$$\sum_{j=1}^{N} j = N(N+1)/2$$

In separation sequencing problem these subgroups define the compositions of all the feasible streams that may occur in any separation sequence. The collection of these feasible streams is called the *feasible stream set.*

Enumeration of Separation Subproblems

Any list containing j digits can be split in $j - 1$ different ways. Therefore,
the number of separation subproblems associated with subgroups containing j digits $= (j-1) \times (N+1-j)$.
[Notice $(N+1-j)$ j-component subgroups can be obtained from an N-digit list.]
Hence the total number of separation subproblems equals

$$\sum_{j=1}^{N} (j-1)(N+1-j)$$

$$= N \sum_{j=1}^{N} (j-1) - \sum_{j=1}^{N} (j-1)^2$$

$$= N \sum_{j=1}^{N-1} j - \sum_{j=1}^{N-1} j^2$$

$$= (N-1)(N)(N+1)/6$$

Enumeration of Separation Sequences

For continuous separation of all components of an N-component mixture it is necessary to use $N - 1$ separators. Each of these separators has two output streams. Thus, there are $[2(N-1)]$ output streams in a separation sequence. Out of these $[2(N-1)]$ output streams, $(N-2)$ streams interconnect the separators.

Number of possible ways for obtaining such connections

$$= \frac{[2(N-1)]!}{(2N-2-N+2)!\,(N-2)!}$$

$$= \frac{[2(N-1)]!}{N!\,(N-2)!}$$

This number also includes the cases when an output stream from a particular separator is connected to the same separator. Such connections are not allowed in real separation sequences. The number of all possible connections that do not include such connections can be obtained simply by dividing the above expression by $(N-1)$. Each of these connections corresponds then to a separation sequence. Therefore,

$$\text{Numer of separation sequences} = \frac{[2(N-1)]!}{N!\,(N-2)!\,(N-1)}$$

$$= \frac{[2(N-1)]!}{N!\,(N-1)!}$$

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Mechanisms of Secondary Nucleation in Agitated Crystallizers

Experiments were designed to identify the mechanism of the secondary nucleation of ice in a vigorously agitated crystallizer. It has been shown that the nucleation rate is proportional to the product of two factors, one characterizing crystal morphology and the other the rate of removal of potential nuclei from the surfaces of the existing crystals. Consequently, the nucleation rate attributable to different mechanisms is additive and the rate is proportional to the number of collisions per crystal. The contribution to the secondary nucleation of ice, by collisions of crystals with the impeller, baffles, and other crystals in an agitated crystallizer have been identified by measurements in a batch crystallizer in which each of the different collision mechanisms could be suppressed.

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SCOPE

Crystal size distribution and the production rate per unit volume are parameters of major importance in the design of industrial crystallizers. However, although the crystal size distribution in continuous crystallizers is controlled by the rates of secondary nucleation and growth of the crystals, little is known about the mechanisms and rates of secondary nucleation.

Previous studies of the secondary nucleation of ice have correlated the nucleation rate $\dot{N}$ with the nth moments of the crystal size distribution:

$$\dot{N} = a_n \mu_n$$

where the moment μ_n is proportional to crystal concentration for $n = 0$, to perimeter for $n = 1$, area for $n = 2$, etc.

The value of n has not been well established and the factors controlling the value of the proportionally constant μ_n have not been adequately understood. Furthermore, the

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mechanisms of secondary nucleation are not clearly identified although Johnson et al. (1972) have shown that the collisions of crystals with the agitator is the dominant mechanism of secondary nucleation for $MgSO_4 \cdot 7H_2O$ at low crystal concentrations. However, it is uncertain whether this mechanism is important for ice, whether crystal-crystal collisions also contribute to secondary nucleation at the higher concentrations of interest in commercial units, and whether mechanisms not involving collisions are significant. Furthermore, it is unknown how any two nucleating mechanisms interrelate to determine the overall nucleation rate. It is these questions that this paper seeks to answer with emphasis on the development of guidelines for the design of commercial continuous crystallizers. Ice was chosen for study because of its importance to the freezing process for desalination; however, the approach and results shed light on the general problem of characterizing secondary nucleation in all crystallizers.

CONCLUSIONS AND SIGNIFICANCE

The secondary nucleation of ice under conditions existing in continuous crystallizers is limited by the rate at which potential nuclei are removed from a crystal surface by collision, shear, or other external forces. This implies that the nucleation rate attributable to different removal mechanisms is additive and that the rate of nuclei removal is proportional to the number of collisions per crystal.

The principal mechanisms for nuclei removal are crystal-crystallizer and crystal-crystal collisions. Coating of the surfaces with coatings such as soft rubber can suppress the contribution of crystal-crystallizer collisions, that is, those attributable to collisions primarily with the impeller and secondarily with the baffles. For conditions expected in a continuous MSMPR crystallizer operated at 10% by weight ice, crystal-crystallizer collisions are responsible for 55% and crystal-crystal collisions for 20% of the overall nucleation rate. The nature of the residual 25% is not understood but is speculatively attributed to fluid shear.

The moment *n* with which the nucleation rate is correlated ($N = a_n \mu_n$) is found to be about 3 for crystal-crystallizer collisions and about 2 for crystal-crystal collisions. As a consequence of the high value of *n*, elimination of one or two major contributors to nucleation results in only a modest decrease in the nucleation rate per crystal β, since it follows from the additivity principle that the β_{1+2} due to two mechanisms is related to the nucleation rates β_1 and β_2 which would prevail if either mechanism acted alone by

$$\beta_{1+2} = \beta_1 \left(\frac{\beta_1}{\beta_{1+2}}\right)^{n_1} + \beta_2 \left(\frac{\beta_2}{\beta_{1+2}}\right)^{n_2}$$

As a consequence, elimination of the crystal-crystallizer contribution to nucleation in a continuous crystallizer by use of surface coatings would result in an increase in the average crystal size of only 15% at constant ice production rate or an increase in ice production of 40% at a constant crystal size.

The contribution to the constant a_n by crystal-crystal collisions is proportional to the concentration of ice crystals. Furthermore, for the limited results obtained in this study with particle addition, the crystal-crystal contribution to a_n is proportional to the 5th power of the size of the particles added. Such a strong dependence of nucleation rate on crystal size implies that attempts to grow large ice crystals will be hindered by the very rapid increase in nucleation rate with increased crystal size.

In the design of crystallizers, two aspects require major consideration: (1) the productivity of the crystallizer per unit volume and (2) the relationship between the performance of the crystallizer and the other unit operations downstream. For a continuous MSMPR crystallizer the productivity of the crystallizer is inversely proportional to the average residence time and proportional to the total mass of crystals within the crystallizer.

The larger the crystals produced in the crystallizer the more readily they are separated and washed. As shown by Kane et al. (1974) the average crystal size ($\bar{r}$) produced in a continuous MSMPR crystallizer under the assumptions:

1. The crystal growth rate (G) is independent of the crystal size
2. All new crystals are nucleated at a size near zero

can be expressed as

$$\bar{r} = G/\beta \tag{1}$$

where

$$\beta = N/\mu_0$$

Since the number of crystals within the crystallizer at steady state is a constant, the nucleation rate per crystal β is equal to the inverse of the average residence time. In order to determine the average crystal size from Equation (1), the nucleation rate and the growth rate must be known. The growth rates of crystals suspended in a crystallizer have been fairly well characterized (Brian et al., 1969). However, little is known about the rates of nucleation or even the mechanisms whereby nuclei are produced in crystallizers.

It is the objective of this paper to attempt to understand the mechanisms of nucleation as it occurs in a crystallizer. In particular, the secondary nucleation of ice will be studied. The choice of ice was predicated by its major application in water desalination by freezing.

SECONDARY NUCLEATION

As demonstrated by Sadek (1965) and Kane et al. (1974), secondary nucleation is the dominant type of nucleation at typical operating conditions of a continuous ice crystallizer. Secondary nucleation by definition occurs only in the presence of a stable parent crystal, thus the original crystal must in some way induce this nucleation. There has been much speculation in the literature on the source of these new nuclei and how the source is displaced into the bulk solution (mechanism of removal).

Sources of New Nuclei

A number of sources of new nuclei have been suggested, including dendrites or microscopic irregularities, molecular clusters, and macro-breakage of the parent crystals. Presently the most accepted source is dendrites or irregularities which are sheared from the surfaces of the parent crystals (micro-attrition). Melia and Moffitt (1964a, 1964b) have observed that convective currents shear tiny dendrites from NH_4Cl and NH_4Br crystals. They have also reported a great increase in the nucleation rate for KCl with the occurrence of dendritic growth on the seed crystals. Though their presence cannot be directly linked to the nucleation, dendrites and other irregularities were observed on the surface of the fixed ice crystal used to seed the crystallizer in the study of Brian et al. (1974). Scallop type growths were seen on the crystals in the studies of Margolis et al. (1971) and Garcia (1974).

Mechanisms of Removal

Given a source of new nuclei, the nuclei must be displaced from the surface of the parent crystal into the bulk. Three mechanisms of removal have been suggested: collisions of the crystals with the crystallizer, the collisions of the crystals with one another, and the fluid shear.

The contribution of crystal-surface collisions to secondary nucleation has been conclusively established by McCabe and co-workers. Clontz and McCabe (1971) grew a stationary $MgSO_4 \cdot 7H_2O$ crystal in a flowing supersaturated solution. No crystals were observed downstream; however, when the crystal was contacted with a metal rod, new crystals were observed downstream. The number of new crystals per contact was found to be proportional to the collision energy but was independent of the fluid velocity past the crystal. In a later paper, Johnson et al. (1972) reported that the replacement of a stainless steel propellor with a plastic one in a batch crystallizer reduced the nucleation rate by a factor of ten. This set of experiments indicate that crystal-crystallizer collisions are the dominant mechanism of secondary nucleation for $MgSO_4 \cdot 7H_2O$ at low crystal concentrations.

When Clontz and McCabe (1971) contacted the stationary crystal with another crystal, new crystals were also produced. This observation indicates that nucleation could possibly be due to collisions between the crystals. The observation of Kane et al. (1974) that the fixed crystal initiated nucleation in the absence of any collisions in the batch crystallizer suggests that fluid shear is also capable of inducing secondary nucleation.

THEORY

The production of potential nuclei at the surface of the parent crystals and the rate of removal of these nuclei from the surface out into the bulk solution must in some way interrelate to determine the overall nucleation rate. Two extreme cases may be visualized. In the first (surface regeneration-limited) the nucleation rate is equal to the rate of production of potential nuclei at the surfaces of the parent crystals, while in the second (removal-limited) the nucleation rate is equal to the rate of removal of nuclei from the surface of the existing crystals.

If the nucleation rate is regeneration-limited, increasing the number of collisions of an individual crystal for the case of removal due to crystal-crystallizer or crystal-crystal collisions or increasing the fluid drag for the case of removal due to fluid shear should not change the secondary nucleation rate. Similarly, if the nucleation is regeneration-limited for one mechanism of removal, then the nucleation will also be regeneration-limited when the removal is due to the first mechanism plus a second mechanism. Since this is so, the secondary nucleation rate will be identical for both cases.

On the other hand, if the secondary nucleation rate is removal-limited, the parent crystals will produce the same number of new nuclei each collision or unit of abrasion independent of the crystal's time history of earlier abrasion. This implies that the overall nucleation rate with two or more mechanisms of removal ($\dot{N}_t$) is the linear sum of the actual nucleation rate attributable to each mechanism of removal ($\dot{N}_i$)

$$\dot{N}_t = \dot{N}_1 + \dot{N}_2 + \ldots \qquad (2)$$

As expressed in Equation (1), the average crystal size produced in a continuous MSMPR crystallizer is inversely related to the nucleation rate per crystal β. Moreover, β is the nucleation parameter that is most readily measured in batch (Kane et al., 1974) or continuous (Margolis et al., 1971) crystallizers. Equation (1) is therefore rewritten in terms of β (see derivation in Appendix)

$$\beta_t = \beta_1 \left(\frac{\beta_1}{\beta_t} \right)^{n_1} + \beta_2 \left(\frac{\beta_2}{\beta_t} \right)^{n_2} + \ldots \qquad (3)$$

where β_t is the total observed nucleation rate per crystal and β_i is the nucleation rate per crystal observed when only the ith mechanism of removal is active, and n_i is the power dependence (n) on the crystal size of the ith mechanism.

Implicit in the derivation of Equation (3) is the assumption that the nucleation rate correlates with the first power of the moments of the particle size distribution [Equation (4)], as was found by Kane et al. (1974) for ice:

$$\dot{N} = a_n \, \mu_n \qquad (4)$$

For the special case when all mechanisms have the same dependency on the crystal size Equation (3) can be rewritten as

$$\beta_t^{n+1} = \beta_1^{n+1} + \beta_2^{n+1} + \ldots \qquad (5)$$

The relationships illustrated by Equations (2) and (3) and the special case expressed by Equation (5) shall be defined as the additivity relationships.

Another important relationship for removal-limited secondary nucleation is that the nucleation rate will be proportional to the number of collisions. For removal-limited secondary nucleation the crystal surface phenomena can be decoupled from the processes of removal. Since the physical processes of removal are essentially independent of the subcooling, the dependency of the nucleation rate on the subcooling is due solely to the crystal surface phenomena.

EXPERIMENTAL APPROACH

The previously discussed implications of the removal-limited nucleation can be used to design experiments to test the applicability of this theory to ice crystallization.

Experiments were designed to evaluate the removal-limited hypothesis and to determine the relative contribution of different mechanisms to the total nucleation rate. This was accomplished by successively suppressing the contributions of different probable sources of nucleation. The contribution of crystal-crystallizer collisions was studied by operating a crystallizer at low enough ice concentrations (< 0.2 wt. %) to suppress crystal-crystal collisions. By coating parts of the crystallizer with a soft rubber, the relative importance of collisions with the different surfaces in a crystallizer could be identified. The contribution of crystal-crystal collisions was studied by the addition of inert particles of varying size and concentration.

As an illustration of how the nucleation rates measured in the experiments described above can be used to test the removal-limited hypothesis and to infer mechanism;

let β designate the nucleation rate per crystal in an uncoated crystallizer and let subscripts A, B, and W indicate coating of the agitator, baffles and walls. If the nucleation rate is removal-limited, it follows from Equation (5) that

$$\beta^{n+1} - \beta_W{}^{n+1} = \beta_A{}^{n+1} - \beta_{A,W}{}^{n+1} = \beta_B{}^{n+1} - \beta_{B,W}{}^{n+1} = \beta_{A,B}{}^{n+1} - \beta_{A,B,W}{}^{n+1} \quad (6)$$

$$\beta^{n+1} - \beta_B{}^{n+1} = \beta_A{}^{n+1} - \beta_{A,B}{}^{n+1} = \beta_W{}^{n+1} - \beta_{W,B}{}^{n+1} = \beta_{A,W}{}^{n+1} - \beta_{A,B,W}{}^{n+1} \quad (7)$$

$$\beta^{n+1} - \beta_A{}^{n+1} = \beta_B{}^{n+1} - \beta_{B,A}{}^{n+1} = \beta_W{}^{n+1} - \beta_{W,A}{}^{n+1} = \beta_{B,W}{}^{n+1} - \beta_{A,B,W}{}^{n+1} \quad (8)$$

The differences given by Equations (6), (7), and (8) represent the contributions to β, raised to the $(n + 1)$ power, by collisions with the walls, the baffles, and the agitator, respectively. It was assumed that n is independent of where the crystals collide. A value for n may be inferred from any one of the nine equalities in Equations (6) to (8). The test of the validity of the removal-limited hypothesis is whether the value of n is the same for all equalities. In practice, only a small number of the above equalities may be so used since the differences in β for the others are too small to provide an accurate value for n.

An additional test of the removal-limited hypothesis for crystal-crystallizer collisions may be obtained if the nucleation rate $\dot{N}$ can be shown to be proportional to the number of collisions. Coating of l blades of an m-bladed impeller should reduce the collision frequency with uncoated blades and hence N by a factor l/m. This implies that

$$\beta^{n+1} - \beta_A{}^{n+1} = \frac{m}{m-l}\left(\beta_{l/m\,A}{}^{n+1} - \beta_A{}^{n+1}\right) \quad (9)$$

where $\beta_{l/m\,A}$ designates the nucleation rate per crystal when l of m blades of the impeller are coated. The removal-limited hypothesis is supported when the value of n obtained by use of Equation (9) is independent of the number of blades coated and agrees with the value obtained from applying Equations (6) to (8).

Further test of the removal-limited hypothesis are provided by varying the contribution of the crystal-crystal collisions. These collisions were simulated experimentally by the addition of plastic particles of different size and concentration. Let β_x, $\beta_{x,A}$, and $\beta_{x,B}$ designate the values of β measured in the presence of x weight percent particles in an uncoated crystallizer, with the agitator coated, the baffle coated, and so on. The additivity relation implies that

$$\beta_x{}^{n+1} - \beta^{n+1} = \beta_{x,A}{}^{n+1} - \beta_A{}^{n+1} = \beta_{x,B}{}^{n+1} - \beta_B{}^{n+1} = \beta_{x,A,B,W}{}^{n+1} - \beta_{A,B,W}{}^{n+1} = \ldots \quad (10)$$

The proportionality of nucleation rate to collision frequency implies that $\beta_x{}^{n+1} - \beta^{n+1}$ for both coated and uncoated crystallizers should be proportional to x.

By suitable variation of particle size and concentration, the particle addition experiments may be used to determine the relative contribution of crystal-crystal collisions to the total nucleation rate in a continuous MSMPR crystallizer under conditions simulating commercial operation and, in addition, to determine the dependence of nucleation rate on particle size and size distribution.

The experiments described above were performed in a batch crystallizer described previously (Kane et al., 1974). The values of β were inferred from temperature-time traces.

RESULTS AND DISCUSSION

Crystal-Crystallizer Collision Secondary Nucleation

Effectiveness of Surface Coatings. The first experiments were designed to test the effectiveness of different surface coatings in suppressing nucleation by absorption of the bulk of the collision energy. Two materials were used as coatings: neoprene and RTV silicone rubber. The moduli of elasticity of these two materials along with those of ice, stainless steel, and polyethylene are given in Table 1. Experiments were performed with these two coatings over a range of solution subcoolings, agitating powers, agitator types and NaCl concentrations. In Figures 1, 2, and 3, the data for an agitation power of 265 J/m^{3}s and 5.3% wt. NaCl solution, and agitation power of 1000 J/m^{3}s and 5.3% wt. NaCl, and an agitation power of 265 J/m^{3}s and tap water, are presented.

There is no question that the nucleation rate per crystal was substantially reduced by the coatings. The fractional reductions of β for the RTV silicone rubber coated crystallizer are presented in Table 2.

The dependency of the nucleation rate per crystal on the subcooling for the RTV silicone rubber coated crystallizer is identical to that for the uncoated crystallizer. This does not appear to be the case for the neoprene coated crystallizer, where the power dependency on the subcooling is somewhat greater than that for the uncoated crystallizer. When compared with the RTV silicone rubber coated and uncoated crystallizers, the values of β for the neoprene coated crystallizer vary depending on the experimental conditions.

For an agitation power of 265 J/m^{3}s and 5.3 wt. % NaCl the nucleation rate for the neoprene coated crystallizer is close to that obtained in the RTV silicone rubber coated crystallizer. As P/V_c is increased to 1000 J/m^{3}s, the nucleation rate moves toward that obtained in the uncoated crystallizer. Finally, for an agitation power of 265 J/m^{3}s and tap water, β for the neoprene coated crystallizer is essentially equivalent to that for the uncoated crystallizer. For agitation powers of 265 and 1000 J/m^{3}s and salt water, the nucleation rate per crystal for the

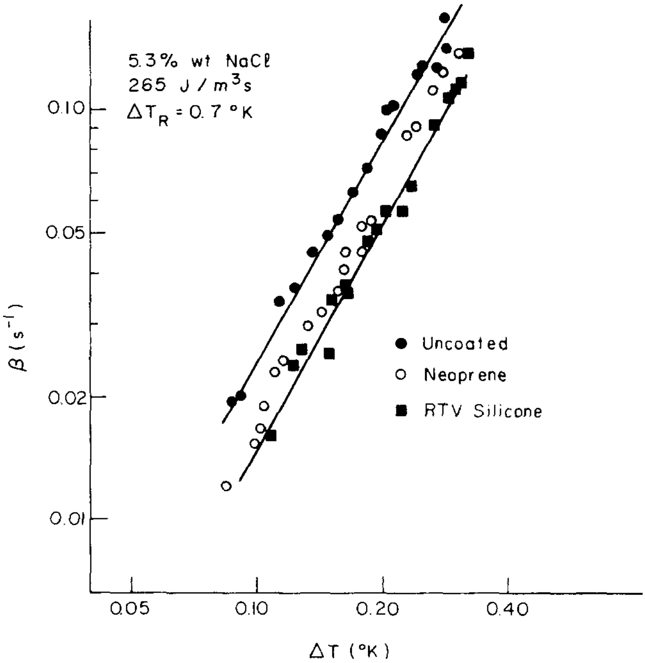

Fig. 1. Nucleation rates per crystal for coated and uncoated crystallizers at an agitation power of 265 J/m^{3}s, in a 5.3% NaCl solution.

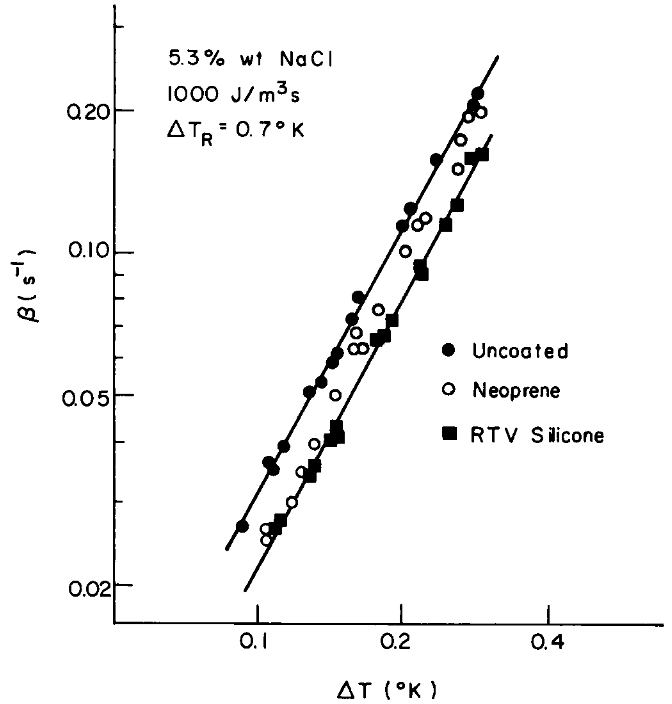

Fig. 2. Nucleation rates per crystal for coated and uncoated crystallizers at an agitation power of 1000 J/m³s, in a 5.3% NaCl solution.

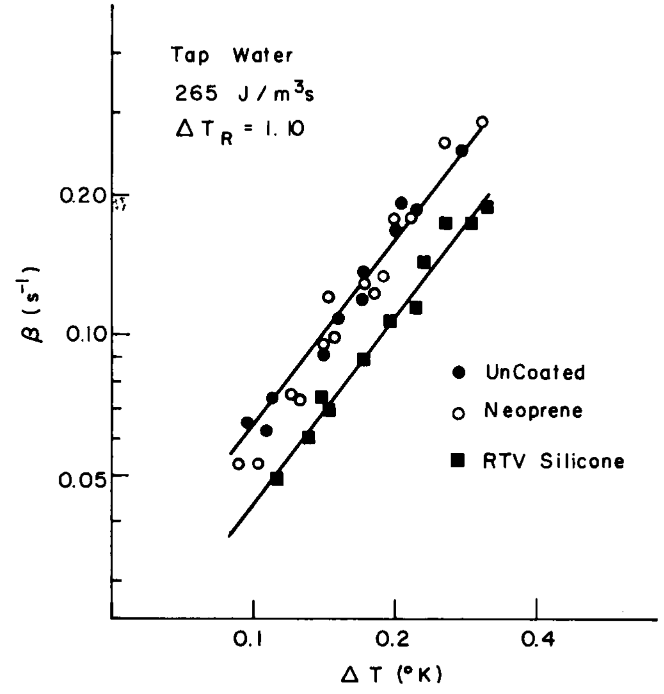

Fig. 3. Nucleation rates per crystal for coated and uncoated crystallizers at an agitation power of 265 J/m³s, in tap water.

neoprene coated crystallizer appears to have asymptotically approached the values of β obtained for the RTV silicone rubber coated crystallizer at low subcoolings. This suggests that reducing the softness of the coating below that of neoprene does not further reduce the nucleation rate, and therefore nucleation due to collisions of the crystals with the crystallizer has been reduced to a level negligible when compared with the overall nucleation rate. If this is true, what mechanism is responsible for the remaining nucleation? It is tempting to conclude that this nucleation is attributable to the fluid shear.

TABLE 1. YOUNG'S MODULI FOR MATERIALS OF INTEREST

Material	Young's modulus
Ice	9.65×10^9 N/m^2
Stainless steel	1.86×10^{11} N/m^2
RTV silicone rubber	4.62×10^5 N/m^2
Neoprene	4.13×10^6 N/m^2
Polyethylene	1.86×10^8 N/m^2

TABLE 2. FRACTIONAL REDUCTION IN β DUE TO RTV SILICONE RUBBER COATING

(P/V_c) J/m³s	Salt concentration wt. % NaCl	$\frac{\beta \text{ RTV silicone}}{\beta \text{ uncoated}} = \frac{\beta_c}{\beta}$
265	5.3	0.64
1000	5.3	0.72
1880	5.3	0.64
265	Tap water	0.71

There appears to be a critical Young's modulus for the coating. At this critical value the nucleation rate is very sensitive to the modulus. However, for moduli much greater than the critical, the nucleation rate is that obtained in the uncoated crystallizer. The nucleation rate should also be insensitive to the modulus for moduli much less than the critical. The critical modulus would be expected to be dependent on the surface morphology of the parent crystals and the collision forces acting on these crystals. Thus this critical modulus may be a function of the subcooling, the agitation power, and the salt concentration. Certainly as the subcooling is increased, the surface morphology will become more delicate and thus possibly more vulnerable to abrasion. Increasing the agitation power serves to increase the abrasive forces acting on the surface of the crystals. It is uncertain exactly what effect the salt concentration will have on the surface morphology. These predicted trends are consistent with the data. Data such as these may be useful in the future in elucidating the source of the new nuclei and the surface characteristics of the crystals which depict the secondary nucleation rate.

Contribution to Nucleation Rate of Crystal-Crystallizer Collisions. Two types of partial coating experiments were conducted, in the first only specific regions of the crystallizer (agitator, baffles, and walls) were coated. The objective of these experiments was to determine the surfaces of the crystallizer where the important collisions occur. In Figure 4 three sets of experiments (agitator coated, agitator and baffles coated, and walls and baffles coated) are compared with the results for the crystallizer completely coated with RTV silicone and the uncoated crystallizer at an agitation power of 265 J/m³s and salt water. When both the agitator and the baffles were coated, the nucleation rate is equivalent to the rate when the entire crystallizer was coated. This suggests that collisions with the walls make a negligible contribution to the overall nucleation rate.

A second set of partial coating experiments were performed in which 2 of the 3 blades of each marine propellor along with the baffles were coated. These results are presented in Figure 5 and Table 3.

From the theory presented earlier

$$\beta^{n+1} - \beta_{B,W}{}^{n+1} = \beta_A{}^{n+1} - \beta_{A,B,W}{}^{n+1} \qquad (11)$$

and

$$\beta^{n+1} - \beta_A{}^{n+1} = 3\,(\beta_{2/3A,B,W}{}^{n+1} - \beta_{A,B,W}{}^{n+1}) \qquad (12)$$

Substitution of the values of β from Table 3 into Equation

(11) suggests that n is greater than 2 within the 95% confidence limits of the data with values of 3 and 4 looking most probable. Since the values of β and $\beta_{B,W}$ are close, the calculation is prone to error and yields only a rough estimate of n. Utilization of Equation (12) yields a value for n greater than 2 and less than 5 given the accuracy of the data. A value of 3 looks most probable.

Given a value of n, it is now possible to determine to what degree the coatings reduced the actual nucleation rate constant (a_n). The fraction of the actual nucleation rate remaining after coating with RTV silicone rubber can be equaled to β_c/β (presented in Table 2) raised to the $n + 1$ power. The percentage of the actual nucleation which was eliminated by the coating is presented in Table 4 for three values of n.

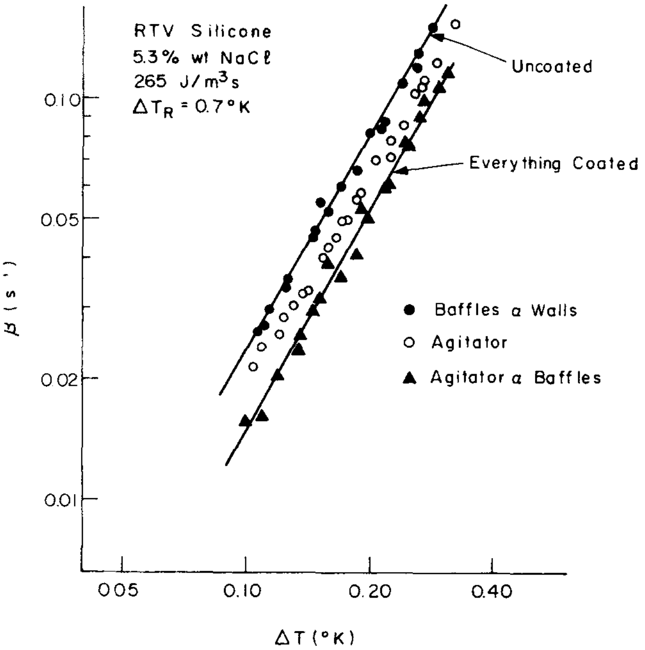

Fig. 4. Nucleation rates per crystal for an agitation power of 265 J/m³s with different combinations of coated surfaces.

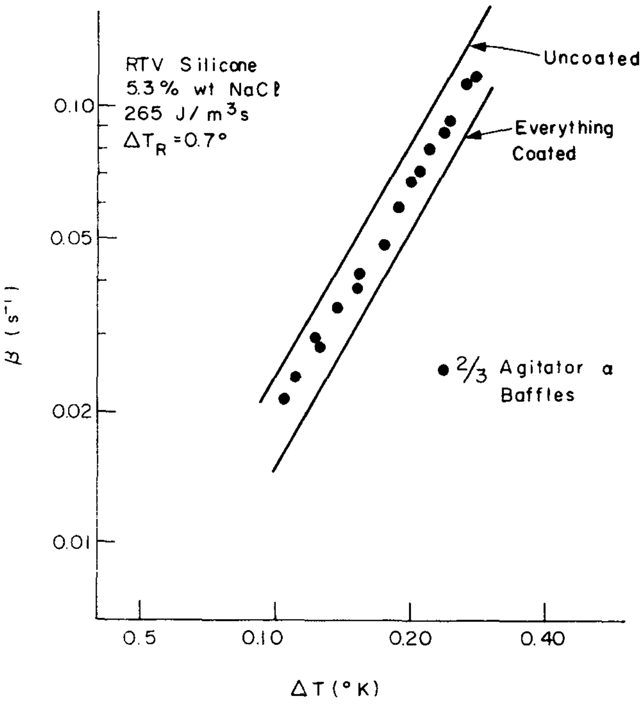

Fig. 5. Nucleation rates per crystal obtained with two of three blades of the agitator and the baffles coated.

TABLE 3. VALUES FOR β FOR VARIOUS COATING EXPERIMENTS
$\Delta T = 0.18°C$
$P/V_c = 265$ J/m³s

	Value (s^{-1})	Error (95% confidence)
β	0.0697	2.05×10^{-3}
β_A	0.0538	1.23×10^{-3}
$\beta_{A,B,W}$	0.0439	2.77×10^{-3}
$\beta_{B,W}$	0.0675	1.83×10^{-3}
$\beta_{2/3A,B,W}$	0.0554	2.27×10^{-3}

TABLE 4. PERCENTAGE OF NUCLEATION ELIMINATED BY COATING

(P/V_c) (J/m³s)	Salt concentration, wt. %	% of overall nucleation eliminated by coating $n = 2$	$n = 3$	$n = 4$
265	5.3	73	83	89
1000	5.3	63	73	81
1880	5.3	73	83	89
265	Tap water	64	74	81

Thus the coatings reduced the overall nucleation rate by 60 to 90% with 80 being a reasonable mean. There is no question that collisions of the crystals with the surfaces of the crystallizer is the dominant mechanism of removal at low ice concentrations.

Given the additivity relationship and a value of n, it is also possible to calculate the relative contributions of collisions with the agitator and the baffles to the actual nucleation rate attributable to this removal mechanism. Either the right-or left-hand side of Equation (11) can be employed to calculate the contribution of the baffles. Similarly the contribution of the agitator can be calculated from either the right- or left-hand sides of Equation (12). For n equal 3 the agitator is found to be responsible for 75% of the nucleation due to this mechanism, while the baffles contribute the remaining 25%.

Crystal-Crystal Collision Secondary Nucleation

The maximum ice concentration during a typical experiment was 0.2%, substantially less than is typical for a continuous MSMPR crystallizer. At these ice concentrations, collisions between the crystals would constitute a minor contribution to the overall nucleation rate. In order to study this mechanism of removal, polyethylene particles with a density (0.92 g/cm³) identical to that of ice were added to the crystallizer at high concentrations (1 to 10% on a weight basis). The deformation properties of polyethylene are compared with those of ice in Table 1. The modulus of elasticity of polyethylene is a factor of 50 less than that of ice. Thus, the experimentally measured rates may be less than the actual case when the crystals collide with one another at these concentrations.

Experiments were performed in RTV silicone coated and uncoated crystallizers with the addition of either a single size or a distribution of particles at various concentrations, subcoolings, and agitation powers. All experiments were performed with a 5.3% wt. NaCl solution.

In Figure 6 the data for the addition of 10 wt. % polyethylene particles with a diameter of 0.9 mm to the uncoated and coated crystallizers are presented along with the rates for these crystallizers with no addition of particles. Compared with the increase for the coated crystallizer, the increase in the nucleation rate per crystal for the uncoated crystallizer is small. The diameter of the polyethylene particles should be contrasted with the average diameter of the crystals being produced in the batch crystallizer of 0.12 mm at a subcooling of 0.2°C.

It is of practical interest to determine the dependency of the nucleation rate per crystal on the concentration of the particles added to the crystallizer. In Figure 7 the measured nucleation rates per crystal for the addition of three concentrations of particles (10, 3.33, and 1%) to the RTV silicone rubber coated crystallizer are presented.

In order to study the effect of the size of the particles which were added to the crystallizer, two sets of experiments were performed. In the first set a 10% by weight polyethylene particles with a diameter of 0.3 mm were added to the coated crystallizer. These data are plotted in Figure 8. The nucleation rate per crystal for this case is approximately identical to that measured when 1 wt. % particles with a diameter of 0.9 mm were added to the coated crystallizer. This suggests that the nucleation rate is proportional to the 5th moment of the particles added. One should not assume that this dependency is applicable over the entire range of particle size.

To determine the contribution of intercrystal collisions to the overall nucleation rate in a continuous MSMPR crystallizer, 10% wt. of particles whose size distribution matched that of the crystals within the coated crystallizer were added (to the batch crystallizer). The distributions were matched on a mass basis under the assumptions that the polyethylene particles were spheres and the ice crystals were disks with an aspect ratio of 0.3. Thus, the relative number of particles of a given mass was identical for the two distributions. The data obtained for this distribution are presented in Figure 9. The mean diameter of the crystal size distribution matched that of the added particles at a subcooling of 0.20°C.

The question to be resolved is whether the rates of removal for the two mechanisms (crystal-crystallizer collision and crystal-crystal collision) and the dependency of the rate of removal attributable to intercrystal collisions on the crystal concentration follow the predictions of the removal-limited hypothesis. First the experimental value of n must be determined.

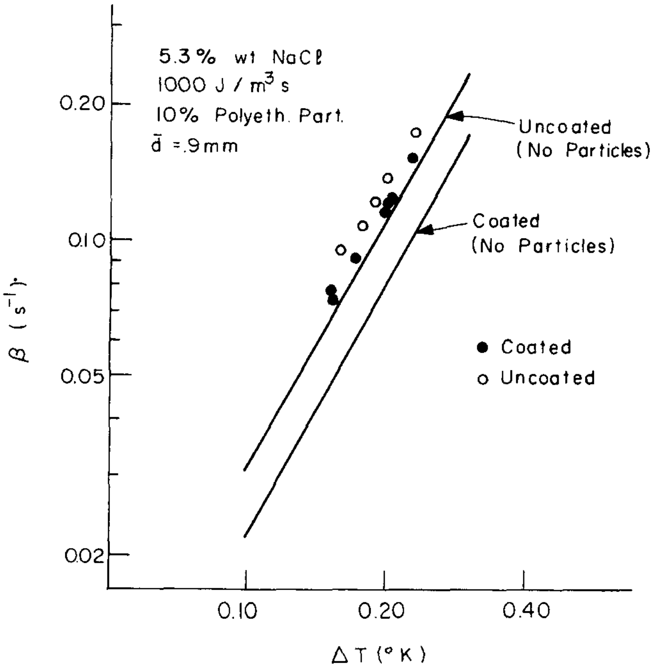

Fig. 6. Effect of particle addition on the nucleation rate per crystal in the coated and uncoated crystallizer at an agitation power of 1000 J/m^{3}s.

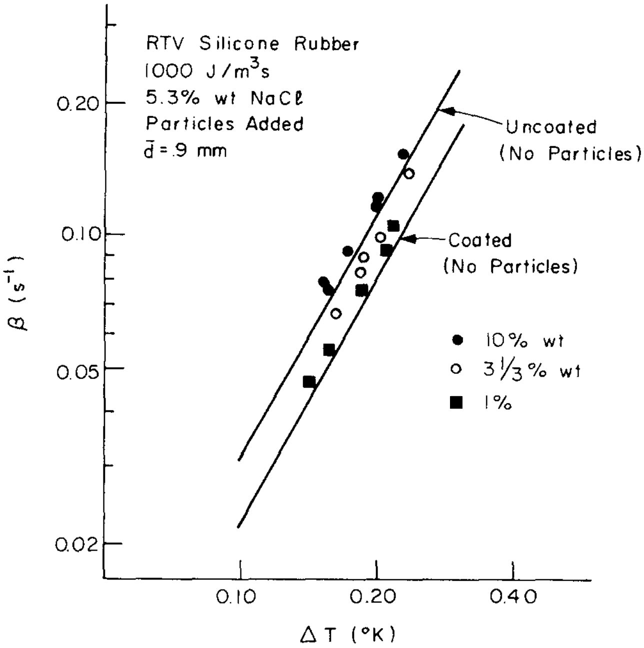

Fig. 7. Effect of added particle concentration on the nucleation rate per crystal in the coated crystallizer.

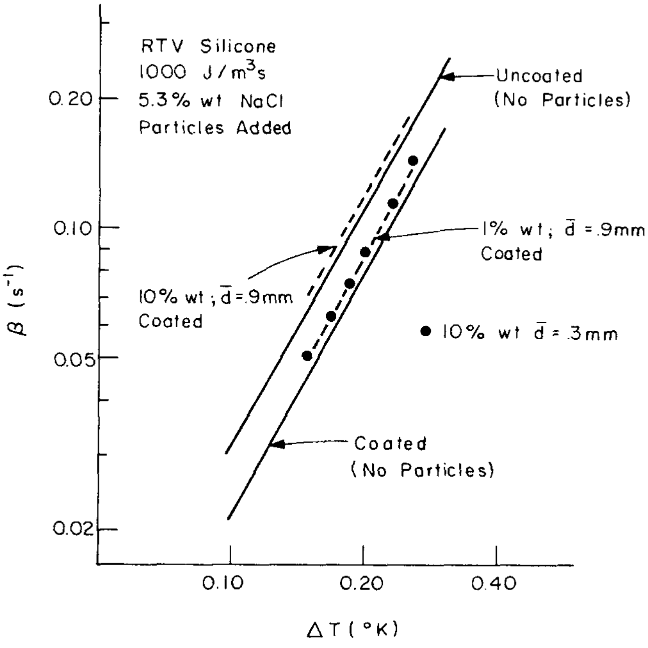

Fig. 8. Effect of size of the added particles on the nucleation rate per crystal.

From Equation (10)

$$\beta_{10}^{n+1} - \beta^{n+1} = \beta_{c,10}^{n+1} - \beta_c^{n+1} \tag{13}$$

All of these β's have been measured and are presented in Table 5.

From this calculation it is concluded that n is greater than 1 and less than 3 with a value of 2 being most probable.

If the nucleation rate is removal-limited, then the term $[\beta_x^{n+1} - \beta^{n+1}]$ presented in Equation (10) should be a linear function of x. These expressions normalized with respect to Equation (13) are plotted against the added particle concentration for a value of n of 2 in Figure 10 and a value of 3 in Figure 11. If the nucleation is removal-limited, all the points should fall on the straight line with slope of unity. Within the accuracy of the experimental data this is true and indeed the assumption of removal-limited is verified. In comparing the two figures a value of n of 2 again appears to be best.

The power dependency of the nucleation rate per crystal on P/V_c for the hypothetical case when removal is due only to collisions of the crystals with the added particles is calculated to be 0.30. This dependency on P/V_c is very close to that measured for collisions of the crystals with the crystallizer of 0.35 (Brian et al., 1974).

For a subcooling of 0.20°C the particle distribution added to the coated crystallizer as presented in Figure 9 matched the crystal size distribution produced within the crystallizer. Thus the difference between the actual nucleation rate $\dot{N}$ for this case and that for the coated crystallizer with no addition of particles is identical to the actual nucleation rate $\dot{N}$ attributable to the collisions of the crystals with one another in a continuous MSMPR crystallizer operated at this subcooling and 10 wt. % ice.

Applying the additivity relationships, the relative contributions of the two mechanisms can be calculated. The results are presented in Table 6 for an agitation power of 1000 J/m^{3}s.

The residual is defined here as the nucleation rate which remains after coating with RTV silicone rubber. It should be noted from Table 2 that at this agitation power the coatings were least effective. Therefore, at either higher or lower agitation powers the crystal-crystallizer collision nucleation will increase at the expense of the residual. These results are for an ice concentration of 10%, for higher concentrations the nucleation due to crystal-crystallizer collisions will increase proportionally and the relative contributions of the other mechanisms will be adjusted accordingly.

TABLE 5. VALUES OF β FOR THE PARTICLE ADDITION EXPERIMENTS $\Delta T = 0.18$°C, $P/V_c = 1000$ J/m^3

	Value (s^{-1})	Error (95% confidence)
β	0.0920	1.50×10^{-3}
β_c	0.0658	1.67×10^{-3}
β_{10}	0.1138	1.67×10^{-3}
$\beta_{c,10}$	0.1005	1.70×10^{-3}
$\beta_{3.33}$	0.1013	1.77×10^{-3}
$\beta_{c,3.33}$	0.0798	2.83×10^{-3}
$\beta_{c,1}$	0.0717	2.57×10^{-3}

TABLE 6. RELATIVE CONTRIBUTION OF REMOVAL MECHANISMS

Mechanism	$n = 2$	$n = 3$
Crystal-crystallizer collision	50%	57.5%
Crystal-crystal collision	20.5%	21.5%
Residual	29.5%	21.0%

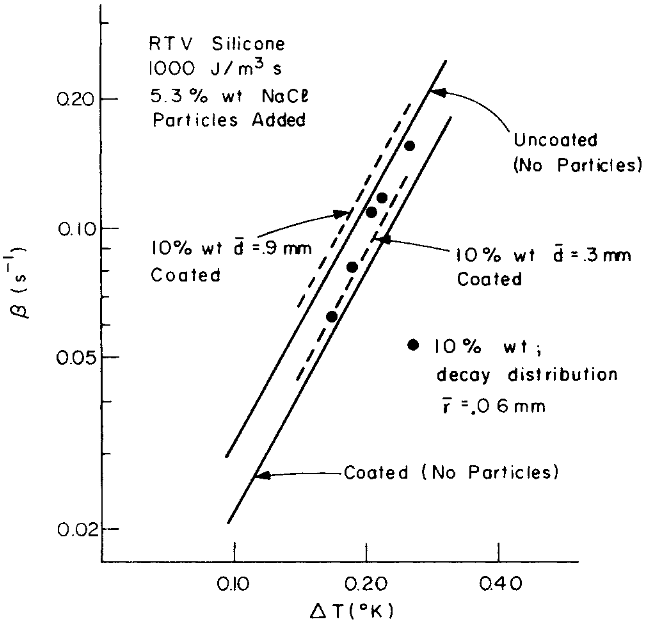

Fig. 9. Effect of addition of particles with a size distribution simulating that expected in a continuous MSMPR crystallizer.

PRACTICAL IMPLICATIONS

Coating the crystallizer has been shown to reduce the actual nucleation rate constant by a factor of 5 at low

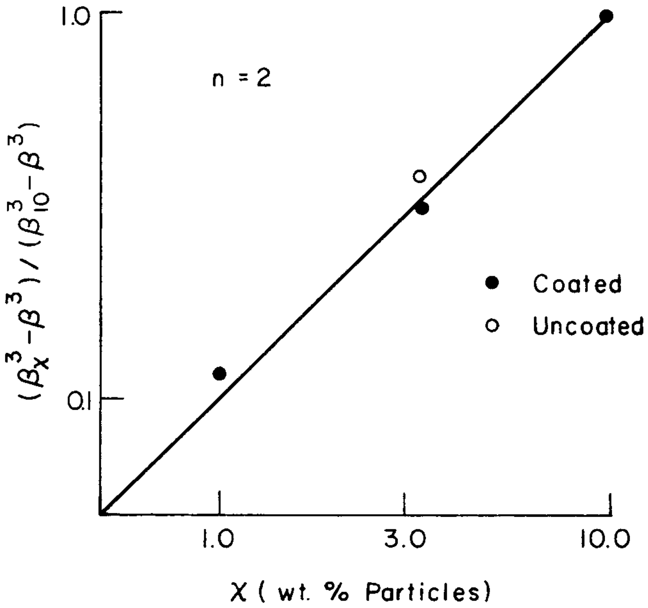

Fig. 10. Dependency of the actual nucleation rate constant on the concentration of added particles for n equals 2.

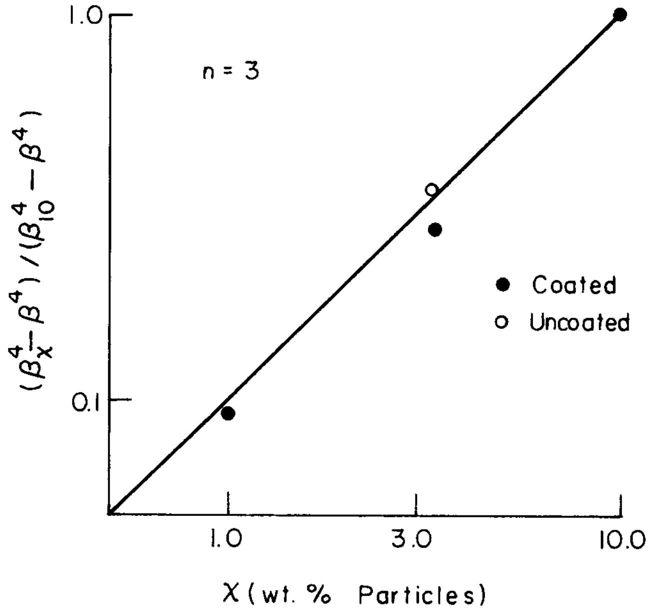

Fig. 11. Dependency of the actual nucleation rate constant on the concentration of added particles for n equals 3.

ice concentrations. Due to the high power dependency of the nucleation rate on the crystal size of approximately 3, this translates into an enhancement of 30% of the average crystal size at a constant residence time or an enhancement of the crystal productivity of 80% at constant average crystal size.

The discouraging implication of this study is the discovery of two mechanisms of removal. Since the crystal productivity is proportional to the ice concentration within the crystallizer, it is desirable to operate at high ice concentrations. Unfortunately, after the elimination of the contribution of crystal-crystallizer collisions to nucleation, that due to crystal-crystal collisions remains. Even though crystal-crystallizer collisions are responsible for over 50% of the nucleation at 10% ice, due to the high value of n, the average crystal size is increased only by 15% at constant residence time or the crystallizer productivity is increased by 40% at constant average crystal size.

Although the nucleation is removal-limited, the nucleation rate could be reduced by modifying the crystal's surface to lower the number of nuclei produced per collision at a given collision energy. This modification must be accomplished without reduction to the crystal growth rate. Omran and King (1973) have reported that the nucleation rate of ice was reduced by the addition of small quantities of pectin to the crystallizer.

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NOTATION

a_n = actual nucleation rate constant, Equation (3), nuclei/s m^n
$\bar{d}$ = diameter of added particles
f = crystal frequency distribution, crystals/m
G = crystal growth rate, m/s
n = power dependency of the actual nucleation rate on the crystal size, Equation (3)
$\dot{N}$ = actual nucleation rate, nuclei/s
P/V_c = agitation power per unit volume
r = characteristic dimension of the crystals, crystal radius
$\bar{r}$ = average crystal size
ΔT = solution subcooling
ΔT_r = refrigerant subcooling
x = weight percentage of added particles
β = nucleation rate per crystal, nuclei/s crystal
μ_0 = zeroth moment of crystal size distribution, total number of crystals
μ_n = $\int_0^\infty r^n f(r)\,dr$, nth moment of the crystal size distribution, m^n

Subscripts

A = only agitator coated
A,B,W = agitator, baffles and walls coated
$2/3A,B,W$ = 2 of the 3 blades of the marine propellors, baffles and walls coated
B,W = baffles and walls coated
c = entirely coated, same as A,B,W
t = total
x = weight percentage of added particles
1 = attributable to the first mechanism
2 = attributable to the second mechanism
10 = 10% wt. added particles

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APPENDIX. Derivation of Equation (3)

Division of Equation (2) by the total number of crystals (μ_0) and application of the definition of β [Equation (1)] yields the following relationship:

$$\beta_t = \frac{\dot{N}_1}{\mu_0} + \frac{\dot{N}_2}{\mu_0} + \text{----} \qquad \text{(A1)}$$

Utilizing the model for the actual nucleation rate [Equation (4)] and the moments for the crystal size distribution produced in a continuous MSMPR crystallizer for size independent growth rates ($\mu_n \propto n!\,\bar{r}^{\,n+1}$), Equation (A1) can be transformed into the following

$$\beta_t = n_1!a_{n_1}\bar{r}^{\,n_1} + n_2!a_{n_2}\bar{r}^{\,n_2} + \text{----} \qquad \text{(A2)}$$

where a_{n_1} and a_{n_2} are the actual nucleation constants for the first and the second mechanisms. From the definition of the average crystal size [Equation (1)]

$$\beta_t = n_1!a_{n_1}\left(\frac{G}{\beta_t}\right)^{n_1} + n_2!a_{n_2}\left(\frac{G}{\beta_t}\right)^{n_2} + \text{----} \qquad \text{(A3)}$$

From the analysis of Kane et al. (1974) the quantity $n_1!a_{n_1}(G)^{n_1}$ is recognizable as the nucleation rate per crystal which would be observed in a crystallizer with only the first mechanism of removal raised to the $n_1 + 1$ power. The similar quantity in the second term can be equated to the nucleation rate per crystal which would be observed in a crystallizer with only the second mechanism of removal raised to the $n_2 + 1$ power. Applying these relationships to Equation (A3), Equation (3) is obtained:

$$\beta_t = \beta_1\left(\frac{\beta_1}{\beta_t}\right)^{n_1} + \beta_2\left(\frac{\beta_2}{\beta_t}\right)^{n_2} + \text{----} \qquad (3)$$

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