R & D NOTES

Importance of Slip Velocity in Determining Growth and Nucleation Kinetics in Continuous Crystallization

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Nucleation and growth kinetics have been investigated for many crystallization systems from analysis of the steady state population density distribution of mixed suspension, mixed product removal (MSMPR) crystallizers (Randolph and Larson, 1971). Plots of the logarithm of crystal population density (CPD) n against particle size L have been shown to be linear for a great many crystallization systems, and for the following relationship:

$$n = \frac{B^0}{G} e^{-L/GT} \tag{1}$$

Growth rate data can be obtained from the slope of the logarithm of n versus L, and nucleation data from the intercept when $L = 0$. Two basic assumptions are important to the derivation of Equation (1): (1) nucleation spontaneously occurs at a size very close to $L = 0$; (2) growth rate is not size dependent.

In more recent years, a careful examination of the small size range of the CPD has shown a break from linearity in the 50 to 100-μm region. Investigations of Glauber's salt (Canning and Randolph, 1967), alum (Timm and Larson, 1968), potassium sulfate (Cise and Randolph, 1967; Randolph and Cise, 1972; Rosen and Hulburt, 1971a), and ammonium sulfate (Youngquist and Randolph, 1972) show considerable departure from Equation (1) below 100 μm. This departure has previously been attributed to secondary nucleation.

This note will look at another aspect of the interpretation of the CPD to evaluate nucleation and growth rate for crystallization systems: the effect of slip velocity on CPD. It is suggested that crystal growth rate can have a dependency on crystal size such that the linearity of the plot of the logarithm of CPD against crystal size is effected only in the smaller size region.

The general equation for an unseeded MSMPR crystallizer at steady state assuming homogeneous nucleation is (Randolph and Larson, 1971)

$$\frac{d(Gn)}{dL} = -\frac{n}{T} \tag{2}$$

Rearranging Equation (2):

$$dn/dL = -\frac{n}{G}\left(\frac{1}{T} + \frac{dG}{dL}\right) \tag{3}$$

If G were not a function of L, Equation (3) could be solved to give Equation (1). However, G is considered a function of L because of the change in growth rate caused by variations in slip velocity which accompanies differences in crystal size.

Although the concepts developed in this paper can apply to any crystallization system, the relationships for the K_2SO_4-water system are used because of the extensive data available. Growth rate data has been obtained from a fluidized bed crystallizer by Mullin and Gaska (1969) and Rosen and Hulburt (1971b). Although the absolute values of the growth rates found for K_2SO_4 by these two investigators differ, they agree on two fundamental points: first, the growth rate increases with increasing solution velocity past the surface of the crystal (slip velocity) until a limiting velocity is reached above which no further increase of growth accompanies an increase in solution velocity; second, the growth rate is second order with respect to supersaturation. Particle size distributions have been obtained by Rosen and Hulburt (1971a) in a vacuum crystallizer and Randolph et al. (Cise and Randolph, 1972; Randolph and Cise, 1972; Randolph and Rajagopal, 1970) in a cooling crystallizer. The studies indicate a considerable departure from Equation (1) in the size range below 60 μm, which is partly explained by secondary nucleation phenomena.

The growth rate of K_2SO_4 in aqueous solution has been found to follow (Rosen and Hulburt, 1971b):

$$G = 0.68\ (1 - 0.92\ e^{-0.41v})\ s^2 \tag{4}$$

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The growth rate of K_2SO_4 is not directly a function of particle size. Although a relationship such as Equation (4) has not been developed for other crystallization systems, there are reports in the literature which qualitatively support this relationship. Single crystal studies of ammonium phosphate (Mullin and Amatavivadhana, 1967), itaconic acid (Pindzola, 1958), and aluminum potassium sulfate (Mullin and Garside, 1967), as well as fluidized bed studies of aluminum potassium sulfate, show an increase in growth rate with increase in slip velocity up to a limiting velocity.

Nienow, Bujal, and Mullin (1972) have studied slip velocities in agitated vessel crystallizers. They found that the slip velocity was related to the terminal velocity v_t, a ratio of the impeller speed N, to the impeller speed just necessary to suspend a particle N_s and an enhancement factor E which compensates for the enhancement of slip velocity due to turbulence in the system.

$$v = E^2 \, v_t \, (N/N_s)^{0.8} \tag{5}$$

Although E was shown to be a slight function of particle size, the scatter of data in the size range of particles of K_2SO_4 was so great that a constant value of 1.15 will be used for this study.

The terminal velocity is calculated over two regions. For $N_{Re} < 2$, the drag force is proportional to the terminal velocities, and Stokes' Law can be applied. The terminal velocities for $N_{Re} \geqq 2$ can be found from a relationship used by Nienow, Bujal, and Mullin (1972) up to a particle size of 500 μm.

$$v_t = 5.44 \times 10^{-5} \, \Delta\rho L^2/\mu \qquad N_{Re} < 2 \tag{6a}$$

$$v_t = 4.06 \times 10^{-3} \, \frac{L^{1.14}\Delta\rho^{0.71}}{\rho^{0.29} \, \mu^{0.43}} \qquad N_{Re} \geqq 2 \tag{6b}$$

The value of N_s related to the physical parameters of an agitated system is given by Zwietering (1958):

$$N_s = \frac{143 \, (\mu/\rho)^{0.1} \, (\Delta\rho/\rho)^{0.45} \, W^{0.13} \, L^{0.2}}{D_s^{0.85} \, f} \tag{7}$$

The parameter f is a function of type of impeller and crystallizer configuration and is determined graphically.

Equations (5), (6), and (7) can be combined to give the necessary relationship between slip velocity and particle size:

$$\begin{aligned} v &= C_s \, L^{1.84} \qquad N_{Re} < 2 \\ v &= C_a \, L^{0.98} \qquad N_{Re} \geqq 2 \end{aligned} \tag{8}$$

where C_s and C_a are complicated functions of the physical parameters of the crystallizer system, but are constant for a particular crystallizer run.

Combining Equations (4) and (8) yields the necessary relationship between growth rate and particle size.

$$\begin{aligned} G &= 0.68 \, (1 - 0.92 \, e^{-0.41} \, C_s L^{1.84}) s^2 \qquad N_{Re} < 2 \\ G &= 0.68 \, (1 - 0.92 \, e^{-0.41} \, C_a L^{0.98}) s^2 \qquad N_{Re} \geqq 2 \end{aligned} \tag{9}$$

Equation (9) can be combined with Equation (3), and the resulting first-order differential equation can be solved by numerical techniques.

An example is given using vacuum crystallizer cumulative number distribution data (Rosen and Hulburt, 1971a-Run 6). The cumulative number distribution data is easily converted to CPD data by differentiation.

Equation (6) was shown to have two branches; the first characterizing flow below a N_{Re} of 2 and the second above a N_{Re} of 2. The two branches do not meet at $N_{Re} = 2$, and thus the discontinuity is smoothed to make a continuous function. The particle size at the break point of the two branches can be calculated by equating Equation (6b) with $N_{Re} = 2$. Using the physical constants $\Delta\rho$ of 1.56 gm/cc and μ of 1.2 cp, the particle size at the break point is found to be 1.35 μm. The value of v_t at 135 μm can be calculated for Equation (6b). The discontinuity between Equations (6a) and (6b) is smoothed by multiplying Equation (6a) by the constant necessary to make v_t equal in both branches of the equation at $N_{Re} = 2$. The constant calculates to 1.039 in this sample. This small difference of less than 4% is not thought to significantly affect the results of the analysis.

The relationship of slip velocity with particle size is plotted in Figure 1 from Equation (8). For L given in μm and v in cm per second, the values of C_s and C_a are 2.75×10^{-4} and 1.87×10^{-2}, respectively (crystallizer dimensions of D_s, C, D_t equal 0.635, 0.635, 0.210 m, respectively, and f equals 7.2). The slip velocity is nearly linear down to a particle size of 135 μm and parabolic below this size.

As calculated from Equation (9), the growth rate approaches a limiting value of 0.342 mm/hr at large particle size, drops sharply with decrease in size below 300 μm, and approaches a stagnant solution growth rate of 0.029 mm/hr at zero size (Figure 1). Although Equation (9) is only valid up to 500 μm, extrapolation of the relationship beyond this point does not effect the results since the growth rate has already reached 98% of the limiting velocity at 500 μm.

The CPD from a typical vacuum crystallization run is presented in Figure 2. The circles represent the data points, the dashed line represents the relationship following Equation (1), and the solid line is the solution of Equation (3) including the correction for slip velocity of Equation (9).

The analysis of the CPD including a slip velocity correction fits the data down to 200 μm. Although the data fit of the slip velocity analysis is not good in the smaller size regions, the trend of the calculated CPD plot is consistent with the experimental data.

Considering the slip velocity analysis, the evaluation of growth rate and nucleation rate from the CPD can be re-

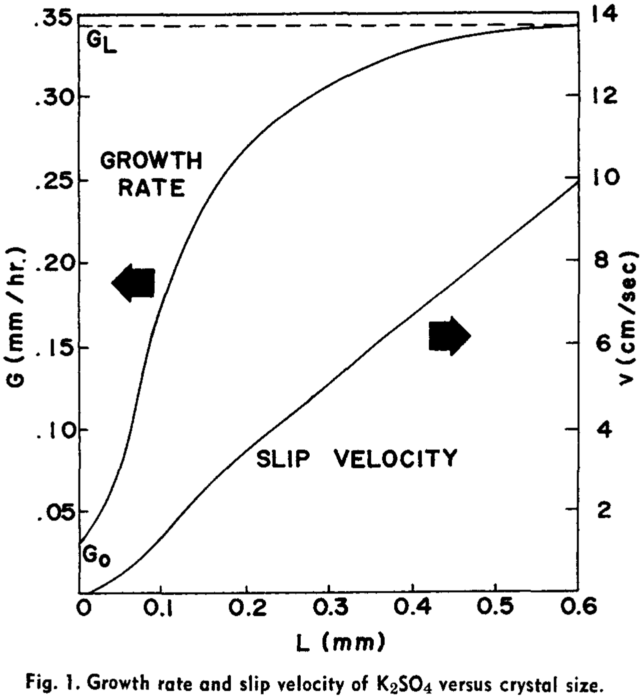

Fig. 1. Growth rate and slip velocity of K_2SO_4 versus crystal size.

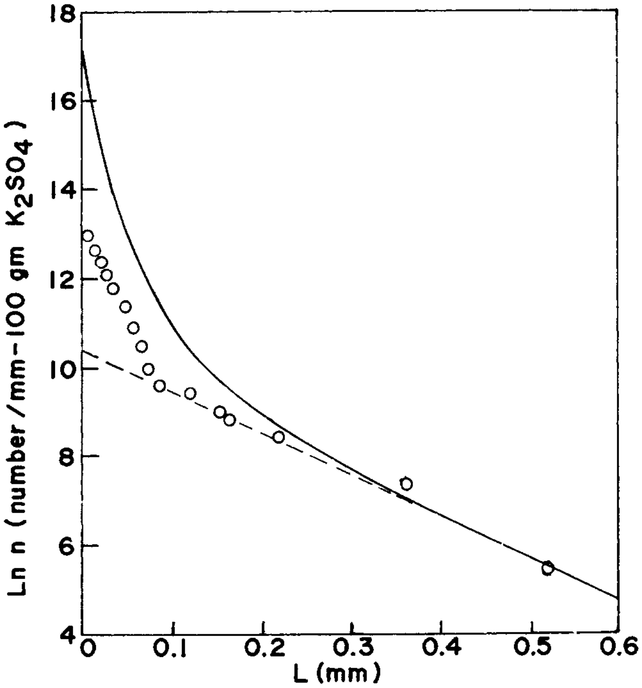

Fig. 2. Population density distribution for vacuum crystallization of K_2SO_4. (T = 0.31 hr, s = 0.71 g/100 g water, N = 1000 rev./min. W = 2.3%)

examined. The dG/dL term in Equation (3) approaches zero at two extremes—large particle size and small particle size. The limiting growth rate, G_L, [G as $v \rightarrow \infty = 0.68\ s^2 = G_L$ by Equation (4)] can be related to the slope of the CPD over the linear portion in the large size range; above 200 μm in the example case. The nucleation rate can be related to the intercept at $L = 0$, and is equal to e^{B/G_0}, where G_0 is the stagnant solution growth rate [G as $v \rightarrow 0 = 0.56\ s^2 = G_0$ by Equation (4)].

The slip velocity analysis can explain a number of apparent conflicting results in the literature concerning the effect of crystal size on the growth rate of K_2SO_4. McCabe's Law states that the growth rate is independent of particle size. Rosen and Hulburt (1971b) confirmed this for particles above 550 μm. For a slip velocity above the limiting velocity, growth rate is independent of size. However, when small particles are suspended in a fluidized bed crystallizer of MSMPR crystallizer, this limiting velocity is not realized, and growth rate becomes an indirect function of size because of the influence of slip velocity. This argument supports results obtained by Mullin and Gaska (1969). The conclusion of Randolph and Cise (1972) that "the growth rate of crystals in the 1.3 to 26 μm size range are markedly size-dependent, decreasing with decreasing size" is also supported by the slip velocity analysis.

The author admits there are a number of model-oriented interpretations that could fit the data of Figure 2, as well or better than the slip velocity analysis. The real mechanisms of the crystallization process are probably a combination of secondary nucleation, diffusional processes, agglomeration, etc., as well as the slip velocity effect. Variation in slip velocity with crystal size which reflects a mass transfer limitation can effect the shape of the CPD plot and consequently should be included in the determination of growth and nucleation kinetics.

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NOTATION

B = nucleation rate per unit volume of suspension, number/cm^3-hr.
C = distance between stirrer and bottom of vessel, m
D_s = stirrer diameter, m
D_t = tank diameter, m
E = enhancement factor
f = dimensionless parameter in Equation (7)
G = growth rate, mm/hr.
G_L = limiting growth rate, mm/hr.
G_0 = stagnant solution growth rate
L = crystal size, μm
n = crystal population density, number/mm-100 gm K_2SO_4
N = impeller speed, rev./min.
N_{Re} = Reynolds number, $Lv_t\rho/\mu$
N_s = impeller speed to just suspend particle, rev./min.
s = supersaturation, g/100 g water
T = drawdown time, hr.
v = slip velocity, cm/s
v_t = terminal velocity, cm/s
W = weight of solids in suspension per weight of liquid × 100
μ = viscosity, cp
ρ = solution density, g/cm^3
$\Delta\rho$ = density difference of solid and liquid phase, g/cm^3

LITERATURE CITED

Canning, T. F., and A. D. Randolph, "Some Aspects of Crystallization Theory: Systems that Violate McCabe's Delta L Law," *AIChE J.*, 13, 5 (1967).

Cise, M. D., and A. D. Randolph, "Secondary Nucleation of Potassium Sulfate in a Continuous-Flow Seeded Crystallizer," *Chem. Eng. Progr. Symp. Ser. No. 121*, 68, 42 (1972).

Mullin, J. W., and A. Amatavivadhana, "Growth Kinetics of Ammonium- and Potassium-Dihydrogen Phosphate Crystals," *J. Appl. Chem.*, 17, 151 (1967).

Mullin, J. W., and J. Garside, "The Crystallization of Aluminum Potassium Sulfate: A Study in the Assessment of Crystallizer Design Data," *Trans. Inst. Chem. Engrs.*, **45**, T285 (1967).

Mullin, J. W., and C. Gaska, "The Growth and Dissolution of Potassium Sulfate in a Fluidized Bed Crystallizer," *Can. J. Chem. Eng.*, 47, 483 (1969).

Nienow, A. W., P. D. B. Bujal, and J. W. Mullin, "Slip Velocities in Agitated Vessel Crystallizers," *J. Crystal Growth*, **13/14**, 488 (1972).

Pindzola, A. D., "Growth Rates of Single Itaconic Acid Crystals, M.S. thesis, Polytechnic Inst. of Brooklyn, New York (1958).

Randolph, A. D., and M. D. Cise, "Nucleation Kinetics of the Potassium Sulfate-Water System," *AIChE J.*, 18, 798 (1972).

Randolph, A. D., and M. A. Larson, *Theory of Particulate Processes*, Academic Press, New York (1971).

Randolph, A. D., and K. Rajagopal, "Direct Measurement of Crystal Nucleation and Growth Rate Kinetics in a Backmixed Crystal Slurry," *Ind. Eng. Chem. Fundamentals*, 9, 165 (1970).

Rosen, H. N., and H. M. Hulburt, "Continuous Vacuum Crystallization of Potassium Sulfate," *Chem. Eng. Progr. Symp. Ser. No. 110*, 67, 18 (1971).

————————., "Growth Rate of Potassium Sulfate in a Fluidized-Bed Crystallizer," *ibid.*, 27.

Timm, D. C., and M. A. Larson, "Effect of Nucleation Kinetics on the Dynamic Behavior of a Continuous Crystallizer," *AIChE J.*, 14, 452 (1968).

Youngquist, G. R., and A. D. Randolph, "Secondary Nucleation in a Class II System: Ammonium Sulfate-Water," *ibid.*, 18, 421 (1972).

Zwietering, T. N., "Suspending of Solid Particles in Liquid by Agitators," *Chem. Eng. Sci.*, 8, 244 (1958).

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