \).

Taking temperature and crystal size effects into consideration and assuming that the mass-transfer coefficient follows the Levins and Glastonbury (1972) equation, Qiu and Rasmuson (1990) changed Eq. (6) to the following equation:

\[
\sigma = \frac{R_g}{K_{d0}(M/400)^{0.62} L^{0.17} \exp(-E_0/RT)}
+ \left( \frac{R_g}{K_{r0} L^r \exp(-E_0/RT)} \right)^{1/r}
\]

They were able to determine the five parameters, \( K_{d0}, K_{r0}, m, E_0 \) and \( r \) simultaneously using a nonlinear optimization technique. Sobczak (1990) also deve-
oped an integral method from Eq. (6) to determine the three parameters.

Further, Tai et al. (1990) suggested a method to determine the surface-reaction order using a lean fluidized bed. When a fluidized-bed crystallizer is operated near the terminal velocity of crystal, the mass-transfer coefficient is constant for a given system and can be estimated from the following equation, which was derived theoretically from the Froessling equation,

\[ Sh = \frac{K_d L}{D} = 0.306 \frac{Ga^{1/3} M_v^{1/3} Sc^{1/3}}{D} \tag{9} \]

where \( Ga, M_v \) and \( Sc \) are Galileo number, density number, and Schmidt number respectively. Note that crystal size in Eq. (9) can be cancelled, thus \( K_d \) is a function of system variables only, including diffusivity of solution, density of crystal and solution, and viscosity of solute. Once \( K_d \) is known, \( \sigma_l \) can be calculated from \( R_e - \sigma \) data according to Eq. (1). Then, \( K_e \) and \( r \) are determined from Eq. (2) by plotting \( R_e \) versus \( \sigma_l \).

2. Kinetic Order of Surface-Reaction Step

In the literature several systems have been carefully studied to explore the crystal growth kinetics using the two-step growth model. As shown in Table 1, second-order kinetics of surface-reaction step was found to be appropriate for most of the systems, including copper sulfate, potassium alum, nickel sulfate, magnesium sulfate, and calcium carbonate. On the other hand, magnesium sulfate and sodium chloride exhibit first-order kinetics. For the systems of magnesium sulfate and glutamic acid with or without impurity, the kinetic order varies from 1 to 2 (Tai et al., 1992c), which is consistent with the BCF theory (Burton et al., 1951). When operated in a stirred tank, the kinetic order of three systems, including potassium sulfate, succinic acid, and calcium carbonate, are higher than 2, which can be explained by the NAM growth model (Ohara and Reid, 1973), which is the only model that predicts a growth order of \( r = 2 \) (Nyvlt et al., 1985). From the results of magnesium sulfate, it can be concluded that the kinetic order is influenced by the level of supersaturation as well as the concentration of impurity.

3. Estimation of Crystal Growth Rate in a Fluidized-bed Crystallizer

For design purpose Eq. (3) is frequently used to estimate crystal growth rate. The inadequacy of the growth rate expression has been discussed, that is, the exponent of supersaturation, \( n \), might be a function of crystal size (Tai et al., 1990) and of supersaturation itself (Tai et al., 1987). Efforts devoted to the investigation of crystal growth in a fluidized bed have made the prediction of crystal growth rate more reliable by using the two-step growth model (Tai et al., 1987; Budz et al., 1984; Tai et al., 1990; Mullin and Garside, 1967). From Eq. (9) it is concluded that the mass-transfer coefficient of crystal growth and dissolution is independent of solution velocity and crystal size when a lean fluidized-bed crystallizer is operated near the terminal velocity of crystals. A similar conclusion has been drawn by Tournie et al. (1979) after analyzing extensive crystal dissolution data for both lean and dense fluidized beds. They expressed the best fit of experimental data by the following equation, using a least squares method.

\[ Sh = 0.245 Ga^{0.323} M_v^{0.300} Sc^{-0.400} \tag{10} \]

The difference between Eqs. (9) and (10) is minimal; however, Eq. (10) is an empirical correlation. After the applicability of Eq. (9) was established, \( K_d \) was estimated and \( r \) and \( K_e \) were determined using the \( R_e - \sigma \) data (Tai et al., 1990).

Since \( r \) and \( K_e \) are related to surface processes, they should be independent of hydrodynamics of the system. Therefore, \( r \) and \( K_e \) obtained from a laboratory-scale fluidized-bed crystallizer should be the same as those in a fluidized-bed crystallizer of any scale. This means that \( R_e - \sigma \) data gathered in a laboratory-scale fluidized bed would be adequate for scale-up purpose.

4. Impurity Effect on the Kinetics of Crystal Growth

The presence of impurities or additives, even in a trace amount, can have a pronounced effect on the crystal growth rate. When the two-step growth model is adopted to explore the kinetics of crystal growth, the presence of impurity would influence the growth rate on the individual rate constant, \( K_d \) and \( K_e \), or on the kinetic order of surface reaction, \( r \).

The mass transfer coefficient, \( K_d \), is usually a function of crystal size, hydrodynamic conditions, and system properties. Any change in \( K_d \) caused by the presence of impurity is related to the solution properties, such as density, viscosity, and diffusivity. It seems that high-molecular dye stuff and chromium ion have no effect on \( K_d \) of magnesium sulfate system (Tai and Lin, 1987; Tai et al., 1992c). On the other hand, the values of \( K_d \) of \( \alpha \)-glutamic acid system are decreased by adding L-asp or L-phe to the system (Tai et al., 1992c). An alteration in solution structure at the solution/crystal interface is suspected for this system, but there is no instrumentation available to detect such a change. Recently, Raman spectros-
Table 1  Kinetic order of surface reaction step

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental method</th>
<th>Supersaturation range</th>
<th>Kinetic order r</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>f.b.</td>
<td>ΔW (kg/kg H₂O) 0.008 - 0.06</td>
<td>2</td>
<td>Karpinski (1980)</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>s.c.</td>
<td>σ (−) 0.117 - 0.187</td>
<td>2</td>
<td>Tai and Pan (1985)</td>
</tr>
<tr>
<td>KAl(SO₄)₂·12H₂O</td>
<td>s.c.</td>
<td>σ (−) 0.02 - 0.10</td>
<td>1.7</td>
<td>Garside et al. (1975)</td>
</tr>
<tr>
<td></td>
<td>f.b.</td>
<td>ΔW (kg/kg H₂O) 0.004 - 0.030</td>
<td>2</td>
<td>Budz et al. (1984)</td>
</tr>
<tr>
<td></td>
<td>f.b.</td>
<td>σ (−) 0.045 - 0.169</td>
<td>2</td>
<td>Tai et al. (1984)</td>
</tr>
<tr>
<td></td>
<td>s.c.</td>
<td>0.108 - 0.175</td>
<td>2</td>
<td>Tai and Lin (1987)</td>
</tr>
<tr>
<td>KAl(SO₄)₂·12H₂O/Fe³⁺</td>
<td>f.b.</td>
<td>—</td>
<td>2</td>
<td>Karpinski et al. (1984)</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>f.b.</td>
<td>ΔW (wt. %) 0.1 - 2.5</td>
<td>2</td>
<td>Sobczak (1990)</td>
</tr>
<tr>
<td>MgSO₄·7H₂O/Fe³⁺</td>
<td>f.b.</td>
<td>σ (−) 0.015 - 0.080</td>
<td>2</td>
<td>Karpinski et al. (1984)</td>
</tr>
<tr>
<td>MgSO₄·7H₂O/Cr³⁺</td>
<td>f.b.</td>
<td>—</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>NaClO₃</td>
<td>s.c.</td>
<td>ΔW (wt. %) 0.3 - 1.5</td>
<td>1</td>
<td>Takeuchi et al. (1979)</td>
</tr>
<tr>
<td>MgSO₄·7H₂O, MgSO₄·7H₂O/dye</td>
<td>s.c.</td>
<td>σ (−) 0.0153 - 0.0757</td>
<td>1</td>
<td>Tai and Lin (1987)</td>
</tr>
<tr>
<td>MgSO₄·7H₂O, MgSO₄·7H₂O/Cr³⁺</td>
<td>s.c.</td>
<td>σ (−) 0.0078 - 0.0336</td>
<td>1 - 2</td>
<td>Tai et al. (1992c)</td>
</tr>
<tr>
<td>Glutamic acid, Glutamic acid/L-asp Glutamic acid/L-phe</td>
<td>s.c.</td>
<td>σ (−) 0.170 - 0.365</td>
<td>1 - 2</td>
<td>Tai et al. (1992c)</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>s.t.</td>
<td>σ (−) 0.01 - 0.10</td>
<td>2.4</td>
<td>Garside et al. (1974)</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>s.t.</td>
<td>ΔC (g/kg H₂O) 0.30 - 5.25</td>
<td>3</td>
<td>Qiu and Rasmuson  (1990)</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>s.t.</td>
<td>σ (−) 0.37 - 2.86</td>
<td>2 - 2.2</td>
<td>Tai et al. (1993)</td>
</tr>
</tbody>
</table>

s.c. = single crystal
f.b. = fluidized bed
s.t. = stirred tank

copy (Hussmann et al., 1984) and Synchrotron radiation (Cunningham et al., 1991) have been applied to study the structure of solution/crystal interface. Although ordered species have been observed at the solution/solid interface, no positive conclusion concerning the structure of adsorbed clusters can be drawn at the present time.

The effect of impurity on Kₗ is much complex. Karpinski (1985) analyzed the growth rate data of impure systems, including K-Alum/Fe²⁺, MgSO₄·7H₂O/Fe³⁺, and MgSO₄·7H₂O/Cr³⁺, with a “standardized r”, which has a value of 2. They found that the surface reaction rate increases and then decreases with the addition of impurity. The dye molecules (quinoline yellow) at a concentration of 150 ppm also decreased the surface reaction rate of potassium alum and magnesium sulfate (Tai and Lin, 1987), in a single crystal experiment. Using an MSMPR crystallizer, in which mass transfer resistance is negligible, Tai (1993) found that Cr³⁺ increased, but Bismarch Brown dye decreased the surface reaction rate of potassium alum in an impurity concentration range from 5 to 550 ppm, and a dispersing agent, (NaPO₄)₆, had no effect at all in the

376 JOURNAL OF CHEMICAL ENGINEERING OF JAPAN
concentration range 5 to 300 ppm. Thus, different types of impurity may have distinct effect on the surface-reaction kinetics of a crystal.

To investigate the impurity effect, Tai et al. (1992c) utilized a modified two-step model, i.e., Eq. (2) was replaced by the BCF equation, which is Eq. (11), to analyze the crystal growth rate data of several systems, including magnesium sulfate/Cr$^{3+}$, α-glutamic acid/L-as, and α-glutamic acid/L-phe.

$$R_g = \frac{c}{\sigma_c} \sigma_{tanh} \left( \frac{\sigma_c}{\sigma_t} \right)$$  \hspace{1cm} (11)

The model parameters $c$ and $\sigma_c$ were influenced by the addition of impurity. In the supersaturation range studied, it is clearly seen that the surface reaction order changed from 1 to 2 for the magnesium sulfate/Cr$^{3+}$ system, and from 2 to 1 for the α-glutamic acid/L-as and α-glutamic acid/L-phe systems. Thus, the change in $K_r$ and $r$ due to surface adsorption or structure incorporation of impurity species may account for the growth rate dispersion of some cases.

5. Effect of Crystal Size on the Individual Rate Constants in an Agitated Tank

There are two types of correlation existing in the literature to estimate mass-transfer coefficient in an agitated tank.

$$Sh = 2 + A_1 \left( \frac{LU}{v} \right)^{1/2} Sc^{1/3}$$ \hspace{1cm} (12)

and

$$Sh = 2 + A_3 \left( \frac{L^{4/3} d^{1/3}}{v} \right)^{0.6} Sc^{1/3}$$ \hspace{1cm} (13)

The former was proposed by Nienow (1975) and the latter by Levin and Glastonbury (1972). In Eq. (12), $U$ is the average relative velocity between particle and fluid. The relative velocity between particle and fluid varies from point to point in an agitated tank and is a function of system geometry. Thus, an average value of $U$ is difficult to estimate (Tai and Yu, 1989). Equation (13) predicts $K_d \propto L^{-0.2}$ for large crystal size, i.e., $K_d$ decreases with an increase in crystal size. This equation has been employed to estimate the mass-transfer coefficient of crystal growth (Qiu and Rasmussen, 1990) or crystal dissolution (Toprac and Rochelle, 1982). By using the two-step growth model to analyze the crystal growth data, however, it was found that the mass-transfer coefficient increased with increasing particle size for several systems, including potassium sulfate (Garside et al., 1974), potassium alum (Tai and Yu, 1989), and calcium carbonate (Tai et al., 1993). Therefore, prediction of mass-transfer coefficient in an agitated tank using either of the correlations mentioned above is not reliable at the present time.

The effect of crystal size on the surface-reaction rate constant has been reported in several studies, including the systems of potassium sulfate (Garside et al., 1974), potassium alum (Tai and Yu, 1989) and calcium carbonate (Tai et al., 1993). The surface-reaction rate increases with increasing crystal size. Similar results were also found when crystals were grown in a fluidized-bed crystallizer (Phillips and Epstein, 1974; Tai et al., 1987; Budz et al., 1984). A possible explanation of size effect on $K_r$ is that larger crystals are likely to suffer more violent collisions, which cause surface damage resulting in more spiral centers and giving a higher growth rate (Garside et al., 1974).

6. Controlling Step in a Crystal Growth Process

The weight of the two resistances, mass-transfer and surface-reaction resistance, in a growth process varies from one case to another. The controlling step can be judged from the effectiveness factor, which was well established in reaction engineering and was introduced to the field of crystal growth by Garside (1971). The surface-reaction effectiveness factor was derived as the following equation for a $r$th-order surface-reaction rate:

$$\eta_r = (1 - \eta_r Da^r)$$ \hspace{1cm} (14)

where $Da = K_d \sigma^{-1} / K_r$. The effectiveness factors are plotted against $Da$ for $r$ being equal to 1, 2, and 3 as shown in Fig. 2. This figure can be used to judge the controlling step of a crystal growth process once the parameters of the two-step model are known. For example, if the calculated $Da$ is 0.05 for a first order surface-reaction rate and the $\eta_r$ is 0.95, the crystal growth process can be considered as surface-reaction control.

The controlling step of a crystal growth process may alter along with a change in a process variable. For example, Tai et al. (1987; 1990) measured the growth rate of potassium alum crystal of various sizes in a batch fluidized bed. After analyzing the crystal growth data with the two-step model, it was found that the mass-transfer coefficient was almost constant for all crystal sizes. When crystal size is smaller than $4\times10^{-4}$ m, the mass-transfer resistance is negligible and the surface reaction is the controlling step. With increasing crystal size, the surface-reaction coefficient increases so that the mass-transfer resistance becomes significant. Then, the crystal growth rate tends to level off. Finally, the crystal size has no effect on the crystal growth rate since both coefficients are constants. In the constant growth rate region, both
resistances are equally important, judging from the effectiveness factor.

7. Judgement on the Adequacy of Over-all Growth Rate Equation

The application of the over-all growth rate expression, Eq. (3), for design purpose was usually confined to a limited range of operating variables. The adequacy of this equation can be judged by using the two-step model. Actually, the exponent of supersaturation, $n$, is the average slope of $R_g - \sigma$ curve in a specified supersaturation range, and is related to $K_d$, $K_r$, and $\sigma$. For illustration two $R_g - \sigma$ curves of a second-order surface reaction system are plotted in Fig. 3; one with $K_d = 2.50 \times 10^{-7}$ kg/m$^2$s and $K_r = 2.78 \times 10^{-9}$ kg/m$^2$s, and the other one with the same $K_d$ but $K_r = 2.78 \times 10^{-7}$ kg/m$^2$s. When the operating supersaturation falls between 0.117 and 0.187, the average slopes of the two curves are 1.4 (curve a) and 1.8 (curve b) respectively. However, if the supersaturation is below 0.01, the average slopes of both
curves are quite close to 2.0 in any supersaturation range.

When impurity is present in a system, the over-all order may or may not change. Tai and Pan (1985) studied the growth kinetics of copper sulfate crystal with the single-crystal growth technique. They found that the addition of quinoline yellow dye did not alter the over-all order as shown in Fig. 4, although a reduction in \( K_r \) is about 40%. It is because the operating range of supersaturation is far from the intersection of the two lines representing pure diffusion and surface reaction as shown in Fig. 5. However, as illustrated in Fig. 6, the over-all order for potassium alum crystal appeared differently when 130 ppm of the same impurity was present (Tai and Lin, 1987). This is because the dye has a greater effect on \( K_r \) of potassium alum, and it is the case shown in Fig. 3.

Solution velocity also has an effect on the over-all order as shown in Figs. 4 and 6; however, the solution velocity effect is minimal when it was set below 0.13 m/s for the impure system of potassium alum.

8. Secondary Nucleation Rate

Strickland-Constable and his co-workers (Lal et al., 1969; Garabedian and Strickland-Constable, 1972) and McCabe and his co-workers (Clontz and McCabe, 1972; Tai et al., 1975) demonstrated the dual role of supersaturation in the determination of secondary nucleation rate, i.e., supersaturation influences the number of nuclei generated by contact and the survival fraction of the generated nuclei. The supersaturation is referred to the overall supersaturation. This concept has been accepted by the researchers of crystallization community. Later on, Tai et al. (1992b) proposed a hypothesis that solute clusters queuing up in an adsorption layer and awaiting incorporation into the growing crystal turned out to be the nuclei after a contact, and the key variable in determining the number of nuclei resulting from a contact event was the supersaturation within the layer, which is identical to the interfacial supersaturation in the two-step growth model. Thus, the dual role of supersaturation is modified to that the number of nuclei generated by contact is influenced by the interfacial supersaturation and the fraction of nuclei survived in the development period is determined by the overall supersaturation.

Based on the hypothesis proposed by Tai et al. (1992b), Tai and Shih (1997) derived a new model of secondary-nucleation rate in a stirred-tank crystallizer,

\[
B^0 = \frac{K_r^{\infty} \sigma_i^b L^3 n^* dL}{L_s}
\]

(15)

Direct integration of Eq. (15) is impossible because \( b \) is usually unknown and \( \sigma_i \) is a complex function of \( L \) and \( \sigma \). However, Eq. (15) can be reduced to a simple form at specific conditions as listed in Table 2. It is noted that Eq. (T1) is the most encountered case; however, both \( \sigma \) and \( \sigma_i \) appear simultaneously in a nucleation rate equation for the case in which the mass-transfer and surface-reaction resistances are significant.

To verify the adequacy of Eq. (T4) in Table 2, Tai and Shih (1997) conducted a crystallization experiment of potassium alum crystal in a fluidized bed, in which both mass-transfer and surface-reaction resistance are important for a crystal growth process. The secondary nucleation rate data were then correlated with \( \sigma \), \( \sigma_i \) and \( Re \) as:

\[
B^0 = 9.55 \times 10^{-4} Re^{2.4} (\sigma)^{1.4} \sigma^{1.0}
\]

(16)

with an error of 15.9%, which is defined as:

\[
\phi = \sqrt{\sum \left( \frac{B^0(\text{exp}) - B^0(\text{cal})}{B^0(\text{cal})} \right)^2}
\]

(17)

where \( B^0(\text{exp}) \) and \( B^0(\text{cal}) \) are the experimental value and calculated value of nucleation rate respectively. However, if the interfacial supersaturation \( \sigma_i \) is omitted, the correlation became

\[
B^0 = 4.80 \times 10^{-4} Re^{2.5} \sigma^{2.1}
\]

(18)

with an error of 34.2%, which is much greater than
Table 2 Expressions of reduced secondary nucleation rate

<table>
<thead>
<tr>
<th>Limiting conditions</th>
<th>Reduced nucleation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal growth process is controlled by surface reaction, $a = a_1$</td>
<td>$K_0 M_0 a'$</td>
</tr>
<tr>
<td>Crystal growth process is controlled by diffusion, $a = 0$</td>
<td>where $r = a + b$</td>
</tr>
<tr>
<td>Surface reaction rate is first order with respect to interfacial supersaturation</td>
<td>$K_0 M_0 a'$</td>
</tr>
<tr>
<td>and McCabe $\Delta L$ law holds.</td>
<td>where $r = a_1 / a_2$, is a constant</td>
</tr>
<tr>
<td>Surface reaction rate is first order with respect to interfacial supersaturation</td>
<td>$K_0 a^2(K + \sqrt{K^2 + 4K_0^2})M_i$</td>
</tr>
<tr>
<td>and McCabe $\Delta L$ law holds.</td>
<td>where $K = K_d / K_r$, is a constant</td>
</tr>
<tr>
<td>Minimum size required for generating secondary nuclei and population density curve</td>
<td>$K_0 a^2 R_0 M_i$</td>
</tr>
<tr>
<td>is nearly straight for crystals larger than the minimum size.</td>
<td>$K_0 a^2 R_0 M_i$</td>
</tr>
</tbody>
</table>

15.9% of Eq. (16). Thus, Eq. (16) is a more adequate form to express the secondary nucleation rate.

Conclusion

Although the two-step model is a simplified scheme for crystal growth, it revealed much useful kinetic information. The parameters of this model can be determined experimentally. Thus, it is more advantageous to use the two-step model than to use the overall growth model for design purposes. Besides, the secondary-nucleation rate data correlates well with the interfacial supersaturation, which is a variable appearing in the two-step crystal growth model. Therefore, we may consider the mechanisms of crystal growth and secondary nucleation as coupled.

Acknowledgment

The author gratefully acknowledge the financial support of the National Science Council of the Republic of China.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>exponent of overall supersaturation in Eq. (15)</td>
</tr>
<tr>
<td>$B^0$</td>
<td>nucleation rate</td>
</tr>
<tr>
<td>$b$</td>
<td>exponent of interfacial supersaturation in Eq. (15)</td>
</tr>
<tr>
<td>$C$</td>
<td>bulk concentration</td>
</tr>
<tr>
<td>$C_i$</td>
<td>solution concentration at solution/crystal interface</td>
</tr>
<tr>
<td>$C^*$</td>
<td>equilibrium concentration</td>
</tr>
<tr>
<td>$c$</td>
<td>parameter in BCF equation</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusivity</td>
</tr>
<tr>
<td>$Da$</td>
<td>Damkohler number</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy of diffusion</td>
</tr>
<tr>
<td>$E_r$</td>
<td>activation energy of surface reaction</td>
</tr>
<tr>
<td>$G$</td>
<td>crystal growth rate of pure diffusion or surface reaction</td>
</tr>
<tr>
<td>$Ga$</td>
<td>Galileo number, $L^3 \rho^2 g / \mu^2$</td>
</tr>
<tr>
<td>$K_d$</td>
<td>diffusion rate constant</td>
</tr>
<tr>
<td>$K_{do}$</td>
<td>diffusion rate constant $[m/s(kg/kg solvent)]$</td>
</tr>
<tr>
<td>$K_r$</td>
<td>overall growth rate constant</td>
</tr>
<tr>
<td>$K_r$</td>
<td>surface-reaction rate constant</td>
</tr>
<tr>
<td>$K_0$</td>
<td>surface-reaction rate constant</td>
</tr>
<tr>
<td>$L$</td>
<td>crystal size</td>
</tr>
<tr>
<td>$L_s$</td>
<td>effective crystal size of secondary nucleation</td>
</tr>
<tr>
<td>$M$</td>
<td>impeller rotation speed</td>
</tr>
<tr>
<td>$M_v$</td>
<td>Density number $(p_v - p)/p$</td>
</tr>
<tr>
<td>$M_i$</td>
<td>magma density</td>
</tr>
<tr>
<td>$n$</td>
<td>parameter in Eq. (8)</td>
</tr>
<tr>
<td>$n$</td>
<td>number of data point</td>
</tr>
<tr>
<td>$n$</td>
<td>overall order of growth rate</td>
</tr>
<tr>
<td>$n^*$</td>
<td>population density</td>
</tr>
<tr>
<td>$P_i$</td>
<td>parameters in Eq. (6), $i = 1, 2, 3$</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number, $nuL/\mu$</td>
</tr>
<tr>
<td>$R_s$</td>
<td>linear growth rate of crystal</td>
</tr>
<tr>
<td>$r$</td>
<td>surface reaction order</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt number, $\mu / \rho D$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$V$</td>
<td>solution velocity</td>
</tr>
<tr>
<td>$U$</td>
<td>relative velocity between solution and crystal</td>
</tr>
</tbody>
</table>

$\varepsilon$ = energy dissipation rate in an agitated vessel $[J/s \cdot k g]

$\eta$ = effectiveness factor of surface reaction $[\text{---}]

$\mu$ = viscosity of fluid $[kg/m/s]

$\nu$ = kinematic viscosity of fluid $[m^2/s]

$\rho$ = solution density $[kg/m^3]

$\rho_p$ = crystal density $[kg/m^3]

$a_o$ = over-all supersaturation, $(C - C^*)/C^*$ $[\text{---}]

$\sigma_i$ = interfacial supersaturation $(C_i - C^*)/C^*$ $[\text{---}]

$\sigma_0$ = parameter in BCF equation $[\text{---}]

$\phi$ = regression error defined in Eq. (17) $[\text{---}]

Literature Cited


Budr, J., P.H. Karpinski and Z. Nuruc; “Effect of Temperature on


Nyvlt, J., O. Sohnle, M. Matuschova and M. Broul; The Kinetics of Industrial Crystallization; p. 186 – 189, Elsevier, Amsterdam, Netherlands (1985)


