Letter to the Editors

A new model relating secondary nucleation rate and supersaturation

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Abstract

A new model of secondary nucleation rate regarding the effects of supersaturation is presented. The model takes account of the interfacial supersaturation, which influences the number of nuclei that is produced, and the overall supersaturation, which determines the fraction of nuclei that survived. The interfacial supersaturation can be replaced by the crystal growth rate so that the nucleation rate equation includes the overall supersaturation and crystal growth rate. This is different from the nucleation models used in the literature with only one of them appearing. Simplified models of the nucleation rate are derived and presented.

Secondary nucleation has been recognized as the dominant mechanism of nucleation in a suspension crystallizer. This was, however, uncertain till the early work on contact nucleation, or collision breeding, was reported. Using different experimental techniques in two separate laboratories, Strickland-Constable and co-workers [1–3] and McCabe and co-workers [4–7] presented evidences showing that contact nucleation was dominating at low supersaturation. They also demonstrated the dual role of supersaturation in the determination of the secondary nucleation rate; both on the generation and development stages of nuclei. The supersaturation is referred to the overall supersaturation, $C - C^*$. However, there is a hypothesis brought up by Tai et al. [8] that the number of nuclei which survive in the development period is determined by the overall supersaturation but the number of nuclei generated by the contact is influenced by the interfacial supersaturation. The interfacial supersaturation is a variable

appearing in the two-step model of crystal growth, which can be expressed mathematically as:

$$G = k_d(\sigma - \sigma_i), \quad \text{diffusion}, \tag{1}$$

$$G = k_r(\sigma_i)^{n_g}, \quad \text{surface reaction}, \tag{2}$$

where σ, i.e., $(C - C^*)/C^*$, is the dimensionless overall supersaturation, and σ_i, i.e., $(C_i - C^*)/C^*$, the dimensionless interfacial supersaturation. Since the driving force $\sigma - \sigma_i$ is for the diffusion, it is no longer effective in generating secondary nuclei which come from the adsorption layer. Thus, the number of nuclei generated by the contact mechanism should be a function of interfacial supersaturation instead of overall supersaturation. It should be noted that the interfacial supersaturation is related to the overall supersaturation in different ways. The interfacial supersaturation will change with the overall supersaturation in the same direction, or in the opposite direction as demonstrated by Tai et al. [8]. The aim of this communication is to show how the interfacial supersaturation would affect the rate of secondary nucleation.

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Ottens and de Jong [9] have developed a model of contact nucleation in a stirred-tank crystallizer. They began with the expression for the nucleation rate of $n \, dL$ crystals between size L and $L + dL$.

$$dB^0 = k_3(C - C^*)^q \omega_L E_L n \, dL, \tag{3}$$

where ω_L is the crystal-impeller contact frequency and E_L the impact energy associated with the contact. They assumed that both the number of nuclei generated and the portion of nuclei survived are functions of the overall supersaturation. According to the hypothesis proposed by Tai et al. [8], however, the number of crystals produced per unit time in the generation stage is

$$dJ = k_4 \sigma_i^{n_b} \omega_L E_L n \, dL. \tag{4}$$

Eq. (4) is similar to Eq. (3), except for $C - C^*$ being replaced by σ_i.

For all sizes of crystals in suspension, the total number of nuclei produced is

$$J = \int_{L_x}^{\infty} k_4 \sigma_i^{n_b} \omega_L E_L n \, dL, \tag{5}$$

where L_x is the minimum crystal size which contributes to secondary nucleation.

Bauer et al. [10] have assumed that the crystal–impeller contact frequency for a homogeneous suspension is a function of the magma circulation rate and target efficiency:

$$\omega_L = k_w(\phi_v/V_c)\eta_t = k_w(k_p n_r D_r^3/V_c)\eta_t, \tag{6}$$

where ϕ_v is the pumping capacity of the impeller, V_c the total volume of the crystallizer, η_t the target efficiency, n_t the impeller speed, and D_t the impeller diameter.

The impact energy E_L is proportional to the crystal mass of size L and the square of the tip speed of the impeller V_t [11]:

$$E_L \propto m_L(V_t)^2 \propto m_L(n_r D_r)^2, \tag{7}$$

and since

$$m_L = k_v \rho_s L^3 \tag{8}$$

Eq. (5) may be written as

$$J = k_5 \int_{L_x}^{\infty} (n_r^3 D_r^5/V_c) \sigma_i^{n_b} \eta_t L^3 n \, dL. \tag{9}$$

For a given crystallizer operating at constant agitation rate, Eq. (9) becomes

$$J = k_6 \int_{L_x}^{\infty} \sigma_i^{n_b} \eta_t L^3 n \, dL, \tag{10}$$

Table 1
Expression of reduced secondary nucleation rate

The general secondary nucleation rate equation

$$B^0 = k_7 \sigma^s \int_{L_x}^{\infty} \sigma_i^{n_b} L^3 n \, dL \tag{11}$$

Limiting condition	Reduced nucleation rate	
Crystal growth process is controlled by surface integration, $\sigma = \sigma_i$.	$k_8 M_T \sigma^r$ where $r = s + n_b$	(12)
Crystal growth process is controlled by diffusion, $\sigma_i = 0$.	Nucleation rate is insignificant	
Surface integration rate is first order with respect to interfacial supersaturation and McCabe Δ law holds.	$k_9 M_T \sigma^r$	(13)
Surface integration rate is second order with respect to interfacial supersaturation and McCabe Δ law holds.	$k_{10} \sigma^s(-K_T + \sqrt{K_T^2 + 4K_T \sigma})^{n_b} M_T$ where $K_T = k_d/k_r$, is a constant.	(14)
Minimum size required for generating secondary nuclei and population density curve is nearly straight for crystals larger than the minimum size.	$k_{11} \sigma^s \sigma_i^{n_b} M_T$	(15)
	$k_{12} \sigma^s G^\beta M_T$	(16)

where J is the production rate of particles in the generation stage. If the effect of supersaturation on the survival stage is considered and the target efficiency is neglected, i.e. $\eta_t = 1$, the nucleation rate can be expressed as:

$$B^0 = k_7 \sigma^{-s} \int_{L_x}^{\infty} \sigma_i^{n_b} L^3 n \, dL. \qquad (11)$$

In Eq. (11) the relation between the survived fraction of nuclei and the overall supersaturation is assumed to be a power-law function as proposed by Garside and Davey [12].

Direct integration of Eq. (11) is impossible because n_b is unknown for most systems and σ_i is a complex function of L and σ; σ_i varies with the particle size of the crystals under the constraint of constant σ. However, Eq. (11) can be reduced to a simple form at limiting conditions. The expressions

of reduced secondary nucleation rate are summarized in Table 1.

To use Eq. (15), σ_i should be determined. In the literature the mass-transfer coefficient can be obtained from the crystal dissolution [13] or it can be estimated by a modified Froessling equation [14]. Practically, Eq. (16) is much easier to use than Eq. (15) because crystal growth rate G can be determined from the nearly straight portion of the population density curve.

So far, only a few experimental results in the literature can be used to support the hypothesis, but they are not conclusive. In order to gather more experimental evidences, experiments should be carefully designed. For instance, both the mass-transfer and surface-reaction resistance should be significant for the chosen system; or a suitable type of crystallizer other than a stirred tank should be used in order not to eliminate the mass-transfer resistance. Effort in this direction is continued in our laboratory.

Nomenclature

J	number of crystals produced per unit time in the generation stage	[no. of crystal/s (m^3 of suspension)]
k_r	surface-integration rate constant	[m/s]
k_v	volume shape factor of the crystal	[–]
L	crystal size	[m]
M_T	magma density	[kg/m^3 of suspension]
m_L	mass of a crystal of size L	[kg]
n	crystal population density	[no. of crystal/m$^3 \cdot \mu$m]
n_r	agitation rate	[rpm]
s	the exponent of overall supersaturation in Eq. (11)	[–]
V_c	crystallizer volume	[m^3]
V_t	tip speed of impeller	[m/s]
β	n_b/n_g	[–]
η_t	target efficiency	[–]
ρ	solution density	[kg/m^3]
ρ_s	crystal density	[kg/m^3]
ϕ_v	pumping capacity of the impeller	[m^3/s]

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