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Influence of Crystal Size on the Rate of Contact Nucleation in Stirred-Tank Crystallizers

The purpose of this study was to investigate the influence of seed crystal size on the rate of nucleation in batch stirred-tank crystallizers. Experimental results confirm the existence of such an effect. Nucleation rate data are correlated with a second-order polynomial in seed crystal size; coefficients of the correlation are functions of the solute-solvent system, crystallizer geometry, and mixing conditions. The empirical correlation is incorporated into a population balance model for determining the nucleation rate in multi-seed crystallizers. The observed results are explained in terms of variations in impact energy, circulation frequency, and target efficiency.

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SCOPE

Secondary crystal nucleation is defined as the formation of crystals in the presence of growing seed crystals—the condition under which most industrial crystallizers operate. Contact nucleation, a subset of secondary nucleation, is defined as the formation of crystals as a result of the collision of a seed crystal with a solid object. Pioneering work on contact nucleation by Clontz and McCabe (1971) and Johnson, Rousseau, and McCabe (1972) has demonstrated that an increase in impact energy results in an increase in the number of nuclei formed as a result of that impact. Furthermore, Ottens and DeJong (1972), showed that the primary source of contact nucleation in stirred-tank crystallizers is the collision of seed crystals with the impeller. When these observations were considered together, it was believed that a variation in impact energy within stirred-tank crystallizers could result from a variation in seed crystal size as well as impeller speed.

However, previous stirred-tank studies on contact nucleation had been conducted in crystallizers whose product streams, and necessarily the in-tank liquor, contained distributions of crystal sizes. Such systems made it difficult to isolate the effect of seed crystal size on the contact nucleation rate from existing data. Therefore, an experimental program was developed to observe and correlate this phenomenon. With the results of this study a better understanding of the variables affecting contact nucleation in batch and continuous stirred-tank crystallizers is to be achieved. Furthering the state of knowledge in this area will lead to better nucleation control in systems where excessive in insufficient nucleation is of concern.

CONCLUSIONS AND SIGNIFICANCE

The influence of seed crystal size on the nucleation rate in batch stirred-tank crystallizers has been demonstrated. Nucleation rates were correlated with seed crystal size at various stirrer speeds and at fixed supersaturation and crystallizer geometry. Expressing the size-dependent nucleation rate as $B_L{}^0\left[\dfrac{\text{nuclei generated}}{(\text{time})(\text{volume})(\text{seed crystal})}\right]$ and the population density as $n\left(\dfrac{\text{number of seed crystal}}{(\text{volume})(\text{size})}\right)$, a model was proposed for incorporating the size-dependent nucleation rate into the determination of an overall nucleation rate for multi-seed crystallizers:

$$B^0 = \int_0^\infty B_L{}^0\, ndL$$

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Modifying the model proposed by Ottens and DeJong (1972), it was further shown that the nucleation rate could be expressed in terms of a target efficiency η_t or the fraction of the particles within a given size range which impact an object placed in a flowing stream of those particles. Specifically

$$B^0 = k_5 \epsilon \int_0^\infty \eta_t L^3 \, ndL$$

Experiments have also shown that the nucleation rates of K_2SO_4 and $MgSO_4 \cdot 7H_2O$ exhibit the same seed crystal size-dependency but that the nucleation rates of $MgSO_4 \cdot 7H_2O$ are roughly 10^2 those of K_2SO_4. This result agrees with studies attributing the variation in contact nucleation characteristics to crystal hardness; that is, the harder the crystal face the lower the contact nucleation rates.

Observation of the crystal dynamics in the stirred-tank crystallizer has shown that the circulation frequency of a seed crystal depends upon the size of that crystal. It is incorrect to assume this quantity a constant and equal to the circulation rate of the fluid, as was done by Ottens and DeJong (1972) in the development of their model.

Contact nucleation results from the contact of growing crystals with a solid object; it is the dominant nucleation mechanism for systems operating at low supersaturations. Crystal contacts which may result in nucleation include crystal-agitator, crystal-wall, and crystal-crystal impacts. Ottens and DeJong (1972) reported that for their work with a stirred-tank crystallizer, crystal-crystal, and crystal-wall contacts contributed negligibly when compared to the nucleation resulting from crystal-agitator impacts. These results are compatible with those of Clontz and McCabe (1971), Johnson, Rousseau, and McCabe (1972), Denk and Botsaris (1972), and Bauer, Larson, and Dallons (1973) all of whom showed that the number of nuclei generated by a crystal-solid contact increased with an increase in the energy of impact; that is, the contacts involving an agitator will impart more energy to the crystal than any of the other forms of impact.

Previous studies have not considered the influence of particle dynamics on the probability of a crystal colliding with an agitator and the concomitant effect on contact nucleation. Bennett et al. (1973) considered the flow of solution through the plane of the impeller (or pump head in a circulation cycle) to carry crystals along in a uniform distribution and assumed all of these crystals had an equal probability of impacting the agitator. However, basic work on the probability of a particle in a moving stream colliding with an object placed normal to the direction of flow has shown this not to be the case. In particular, Lapple (1950) defines a term called *target efficiency* η_t as the fraction of the particles in a stream that strikes a solid object placed in the path of the stream. The target efficiency is a function of the shape of the target and can be correlated with a dimensionless parameter, the separation number N_{sep} defined as

$$N_{sep} = u_t \, u_0 / g \, D_b \qquad (1)$$

Lapple's correlation for a ribbon-shaped target shows that as the terminal velocity of a particle in a static layer of the liquid carrier decreases, which corresponds to a reduction in its size while holding the shape constant, its chance of striking the target diminishes. Eventually some particle size is reached where a further reduction in size gives no collisions. Clearly then, the probability of a particle striking the impeller is a function of the particle properties, particularly those which determine terminal velocity.

The analysis in the previous paragraph assumes that all particles (crystals) are uniformly distributed and have an equal probability of passing through the plane of the impeller. Nienow (1968) and Aeschback and Bourne (1972) have shown that a homogeneous suspension of particles of various sizes can only be achieved at agitation intensities greater than some system-dependent minimum; at low agitation, larger particles settle to the bottom of the vessel and are not circulated. If the two concepts of target efficiency and minimum agitation levels for uniform particle suspension are considered together, it is to be expected that the relation between nucleation rate and crystal size would be as follows: nearly zero until some minimum crystal size is reached after which the nucleation rate would increase with increasing crystal size, pass through a maximum and decrease until a limiting crystal size was obtained where crystal circulation ceased. Nucleation due to the presence of these large seed crystals would then be due only to their sliding along the bottom of the crystallizer. This expected relationship assumes that contact nucleation is the dominant nucleation mechanism.

Since the size of a crystal would seem to have a dramatic influence on the nucleation rate, it was the purpose of this study to begin an analysis of this phenomena with the goal of incorporating the results into a model that would be useful in the design, scale-up, and control of stirred-tank crystallizers.

EXPERIMENT

The crystallizer used in this investigation was a circular jar with an inside diameter of 13.3 cm. It was equipped with three vertical baffles and a tight fitting plastic cover which was constructed to accommodate the agitator shaft, a thermometer, and a pipette for sampling. Each of the baffles was 15.2 cm long, 1.59 cm wide, and were mounted 120° apart about 3.2 cm from the floor of the vessel. Agitation was with a 5-cm stainless steel marine propeller having a 1:1 pitch and driven by a variable speed motor. For all experiments the distance between the propeller and the bottom of the crystallizer was 7.25 cm. The flow of the solution through the propeller was downward.

The crystallizer was immersed in a constant temperature bath in which the temperature was controlled to ±0.05°C. The volume of the solution filled the crystallizer to a level of about 0.6 cm above the top of the baffles. Solution concentrations were determined from refractive index vs. concentration calibration curves. The solubility data of Ting and McCabe (1934) were used for $MgSO_4$ while that of Mullin (1972) was used for K_2SO_4.

An experimental run involved the determination of the solute concentration in the aqueous solution followed by cooling to a supersaturation level of 3.0°C (the $MgSO_4$ concentration was in the range of 28 to 30 wt. %, while that of K_2SO_4 was 11 to 12 wt. %); when the proper supersaturation was achieved, the agitation was stopped and a cured seed crystal was dropped into the solution and allowed to settle to the floor of the crystallizer. Agitation at the desired stirrer speed was then started.

The instant the crystal began to moved around on the floor of the vessel was designated as the beginning of the experiment. At the end of a 2-min. period, agitation was stopped and the seed crystal was carefully retrieved from the solution.

The solution was then allowed to remain unagitated at the run temperature for 2¼ hours. This was sufficient time for the nuclei formed during the 2-min. experiment to grow large

enough to be counted visually. On several occasions the crystallizer was returned to the water bath at the run temperature and the crystals were recounted after 2 hours to check the initial count. Normally the two counts agreed within 10%.

In several experiments the $MgSO_4$ solution in the crystallizer was sampled at the end of the growth period to determine if the concentration had undergone any significant depletion as a result of crystal growth. The concentration was found to be constant during the experiment.

Immediately after removal from the crystallizer, excess solution was wiped from the seed crystal, the crystal was weighed, and its major dimensions measured with the aid of a microscope.

The result of the experiments was the determination of the number of crystals produced per minute as a function of the crystal size for a fixed crystallizer geometry, stirrer speed, and supersaturation.

EXPERIMENTAL RESULTS

No nuclei were formed in control experiments (experiments without the addition of a seed crystal) which confirmed that the nuclei formed in the seeded experiments were a result of the presence of the cured seed crystal and not the result of homogeneous or heterogeneous nucleation.

During the course of the experiments, it was observed that the seed crystal would often bounce along the floor of the crystallizer and that the amount of time the crystal spent on the crystallizer floor depended on its size—just a few seconds for the smaller crystals to as long as one-half of the 2-min. run time for the largest crystals. When the smaller crystals did lift off the floor, they made as many as 45 to 60 passes during the 2-min. experiment while the larger crystals made as few as 12 passes. A pass is defined as one complete cycle from the floor of the crystallizer upward along the wall and then downward near the propellor. Not all passes of the crystal resulted in a crystal-agitator collision. Frequently, especially in cases where the crystal was 8 mm or larger, an audible impact was heard as the crystal passed downward in the vicinity of the propellor. For crystals 8 mm and larger, 8 to 15 of these impacts were noted during the course of the 2-min. experiment. Audible crystal-agitator collisions did not occur for crystals smaller than approximately 8 mm, but this does not mean that impeller-crystal impacts did not occur, only that they were inaudible. Generally, the larger the crystal the greater the frequency of known crystal-agitator collisions.

Inspection of Table 1 shows that both the potential and known crystal-agitator contacts increase with an increase

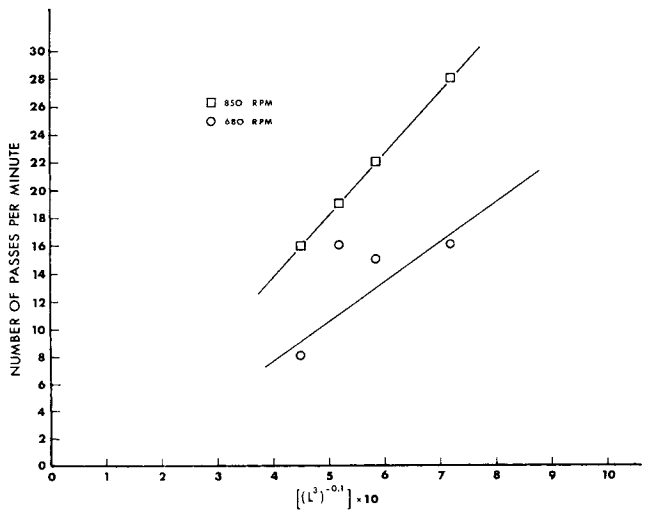

Fig. 1. Correlation of circulation frequency.

TABLE 1. AVERAGE NO. OF PASSES/MIN.—AVERAGE NO. OF KNOWN CONTACTS/MIN.

Crystal size, mm	Agitation rate, rev./min. 350	600	850
3	3-0	16-0	28-0
6	—	15-0	22-0
9	—	16-3	19-6
14	—	8-5	16-9

in the agitation rate for a given crystal size. It is clear then that, for a fixed crystal size, more crystal-agitator collisions occur as the stirrer speed is increased, and these occur at higher contact energies. It is equally important that for a fixed agitation level the number of passes a crystal makes through the plane of the impeller decreases as the crystal size increases. Assuming the data of Table 1 may be represented by a relationship in which the number of passes is proportional to $(m_L)^s$ or to $(L^3)^s$, data may be plotted as in Figure 1 for $s = -0.1$. A linear relationship is noted for the 850 rev./min. curve, but the data for the 680 rev./min. curve is somewhat scattered. These curves suggest that the number of passes per minute, at a fixed agitation level, is inversely proportional to the mass of the crystal to the 0.1 power. Such is expected to be the case as long as the prevailing agitation is less than the minimum agitation level necessary to provide a uniform suspension throughout the vessel. Once this minimum rate is exceeded, the number of passes is expected to be independent of crystal size.

It is likely that the nuclei formed in these experiments were produced by the seed crystal sliding across the floor of the crystallizer as well as by impacting the agitator. However, in view of the vast difference in contact energies between the sliding contact and a crystal-agitator contact, and the relatively few nuclei produced by crystals too large to be lifted off the floor of the vessel, it is believed that virtually all the nuclei produced by the larger crystals (those greater than 8 mm) are the result of crystal-agitator collisions.

Crystals smaller than 8 mm were in suspension for almost the entire 2-min. run. Furthermore, a careful observation of crystals of this size range revealed that crystal-vessel floor contacts were nil even though a crystal would occasionally be thrown against the wall of the crystallizer. Usually a crystal would be drawn into the agitator and appear to strike it on the downstream side (back side) of the propellor. This is strong evidence that crystal-impeller impacts are the major source of nucleation for smaller seed crystals.

The results of these experiments are shown in Figures 2 and 3. In the former, the size-dependent nucleation rate is indicated for crystals up to approximately 15 mm in length. At the larger sizes the number density of the crystals produced was so great that accurate counting was prohibited. For this reason, and because industrial crystallizers seldom produce crystals larger than a few mm, experiments at larger sizes were not attempted.

The data of Figure 2 are truncated at a crystal size of 8 mm and presented in Figure 3. The curves shown in Figure 3 are second-order polynomials in seed crystal size which were obtained using a least squares curve fitting criterion. The correlation coefficient for the 850, 680, and 350 rev./min. curves at 0.986, 0.979, and 0.782, respectively. Defining B_L^0 as the size-dependent nucleation rate with units of number per min per unit number of crystals of size L, the correlations at various agitation rates are

$$B_L^0 = 0.405L - 2.85 \times 10^{-5}L^2 \quad \text{for} \quad 850 \text{ rev./min.} \quad (2)$$

$$B_L^0 = 0.192L - 1.16 \times 10^{-5}L^2 \quad \text{for} \quad 680 \text{ rev./min.} \quad (3)$$

$$B_L^0 = 0.054L - 4.25 \times 10^{-6}L^2 \quad \text{for} \quad 350 \text{ rev./min.} \quad (4)$$

where L is in microns.

Figures 2 and 3 show that, for a given agitation rate, the number of crystals produced increases with increasing seed crystal size, which is in agreement with the target efficiency concept. However, such results may also be explained by the increase in contact energy associated with the crystals at the larger sizes. It can be seen also from Figure 3 that the number of crystals produced increased with an increase in the agitation rate, at a fixed crystal size.

To determine whether or not size-dependent nucleation was peculiar to $MgSO_4 \cdot 7\ H_2O$ crystals, several experiments were conducted using K_2SO_4 seed crystals. At identical conditions of crystallizer geometry, agitation rate and supersaturation, $MgSO_4 \cdot 7\ H_2O$ crystals produced nearly two orders of magnitude more nuclei than did K_2SO_4 crystals; in the case of seed crystals weighing 2 mg, 730 $MgSO_4 \cdot 7\ H_2O$ crystals were produced compared to 10 K_2SO_4 crystals, at an agitation rate of 850 rev./min. The experiments using K_2SO_4 gave similar results to those where $MgSO_4 \cdot 7\ H_2O$ crystals were used; that is, the number of nuclei produced increased as the crystal size increased. The difference between the observed nucleation rates for $MgSO_4 \cdot 7\ H_2O$ and K_2SO_4 is consistent with the studies of Johnson, Rousseau, and McCabe (1972) showing that nucleation by crystal contacts resulted in a much larger number of crystals for $MgSO_4 \cdot 7\ H_2O$ than for K_2SO_4. These authors attributed this to the difference in crystal surface hardness; K_2SO_4 has a much harder surface than $MgSO_4 \cdot 7\ H_2O$ and is apparently less susceptible to contact nucleation.

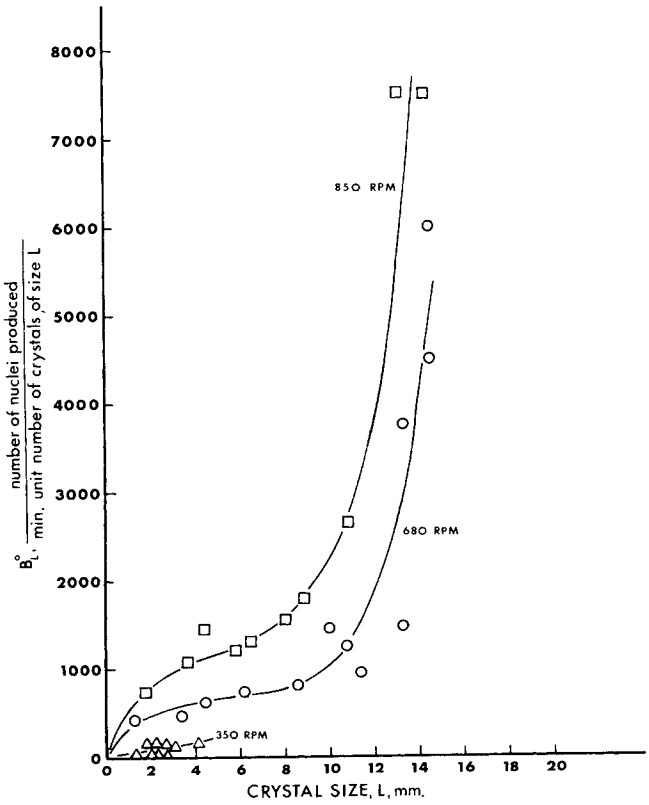

Fig. 2. Least squares fit of nucleation rates for all seed crystals (L_{max} = 15 mm).

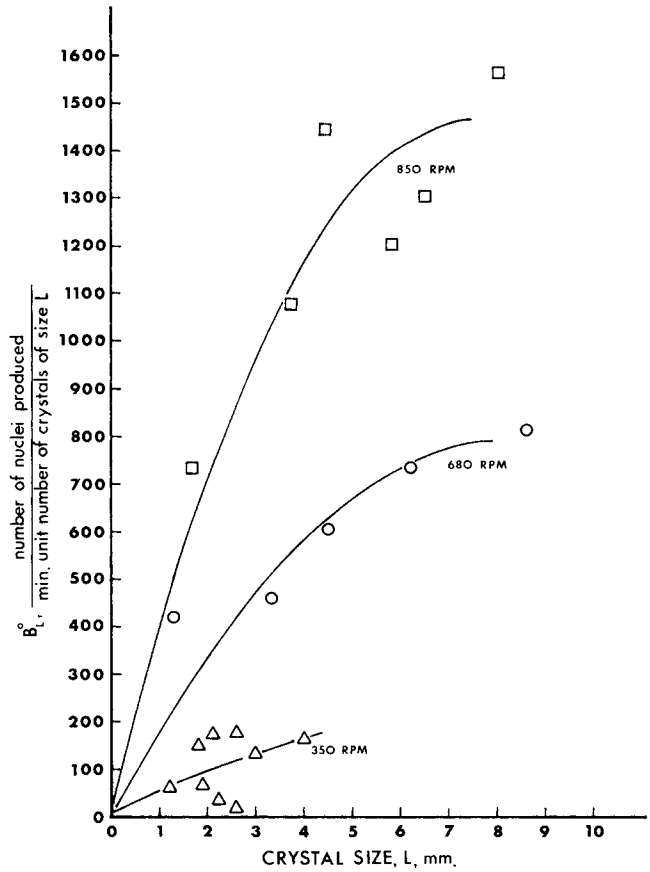

Fig. 3. Least squares fit of nucleation rates for seed crystals less than 8 mm in length.

A MODEL FOR CONTACT NUCLEATION IN CONTINUOUS CRYSTALLIZERS

If the number of crystals of a given size, say L, and the number of nuclei produced per minute per crystal of size L were known, the nucleation rate for the entire crystallizer could be expressed as

$$B^0 = \sum_{L=0}^{\infty} B_L^0 N_L \quad (5)$$

where B_L^0 is the size dependent nucleation rate and N_L is the number of crystals of size L per unit volume. Alternatively, the rate of contact nucleation due to crystals in the size range L to $L + dL$ can be expressed as the product of the number of crystals of size $L_1 (L < L_1 < L + dL)$ and the number of nuclei generated per minute per unit number of crystals of size L_1. For a mixed-suspension mixed-product removal (MSMPR) crystallizer this becomes

$$dB^0 = B_L^0\, n dL \quad \text{and} \quad B^0 = \int_0^{\infty} B_L^0\, n dL \quad (6)$$

Equation (6) can also be written as

$$B^0 = \int_0^{\infty} \nu_L\, f_L\, n\, dL \quad (7)$$

where ν_f is the size-dependent nuclei generating function and f_L is the size-dependent crystal-agitator contact frequency. Clearly

$$B_L^0 = \nu_L\, f_L \quad (8)$$

Equation (6) is similar in form to an equation presented by Ottens and deJong (1972) and Ottens (1973).

To compare the nucleation rate predicted by Equation (6) with the experimentally determined values reported in the literature, an examination of MSMPR data presented by Genck and Larson (1972) and by Ottens (1973) was undertaken. These authors reported the necessary parameters of n, B^0, and agitation rate that allowed the desired comparison to be made. Recalling from Figure 3 that $B_L{}^0$ is a function of the agitation rate, the relationship for $B_L{}^0$ used in Equation (6) was chosen so as to approximate (as closely as possible) the agitation rate reported by these investigators. The limits of integration used in conjunction with Equation (6) were an upper limit of 8 mm and a lower limit of zero.

The initial comparison was made using the data of Genck and Larson whose experimental systems were KCl and KNO_3 in a draft tube crystallizer operated at a maximum agitation rate of 1725 rev./min. They reported nucleation rates in the order of 1×10^5 nuclei per minute; values of the nucleation rates given by Equation (6), using the $B_L{}^0$ function evaluated at 850 rev./min., were a factor of 500 greater than those reported by Genck and Larson. Several factors could account for the difference between the calculated and experimentally determined nucleation rates:

1. There is a significant difference in the nucleation characteristics of KCl and KNO_3 as compared to those of $MgSO_4 \cdot 7H_2O$. Lal, Mason, and Strickland-Constable (1969) reported that KCl nucleated more easily than $MgSO_4 \cdot 7H_2O$ under the same conditions.

2. The experiments on which the comparison is based were performed at different supersaturations; $B_L{}^0$ was evaluated at a higher supersaturation than used by Genck and Larson. The maximum supersaturation used by Genck and Larson was about 1°C, while that used to evaluate $B_L{}^0$ was 3°C.

3. Genck and Larson operated their crystallizer (a) at agitation rates corresponding to a maximum mixing Reynolds number of about 67,000, (b) a propeller diameter to tank diameter ratio of 0.278, and (c) with a draft tube. In this investigation (a) the mixing Reynolds number was 10,000, (b) the propeller diameter to tank diameter was 0.376, and (c) no draft tube was used. All these factors, in addition to the particle density differences—1.68 ($MgSO_4 \cdot 7H_2O$), 1.99 (KCl), 2.11 (KNO_3)—contribute to making the circulation rates different in each of these systems.

4. In the MSMPR system used by Genck and Larson, washout of small crystals allowed them to go undetected and results in an observed nucleation rate that is smaller than the true nucleation rate. The magnitude of the loss of nuclei due to washout is unknown; further, its effect on the evaluation of the nucleation rate is not clear.

A similar comparison was made between the calculated nucleation rate using Equation (6) and the nucleation rates obtained by Ottens (1973) who investigated the crystallization of potassium alum in a baffled MSMPR crystallizer with cooling coils immersed in the solution. The comparisons were made using data that Ottens obtained from a 10-liter crystallizer operating at agitation rates of 1000 to 1500 rev./min. At these conditions it was determined that nucleation rates were about 1×10^8 nuclei/s/m^3 of solution. The calculated nucleation rate using Equation (6) was about a factor of 100 higher than what Ottens had measured. The principal factors causing this difference are believed to be the same as those given in discussing Genck and Larson's data.

REFINEMENT OF THE OTTENS MODEL FOR CONTACT NUCLEATION

Ottens developed a model for contact nucleation in stirred-tank crystallizers that is similar to that used to produce Equation (6); his model results in the expression

$$J = k_n \, \epsilon M r^q \tag{9}$$

where

$$\epsilon = \frac{n_r{}^3 \, D_r{}^5 \, N_{Po}}{V_{tc}} \tag{10}$$

The nomenclature is that used by Ottens. In the development of this equation, Ottens began with the expression

$$dJ = k\omega_L E_L (\Delta c)^p \, n \, dL \tag{11}$$

which says that the nucleation rate caused by particles within the size range L to $L + dL$ is proportional to the number of crystal-agitator contacts and the energy associated with these contacts.

Assuming that the contact frequency between the crystals and the agitator is equal to the circulation frequency of an element of fluid volume, and therefore independent of crystal size,

$$\omega_L \simeq \omega = \frac{k_p n_r D_r{}^3}{V_{tc}} \tag{12}$$

Relating contact energy to the mass of the impacted crystal and the impeller tip speed

$$E_L = k_E m_L \, v_r{}^2 = k_E \, n_r{}^2 \, D_r{}^2 \, m_L \tag{13}$$

and since

$$m_L = k_v \, \rho_s \, L^3 \tag{14}$$

Equation (11) may be written

$$dJ = k \left(\frac{n_r{}^3 \, D_r{}^5}{V_{tc}} \right) (\Delta c)^p \, n \, L^3 \, dL \tag{15}$$

Since $dJ = dB^0$, rearrangement of Equations (6) and (15) gives

$$B_L{}^0 = k \left(\frac{n_r{}^3 \, D_r{}^5}{V_{tc}} \right) (\Delta c)^p \, L^3 \tag{16}$$

For a given crystallizer and constant supersaturation

$$B_L{}^0 = k_1 \, n_r{}^3 \, L^3 \tag{17}$$

This equation is in agreement with Figures 2 and 3 which show that $B_L{}^0$ is a function of crystal size and agitation rate. Further, if $B_L{}^0$ were plotted against L^3 at a fixed level of agitation as shown in Figure 4, a straight line should result if k_1 is a true constant with respect to L. Note, however, that linearity holds over the range $L = 4$ to 8 mm but not at smaller sizes; necessarily then k_1 is a function of crystal size below $L = 4$ mm. Since k_1 contains several constants, it is possible to assign the variation of k_1 to a number of factors; however, the most questionable assumption appears to be that contained in Equation (12) which postulates that the frequency of crystal-agitator contact is proportional to the circulation frequency of the magma in passes per unit time and is independent of crystal size. The concept of target efficiency and the data presented in Figure 1 challenge the validity of this assumption.

The crystal-agitator contact frequency is, therefore, a function of: (1) the magma circulation rate, (2) the mass of the seed crystal, and (3) the target efficiency associated with the given system and the crystal size. Mathematically

$$\omega_L = k_2\left(\frac{k_p\, n_r\, D_r^3}{V_{tc}}\right)\eta_t\, m_L^s \qquad (18)$$

where $s = 0$ for a uniform suspension. Substituting Equations (13) and (18) into Equation (11)

$$dJ = k_3\,\frac{n_r^3\, D_r^5}{V_{tc}}\,\eta_t\, m_L^{1+s}\,(\Delta c)^p\, n\, dL \qquad (19)$$

from Equation (10)

$$dJ = k_3\left(\frac{\epsilon}{N_{Po}}\right)\eta_t\, m_L^{1+s}\,(\Delta c)^p\, n\, dL \qquad (20)$$

If supersaturation and the power number are constant:

$$dJ = k_4\,\epsilon\,\eta_t\, m_L^{1+s}\, n\, dL \qquad (21)$$

For homogeneous suspension, $s = 0$ and

$$J = k_4\epsilon\int_0^\infty \eta_t\, m_L\, n\, dL = k_5\epsilon\int_0^\infty \eta_t L^3\, n dL \qquad (22)$$

For systems where $s \neq 0$, such as the case discussed earlier where $s = -0.1$, an equation analogous to Equation (22) could be obtained simply by integrating Equation (21) with the appropriate value of s.

TARGET EFFICIENCY

The effect of particle size on target efficiency is illustrated by Figure 5 which is based on the $MgSO_4 \cdot 7H_2O$ system used in this investigation; the particles are assumed to be spherical and the agitation is set at 700 rev./min. In developing this plot, the separation number N_{sep} is calculated as given by Equation (1). The fluid velocity can be estimated using a correlation proposed by Rushton and Oldshue (1953) for marine impellers

$$u_0 = 0.4\, n_r D_r^3/A \qquad (23)$$

where A is the area of the circle with a diameter equal to D_r. The terminal velocity is determined for the appropriate flow regime depending on the particle size, and once N_{sep} has been determined for a given particle diameter, the target efficiency can be obtained from Lapple (1950). Although the plot of η_t vs. N_{sep} given in Lapple is strictly applicable only to particles in the Stokes flow regime, it may be assumed to give a reasonable approximation of the dependence of η_t on particle size for other

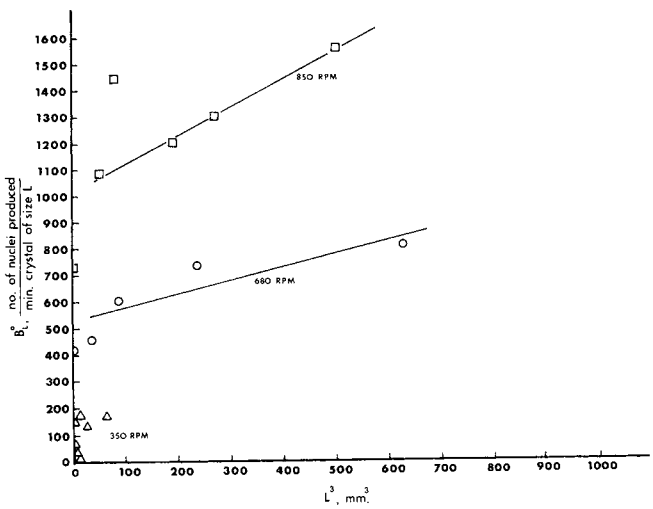

Fig. 4. Correlation of size effect on nucleation rate.

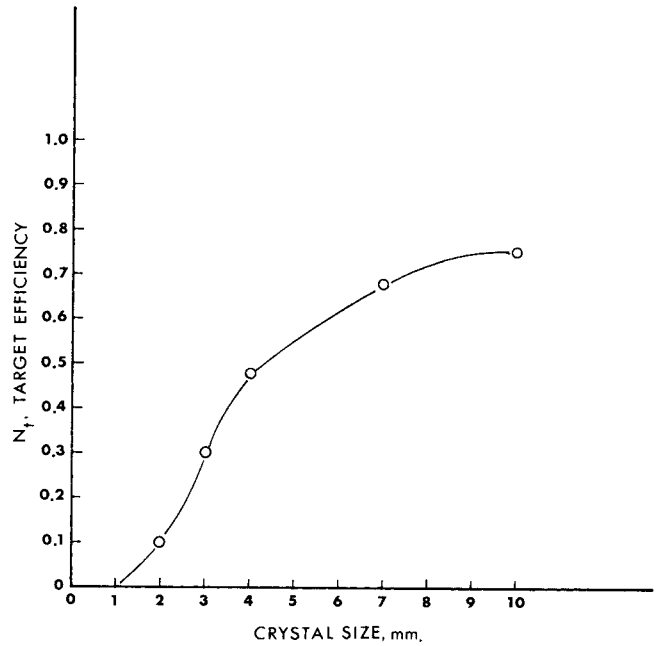

Fig. 5. Target efficiency for $MgSO_4 \cdot 7H_2O$ systems.

flow regimes. The actual flow regime (which must be known in order to determine the drag coefficient) for all the particle sizes shown in Figure 5, is the intermediate range, excepting at $L = 10$ mm which is in the Newton's Law regime. Figure 5 shows that particles of about 4 mm or larger have at least a 50/50 chance of striking the impeller, while particles smaller than 1 mm in diameter will not strike the agitator.

Cayey and Estrin (1967) reported that "secondary particles are not generators until they reach a certain critical size." A group of experiments which they ran at constant supersaturation is of particular interest. In these experiments a single crystal was attached to a rod and immersed in a supersaturated solution until the particles which resulted from initial breeding had grown large enough to exhibit the Tyndall effect. The seed crystal was then withdrawn from solution, and the system was monitored until still more new crystals were formed. An analysis of the number of particles vs. time data led to the conclusion that no new crystals were generated until the first generation particles reached approximately 225 microns in size.

Using Cayey and Estrin's data, the minimum particle size which would impact the impeller blades was calculated using Lapple's target efficiency as follows: Cayey and Estrin used an impeller speed of 350 rev./min., an impeller diameter of 6.35 cm, and a projected impeller blade width of approximately 1.3 cm. Lapple (1950) has shown that η_t becomes greater than zero at $N_{sep} = 0.0625$. From Equations (1), (19), and (20), the terminal velocity u_t of these minimum size particles was evaluated to be 4.15 cm/sec.

Since

$$u_t = \left[\frac{4}{3}\,\frac{g(\rho_p - \rho)\, D_p}{\rho\, C_D}\right]^{1/2} \qquad (24)$$

and for

$$2 \leq N_{Re} \leq 500$$

$$C_D = 18.5/N_{Re}^{0.6} \qquad (25)$$

Equations (24) and (25) may be solved to give $D_p \simeq 700$ microns. Even with the approximations involved in these calculations, the agreement between this figure and

that observed by Cayey and Estrin seems to be exceptional. Further, these calculations are based solely on crystal-impeller impacts and do not consider crystal-wall contacts, which did occur in the experiments of Cayey and Estrin.

CONCLUSIONS

1. For a fixed crystallizer geometry and agitation rate, the number of nuclei generated by $MgSO_4 \cdot 7H_2O$ and K_2SO_4 crystals is a function of the size of the seed crystal.

2. For identical conditions of crystallizer geometry, agitation rate and supersaturation, $MgSO_4 \cdot 7H_2O$ crystals produced nearly two orders of magnitude more nuclei than did K_2SO_4 crystals. This result corresponds to work by Johnson et al. (1972) showing crystal hardness to influence markedly the contact nucleation of inorganic crystals.

3. The number of nuclei produced increases with an increase in the agitation rate for a fixed crystallizer geometry, supersaturation, and crystal size.

4. The size dependent nucleation rate $B_L{}^0$ can be expressed as a second-order polynomial of the crystal size L. It is a function of the particular chemical system, the agitation rate, the crystallizer geometry, the supersaturation and the crystal size; once determined, it may be used to estimate the total nucleation rate using Equation (6).

5. The nucleation rate models proposed by Bennett, Fiedelman, and Randolph (1973), and Ottens (1973) show nucleation rates in MSMPR systems to be dependent upon the fourth moment of the crystal size distribution. However, the development of their models assumes (1) that the crystal-agitator contact frequency is proportional to the solution circulation rate and (2) that the probability of a given seed crystal impacting an impeller is independent of the size of that crystal. This work has shown that contact frequency is a function of crystal size, and models such as that of Ottens, Equation (9), should be modified to take this into account, as shown by Equations (19) through (22).

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NOTATION

A = projected area of impeller
B^0 = nucleation rate, number/min. · cm³
$B_L{}^0$ = size dependent nucleation rate, number/min/unit number of size L
c = solute concentration, g hydrate/g solution
c_s = solute concentration at saturation, g hydrate/g solution
D_b = characteristic dimension of target, cm
D_{prop}, D_r = diameter of propeller, cm
D_{tank} = diameter of tank, cm
E_L = impact energy associated with a crystal-agitator contact when the crystal is of size L, ergs
f_L = size dependent crystal-agitator contact frequency, number/min
g = gravitational acceleration constant, cm/s²
J = nucleation rate, number/cm³ · min
$k, k_m, k_p, k_1, k_2, \ldots$ = proportionality constants
k_v = volumetric shape factor
L = crystal size, mm
M = crystal mass concentration, g/cm³
m_L = mass of a crystal of size L, g
N_L = number of crystals of size L
N_{Po} = power number, dimensionless
N_{sep} = separation number, dimensionless
n = crystal population density, number/cm³ · μ
n_r = agitation rate, RPM, RPS
n_t = target efficiency, dimensionless
p = empirical constant
Q = pumping rate, cm³/s
q = empirical constant
r = crystal growth rate, μ/min, μ/s
s = empirical constant
u_0 = solution velocity, cm/s
u_t = crystal terminal velocity, cm/s
V, V_{tc} = crystallizer volume, cm³
V_r = tip speed of impeller

Greek Letters

Δc = supersaturation, g hydrate/g solution
ϵ = power dissipation
ρ_s = crystal density, g/cm³
ν_L = size dependent nuclei generation function, number/crystal of size L
ω = circulation frequency of a fluid volume element, cycles/unit time
ω_L = size dependent crystal-agitator contact frequency

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