Numerals

0 = mid axis origin
1 = initial condition or upper phase
2 = final condition or lower phase
½ = experimental

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The Mixed Suspension, Mixed Product Removal Crystallizer as a Concept in Crystallizer Design

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Simultaneous population and mass balances have been solved together with a generalized form of nucleation-growth rate kinetics to obtain the form of crystal size distribution (CSD) for several idealized modes of crystallizer operation, including seed crystal removal, product classification, arbitrary solids concentration, and staged vessels. The effect of holding time and feed supersaturation on crystal size in a mixed suspension, mixed product removal (MSMPR) crystallizer was also studied. A representative CSD from an MSMPR crystallizer plus the relative kinetic order of nucleation to growth rate can be used to predict CSD from any of the above modes of operation.

Crystal size distribution (CSD) is one of the most important and troublesome properties of an operating crystallizer and is a property which cannot presently be designed without prior experience with the crystal system and the type of crystallizer used. Saeman (*1*), in a classical contribution to crystallization theory, published equations for the form of steady state size distributions in mixed crystal suspensions. These equations had been derived as early as 1931 by Peet (*2*) in an unpublished report and by Bransom et al. (*3*) in 1948. However, the chief importance of Saeman's work was the presentation of these equations in an engineering context and the evolution of a philosophy (*4*) which regards crystallization as "a crystal suspension on which is maintained certain constraints." Robinson and Roberts (*5*) published a study of residence time distributions, and hence CSD, for a series of perfectly mixed tanks. These equations reduce to those of Saeman for one tank. Randolph and Larson (*6*) used the concept of conservation of population to derive a general equation relating crystal population density to crystal size in a transient system. Transient CSD for various upsets was studied with a model for a single tank mixed suspension crystallizer and assumed nucleation-growth kinetics used. The problem of steady state CSD from staged tanks was also studied, but in this case nucleation in each tank was accounted for. It should be pointed out that in all of the above references only the form or dimensionless behavior of the distribution was predicted; kinetic growth and nucleation rates are necessary to obtain actual CSD for a particular system.

A notable addition to the recent literature is a paper by Bennett (*7*) which tabulates experimental CSD data from a large class of crystallizers and crystal systems. A property of any CSD is the so-called *coefficient of variation* (C.V.),* or *relative size spread* over which the majority

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* Not to be confused with coefficient of velocity, also referred to as C.V.

of crystal mass is distributed. In the case of the theoretical exponential distribution of a mixed suspension, mixed product removal (MSMPR) crystallizer, C.V. is equal to 52 and is independent of absolute size (independent of growth and nucleation rates). In the above work Bennett points out that C.V.'s calculated from experimental CSD data seldom are as great as 52, implying a certain amount of product classification and/or a lowering of growth rate with size because the larger particles settle away from the boiling surface where greater supersaturation (and hence growth rate) exist. Bennett cites an equation derived by Bransom (*8*) for the case where growth rate is size dependent and points out that classical diffusion theories predict crystal growth rate should increase with size, giving C.V.'s greater than 52. Unfortunately, Bransom uses an incorrect starting differential equation* which he then integrated to obtain CSD with growth rate size dependent. However, the conclusions of Bennett using Bransom's equation are qualitatively correct and do indicate that classification in both the product take off and at a boiling surface dominates the opposite natural tendency of the larger crystals to grow faster because of less diffusion resistance.

Two approaches to lessen the discrepancy between theoretical and actual CSD would be to learn more about actual residence time distributions and crystal growth rates as a function of hydrodynamic environment, or change the environment to conform to the ideal assumptions. The philosophy which considers crystallization as a crystal suspension upon which certain constraints are maintained would favor the latter approach. In practice both approaches will be necessary if continuous crystallization is to be put on a firm theoretical design basis comparable to other important unit operations.

This paper adopts the philosophy that crystallization can be thought of as the art of constraining a suspension of crystals and attempts to set forth a complete rationalization of CSD for the major types of crystallizers and crystal systems, as given by their ideal constraints.

It should be pointed out that the resulting equations describing CSD will be no better than the nucleation-growth rate kinetics going into them, and such data are woefully lacking at this time. However, there are currently several encouraging investigations of nucleation-growth rate kinetics in environments resembling a mixed crystal suspension, and it is probable that more and better information of this type will become available. In any case, the fundamental equations can readily be used with the kinetic data at hand. It is hoped that the general principles suggested in this paper will be used as a set of ground rules to interpret CSD in operating crystallizers and to utilize kinetic data as they become available.

GENERAL APPROACH

Crystal size distribution, and where important, yield, can be thought of as the interaction of three factors: residence time probabilities of mother liquor vs. solids and solids as a function of size, kinetics of nucleation and growth rate, and other.

The classification other is included to account for such devious phenomena as multicrystal growth, agglomeration, chemical effects such as habit modifiers, etc. These are very real phenomena in some crystal systems and give rise to much of the art involved in crystallization. It is not the purpose of this paper to discuss phenomena such as these which are not general to all systems, and it will be assumed that if such factors are important to a particular application, due consideration for their effects will be made. This paper will be concerned with the study of interactions of residence time distributions with nucleation-growth kinetics to give CSD in various constrained systems.

Population Balance

Any real crystallizer must satisfy relationships guaranteeing the conservation of mass and energy, but, in addition, the CSD which can be obtained is constrained by the conservation of population of particles present. Unfortunately, a statement of the conservation of population cannot be made in as exact and unequivocal manner as can the conservation of mass and energy because of an involvement with kinetics of nucleation, of which little is known experimentally. Regardless of the state of knowledge of nucleation kinetics, appropriate forms of the mass, energy, and population balance equations can be solved together to obtain yield and CSD in terms of selected types of nucleation-growth rate kinetics. A population balance for an arbitrary suspension has been given (*6*) and becomes

$$V \frac{d}{dL}(rn) = \sum_i \vec{Q}_i n_i \tag{1}$$

for the steady state case of a constant volume crystallizer.

Mass Balance

A mass balance of the crystallizable solute can be expressed simply as

$$\sum_i \vec{Q}_i (C_i + M_i) = 0 \tag{2}$$

Energy Balance

On the assumption that the suspension is backmixed to an isothermal condition, energy requirements do not enter directly into CSD and yield equations except to determine exit flow rates. From a practical standpoint, however, such things as vapor release area (in the case of evaporative or flash cooling crystallizers) and per-pass superheat of circulating liquor (from heaters or superheated feed) are of course important design considerations. The importance of suspension turnover time in systems with small supersaturation decay time constants has been discussed elsewhere (*4*, *9*).

Nucleation and Growth Kinetics

It is convenient to divide crystallization processes into two classes: those in which per-pass yield is a factor and those in which the yield is essentially quantitative. A simple experiment in which supersaturated liquor is equilibrated in the presence of seed crystals can easily distinguish such systems. As a concrete example one could cite the sodium tetraborate pentahydrate system vs. potassium chloride as systems where yield is or is not a variable.

Class I system, yield a variable

$$\text{Nucleation rate} = \frac{dN^\circ}{dt} = f(s) \quad \text{nuclei/sec.-cu. ft.} \tag{3}$$

$$\text{Growth rate} = r = g(s) \quad \text{ft./sec.} \tag{4}$$

where the kinetic functions f and g would have to be determined experimentally.

Class II system, quantitative yield

$$\frac{dN^\circ}{dt} = h(r) \tag{5}$$

or

$$n^\circ = [1/r][h(r)] \tag{5a}$$

and the kinetic function h would have to be determined experimentally. Equations (3) and (4) may be combined to give Equation (5) for a class I system if only CSD and not yield is of interest, that is by eliminating s as a

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* See Appendix for the solution of correct differential equation.

parameter. The per-pass yield can be calculated directly from the value of supersaturation when the kinetics of nucleation-growth rate are given in terms of supersaturation, but the CSD is only a function of relative growth and nucleation rates, not supersaturation. It should be pointed out that in spite of the general functional notation of Equations (3) and (4) or (5), certain limitations are implied as they are written. Thus they are written for a constant temperature suspension (usually an excellent assumption) and do not include any functional dependence on solids concentration, degree of agitation, seeding, etc., and as such the supersaturation is considered the only driving force producing crystal formation and growth. This is in no way a fundamental limitation, and the general form of kinetics presented is considered sufficient until more data are obtained.

Very little quantitative data on nucleation and growth rates in mixed crystal suspensions have been published, but what data have appeared are consistent with simple power models of the form

$$\frac{dN^\circ}{dt} = k_N r^i \tag{6}$$

or

$$n^\circ = k_N r^{i-1} \tag{6a}$$

This specific form of nucleation-growth rate kinetics, Equation (6), has been shown to hold over a considerable operating range for several inorganic systems, the results of which are as yet unpublished. Equation (6) has also been shown to represent nucleation-growth rate kinetics for the alum-ethanol-water system over a threefold range of holding times (*10*). The exponent i in Equation (6) is actually the relative kinetic order of nucleation rate to growth rate when both are expressed as powers of the supersaturation. Thus values from zero to very large numbers might be expected. The specific rate constant k_N would in general be temperature dependent and might also vary with agitation and solids concentration in the suspension.

IDEALIZED CRYSTALLIZER MODELS

MSMPR Crystallizer

The theoretical CSD for an MSMPR crystallizer has been shown (*1, 2, 6*) to be given as

$$w(x) = 1/6 \int_0^x \exp\,(-p) p^3\, dp \tag{7}$$

when growth rate is independent of size and where $x = L/rT$. It can be easily shown (*6*) that the dominant crystal size (on a weight basis) from distribution (7) is given as

$$L_D = 3rT \tag{8}$$

where rT can be thought of as a characteristic crystal size of the system. Equation (8) provides a basis for quantitatively predicting the effect on size of various crystallization modes.

In order to conserve mass in the system, the growth rate must satisfy the constraint

$$r^4 = \frac{M_T}{6\rho_c\, k_L\, n^\circ\, T^4} \tag{9}$$

Equation (9) emphasizes the necessity of obtaining growth and nucleation kinetics in order to a priori design CSD, even in such simple cases as the MSMPR crystallizer where the form of the distribution is known. When the assumptions going into Equation (7) are realized, this equation fits experimental distributions very well. Figure 1 shows a typical screen analysis from a small laboratory MSMPR crystallizer fitted to Equation (7). The crystal system was sodium tetraborate pentahydrate.

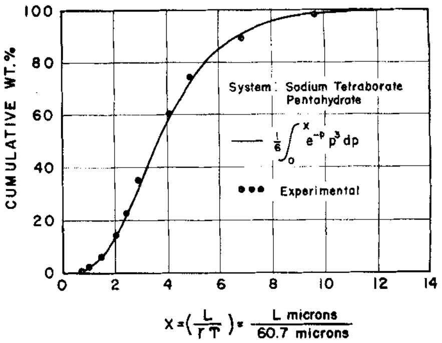

Fig. 1. Theoretical and experimental CSD from MSMPR crystallizer.

The effect of holding time on crystal size from an MSMPR crystallizer can be predicted (in terms of nucleation-growth kinetics) as follows.

For an exponential population distribution [as in Equation (7)], the proposition

$$L_D \equiv 3rT = \frac{\int_0^\infty nL^3\, dL}{\int_0^\infty nL^2\, dL} \tag{10}$$

can easily be demonstrated. Upon substitution of the mass balance, Equation (2), in the numerator and direct integration of the denominator, Equation (10) becomes

$$L_D = K_1[C_iQ_i/Q_o - C]^{1/i+3}\,[T]^{i-1/i+3} \tag{11}$$

where

$$K_1 = \left[\frac{3^{i+2}}{2\rho_c\, k_L\, k_N}\right]^{1/i+3} \tag{12}$$

For constant feed conditions and a class II crystal system (quantitative yield), Equation (11) becomes

$$L_D = K_2T^{i-1/i+3} \tag{13}$$

where K_2 is a constant depending on feed concentration. Equation (13) indicates that crystal size can increase, decrease, or remain constant with changes in holding time, depending on the relative kinetic order of nucleation to growth rate. For the case $i > 1$ crystal size increases with holding time, for $i < 1$ crystal size decreases, and for $i = 1$ crystal size is independent of holding time. Furthermore, in a class I system (yield a variable) crystal size is very small at low holding times (low yield), and for the case $i < 1$ crystal size actually undergoes a maximum. These situations are illustrated for various values of i in Figure 2.

The maximum dominant crystal size obtainable from an MSMPR crystallizer for a class I system with $i < 1$ can be found by substituting for C in Equation (11) from Equation (4) and then finding the maximum in the resulting equation. If growth rate in Equation (4) can be represented as

$$r = g(s) = k_g\,(C - C_o)^j \tag{14}$$

then applying calculus procedures to find the maximum gives

$$L_{D_{\max}} = \left\{\frac{3^3\, s_i^{\,1+j-ij}\, k_g^{\,1-i}}{(2\, k_Lk_N)\,(1 + j - ij)\left(\dfrac{i - 1 - 1/j}{i - 1}\right)^{j-ij}}\right\}^{\frac{1}{4-i}} \tag{15}$$

for $i < 1$ and where s_i is the apparent feed supersaturation equal to

$$s_i = C_iQ_i/Q_o - C_o \tag{16}$$

The holding time which corresponds to this maximum dominant crystal size is given as

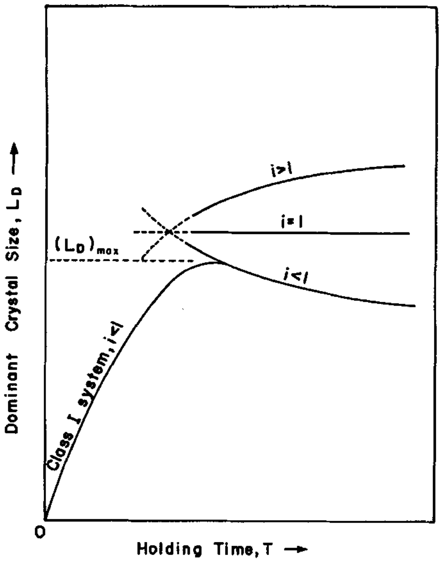

Fig. 2. Effect of holding time on dominant crystal size in MSMPR crystallizer.

$$T_{\max} = 1/3\, k_g \left[\frac{i-1-1/j}{s_i(i-1)}\right]^j [L_D]_{\max} \tag{17}$$

Equation (15) indicates that the maximum dominant crystal size obtainable in such a system increases with the fraction of crystallizable input, thus indicating that the crystals are starved for additional solute to grow to larger size. This effect is indeed observed. However, if feed concentration is increased too much, with solids concentration rising accordingly, there is a tendency for additional nucleation to occur, with the result that size finally begins to decrease. Equation (11) also gives the effect of feed concentration on crystal size for class II systems. This effect is qualitatively the same; that is, crystal size is predicted to increase with the amount of crystallizable solute per unit volume of feed material.

Seed Crystal Removal

The practice of keeping population in control by preferential seed crystal removal and destruction has been shown (*1*) to be effective in increasing crystal size. Essentially, such an operation changes the residence time probability of the solids as a function of size, with the smaller crystals having a smaller residence time probability. If the exact size range and rate of removal of the seed crystals is known from the operation of a seed trap, the product CSD can be predicted rigorously by solving the appropriate mass and population balance equations together with nucleation-growth kinetics. However, by making a few simple assumptions, the MSMPR concept can be used to obtain the limiting ideal behavior of such a system. The author assumes that operation of a seed crystal trap is as follows:

1. The seed crystals removed are small enough to be considered nuclei, that is small compared with $2rT$.
2. The seed crystals are removed proportional to their population (a valid assumption for a flow system of removal).
3. Assume a class II system.

Thus, letting subscripts (2) and (1) refer to the same crystallizer operating with identical feed conditions but with and without seed crystal removal, the net population density in the second case can be represented as

$$[n_2^\circ]_{\text{net}} = u\, n_2^\circ \tag{18}$$

where u is the fraction of crystals left to grow in the suspension.

Rewriting Equation (10) for this situation one gets

$$L_{D2}/L_{D1} = \frac{\int_0^\infty n_2 L^3\, dL \int_0^\infty n_1 L^2\, dL}{\int_0^\infty n_2 L^2\, dL \int_0^\infty n_1 L^3\, dL} \tag{19}$$

As the population distribution remains exponential because of assumption 1, these integrations can easily be performed to give

$$[L_{D2}/L_{D1}]^4 = 1/u \left[\frac{n_1^\circ}{n_2^\circ}\right] \tag{20}$$

Or, substituting nucleation kinetics from Equation (6*a*) one obtains

$$[L_{D2}/L_{D1}]^4 = 1/u \left[\frac{r_1}{r_2}\right]^{i-1} \tag{21}$$

Multiplying top and bottom by T^{i-1} and using the definition of L_D from Equation (8) one gets the final limiting case of size improvement as a function of the fraction of seed crystals removed and nucleation-growth kinetics. Thus

$$L_{D2}/L_{D1} = [1/u]^{1/i+3} \tag{22}$$

The significance of Equation (22) is that for a given fraction of seed crystals removed, as given by $1-u$, the amount of size improvement to be expected depends on nucleation sensitivity as given by the parameter i. The lower the value of i, the more size improvement that occurs with a given fraction of seed crystals removed.

Classified Product Removal

The dimensionless CSD of the MSMPR crystallizer is also useful for predicting the CSD obtainable from a crystallizer operated with classified product withdrawal. Actually, classified product removal can be thought of as a reversal of seed crystal removal; the residence time probabilities of the crystals are again dependent upon size, but crystals above the classification size have a smaller residence time probability than small crystals.

Product classification can be achieved, in a mechanical sense, by several types of equipment such as elutriators, hydroclones, Dutch State Mines (DSM) screens, etc. If a solid-free liquor is available for counter washing, classification by elutriation can limit product draw off to essentially those crystals above a given size. The limiting case of such classification, where the mean residence probability of crystals is infinity below size L_o and is equal to zero above size L_o, has been studied previously (*1*). In actual practice, devices of the DSM or hydroclone type preferentially remove particles larger than the classification size from the suspension rather than removing particles less than the classification size from the product. For the purposes of this study a classification model is used which is both idealized and yet realistic, especially with respect to the latter two previously mentioned classification devices.

The idealized model for classified product removal is as follows. Assume crystals smaller than the classification size L_o are removed at a rate Q_o, while those greater than size L_o are removed at a rate zQ_o. The flow rate Q_o maintains liquid level in the system.

Solving the population balance for this case one obtains

$$n = n^\circ \exp(-L/rT_o) \qquad L < L_o$$

and

$$n = n^\circ \exp[(z-1)L_o/rT_o] \exp(-zL/rT_o) \qquad L > L_o \tag{23}$$

where $T_o = V/Q_o$. Cumulative weight distribution is given as

$$W(L) = \frac{\int_0^L n\, L^3\, dL}{\int_0^\infty n\, L^3\, dL} \qquad (24)$$

Thus, using the population distributions from Equation (23) and making the dimensionless substitution $x = L/rT_o$, one gets the weight distribution in suspension as

$$W_s = \frac{w(x)}{w(x_o) + \frac{[1 - w(zx_o)]}{z^4} \exp[(z-1)x_o]} \qquad L < L_o$$

and

$$W_s = \frac{w(x_o) + \frac{[w(zx) - w(zx_o)] \exp[(z-1)x_o]}{z^4}}{w(x_o) + \frac{[1 - w(zx_o)]}{z^4} \exp[(z-1)x_o]} \qquad L > L_o \quad (25)$$

where $w(x)$ is the MSMPR distribution as given by Equation (7). The CSD of the product is calculated simply by mixing z parts of oversize with one part of undersize. Thus, the factor z^4 is replaced by z^3. In terms of the foregoing nomenclature the product CSD is given as

$$W_p = \frac{w(x)}{w(x_o) + \frac{[1 - w(zx_o)] \exp[(z-1)x_o]}{z^3}} \qquad L < L_o$$

and

$$W_p = \frac{w(x_o) + \frac{[w(zx) - w(zx_o)] \exp[(z-1)x_o]}{z^3}}{w(x_o) + \frac{[1 - w(zx_o)] \exp[(z-1)x_o]}{z^3}} \qquad L > L_o \quad (26)$$

Equations (25) and (26) only predict the form of CSD with classified product removal; in order to obtain the actual CSD going from mixed to classified product removal the growth rate must be constrained by solution of the mass balance equation with appropriate nucleation-growth kinetics. This procedure is as follows. Let subscripts (m) and (c) refer to mixed and classified product removal. The mass balance for mixed product removal is given as

$$Q_i C_i / Q_o - C = 6 \rho_c k_L n_m^o r_m^4 T^4 \qquad (27)$$

and for the classified case

$$Q_i C_i / Q_o - C = 6 \rho_c k_L n_c^o r_c^4 T^4 \left[w(x_o) + \frac{[1 - w(zx_o)] \exp[(z-1)x_o]}{z^3} \right] \qquad (28)$$

A comparison of the two cases of mixed vs. classified product removal under identical feed conditions enables the right-hand side of Equations (27) and (28) to be equated. Thus

$$[r_m/r_c]^4 = n_c^o / n_m^o \left[w(x_o) + \frac{[1 - w(zx_o)] \exp[(z-1)x_o]}{z^3} \right] \qquad (29)$$

For a class II system using nucleation-growth kinetics given by Equation (6*a*) the constraint on the growth rate becomes

$$r_m/r_c = \left[w(x_o) + \frac{[1 - w(zx_o)] \exp[(z-1)x_o]}{z^3} \right]^{1/i+3} \qquad (30)$$

Using the form of CSD from Equation (26) and the constraint on growth rate, Equation (30), it is possible for one to predict CSD for classified product removal knowing only the CSD from an MSMPR crystallizer and the relative nucleation-growth sensitivity i. The effect of product classification is to narrow the distribution and produce crystals that are more uniform but somewhat smaller in size. Solids concentration is decreased and growth rate increased as compared with the mixed product case.

Arbitrary Solids Concentration

In the so-called *growth type* of crystallizers solids concentration is held at an arbitrary level (within limits) by taking off a more or less clear settled overflow stream and a mixed suspension underflow from the crystal suspension. This mode of operation is particularly effective in raising per-pass relief of supersaturation in a class I system with low crystallizable solute content in the feed. The effect of such operation on crystal size in an idealized growth type of crystallizer can be obtained in terms of the MSMPR model. Assume a class II system and no seed crystal removal in clear liquor overflow.

Let z be the ratio between overflow and underflow streams on a clear liquor basis and let subscripts (m) and (g) refer to MSMPR and growth types of crystallizers. The population distribution is again given by the exponential relationship

$$n_g = n_g^o \exp[-LQ_o/(1+z) r_g V_g] \qquad (31)$$

Mass of solute is conserved by the relationship

$$C_i Q_i / Q_o - C = (1+z)^3 r_g^4 T_m^4 6 \rho_c k_L n_g^o \qquad (32)$$

Under constant feed conditions the right-hand member of Equations (27) and (32) can be equated to give a relationship between the growth rates in the two cases. Thus

$$[r_g/r_m]^4 = [1+z]^{-3} [V_m/V_g]^4 [n_m^o/n_g^o] \qquad (33)$$

which after substitution of nucleation-growth kinetics from Equation (6*a*) becomes

$$r_g/r_m = [1+z]^{-3/i+3} [V_m/V_g]^{4/i+3} \qquad (34)$$

Multiplying Equation (34) top and bottom by $V_g V_m (1+z)/Q_o$ and recognizing that

$$L_{Dg} = (1+z) r_g V_g / Q_o \qquad (35)$$

one obtains the final relationship between dominant crystal size from mixed product and growth types of crystallizers as

$$L_{Dg}/L_{Dm} = (1+z)^{i/i+3} [V_g/V_m]^{i-1/i+3} \qquad (36)$$

The variation of dominant size with crystallizer clear liquor volume V would be slight as the ratio $V_g/V_m \approx 1$ for any reasonable change in solids concentration going from mixed to growth type of operation. Thus the major variation in size would be given as

$$L_{Dg} = L_{Dm} (1+z)^{i/i+3} \qquad (37)$$

It should be emphasized that Equation (37) does not include any possible changes in nucleation mechanism with changes in solids concentration. However, this variation could easily be handled by retaining the specific rate coefficient k_N which would then be a function of solids concentration.

Equation (37) indicates that the expected improvement in crystal size in a growth type of crystallizer will depend on the nucleation sensitivity i and would be greater in a system with sensitive nucleation behavior. With a class I system additional size improvement would result because of an increase in per-pass yield with the growth type of crystallizer.

Staged Vessels

Crystallization is sometimes performed in staged vessels with the entire suspension of one vessel discharging as feed to a subsequent vessel. Nucleation and growth occur in each stage. Variations of this problem have been treated previously (*5*, *6*). However, the MSMPR ideal model can be useful in analyzing such a system with two stages. Consider the following allocation problem. A fixed amount of crystallizer volume V is to be allocated as a single MSMPR crystallizer or as two staged MSMPR crystallizers of equal volume. A fraction α of the total crystallization is to occur in the first stage. (This could be achieved by adjusting evaporation or cooling profiles.) A class II system is assumed. Let subscript (m) refer to single stage MSMPR and subscripts (1) and (2) refer to first and second stages of staged system. Product CSD and a mass balance for the single-stage case are as given previously by Equations (7) and (27). The population balance equation can be solved for each of the two stages to give

Stage 1

$$n_1 = n_1^\circ \exp(-2L/r_1T) \tag{38}$$

Stage 2

$$n_2 = \left[n_2^\circ - \frac{n_1^\circ}{(1-r_2/r_1)} \right] \exp(-2L/r_2T) + \frac{n_1^\circ}{(1-r_2/r_1)} \exp(-2L/r_1T) \tag{39}$$

where $T = V/Q_o$.

The overall solute balance can be expressed as

$$C_iQ_i/Q_o - C = M_{T2} \tag{40}$$

which is identical to the single tank situation. Thus the two relationships which constrain the growth rates are given as

$$M_{T2} = M_{Tm} \tag{41}$$

and

$$M_{T1} = M_{Tm}\alpha \tag{42}$$

Performing the required integrations in (41) and (42) using population distributions (38) and (39) and nucleation-growth kinetics (6*a*) (and assuming $k_{N1} = k_{N2}$ if stage temperatures are different) one gets the following relationships that constrain growth rates r_1 and r_2:

$$r_m^{i+3} = \left[r_2^{i-1} - \frac{r_1^{i-1}}{(1-r_2/r_1)} \right] \frac{r_2^4}{2^4} + \frac{r_1^{i+3}}{2^4(1-r_2/r_1)} \tag{43}$$

and

$$r_1 = r_m\,\alpha^{1/i+3}\,2^{4/i+3} \tag{44}$$

Finally, product CSD can be calculated from the definition of cumulative weight fraction, Equation (24), in terms of the dimensionless MSMPR CSD, Equation (7). Thus

$$W_2 = \frac{\left[r_2^{i-1} - \dfrac{r_1^{i-1}}{(1-r_2/r_1)} \right] r_2^4\, w(x_2) + \dfrac{r_1^{i+3}\, w(x_1)}{(1-r_2/r_1)}}{\left[r_2^{i-1} - \dfrac{r_1^{i-1}}{(1-r_2/r_1)} \right] r_2^4 + \dfrac{r_1^{i+3}}{(1-r_2/r_1)}} \tag{45}$$

where $x_1 = 2L/r_1T$, $x_2 = 2L/r_2T$, and where r_1 and r_2 satisfy Equations (43) and (44).

Numerical evaluation of Equation (45) for the case where $\alpha = 0.5$ and $i = 2$ indicates that the two-stage system produces a considerably smaller and somewhat more uniform CSD than a single stage of equal total volume (C.V. 49 vs. 52 for the single stage). This difference, which would be expected to increase for higher values of nucleation sensitivity, i, is shown clearly in Figure 3. This figure plots the weight distribution of product vs. $x = L/r_mT$, the dimensionless crystal size in the MSMPR case. The curves were obtained by differentiating W_2, Equation (45), with respect to x. Growth rate in the first and second stages was, respectively, 1.52 and 0.80 times the growth rate of the single stage MSMPR. The two-stage crystallizer produces smaller crystals because nucleation was much heavier in the first tank of the staged system as an equal volumetric crystallization rate (pound per hour-cubic feet) had to be deposited on a solids concentration one half that of the single tank case, thus creating higher driving forces. This distribution of fine crystals, which would then be advanced to the second stage, could not grow to large average size because there was not enough available solute in the second stage. It appears that the use of a growth type of crystallizer for the first stage would greatly increase crystal size in a two-stage system.

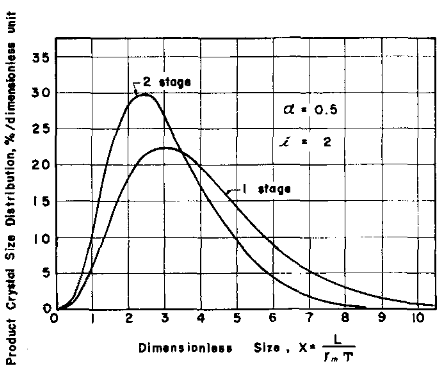

Fig. 3. Comparison of CSD from two- and one-stage crystallizers of equal total volume.

SUMMARY

Simultaneous population and mass balances have been solved together with an assumed generalized form of nucleation-growth kinetics to obtain the form of CSD for several idealized modes of crystallizer operation, including seed crystal removal, product classification, arbitrary solids concentration, and staged vessels. The effect of holding time and feed supersaturation on crystal size in an MSMPR crystallizer was also studied. The power model form of nucleation-growth rate kinetics which was assumed has little to recommend itself other than that it fits such limited data as are available, it can be expressed in terms of a single parameter capable of physical interpretation, and it permits simple analytical solutions of the problems considered. It is hoped that the work presented here will stimulate interest in the very difficult problem of determining nucleation and growth rate kinetics in environments resembling that of a mixed crystal suspension.

Finally, it was shown that with a representative CSD from an operating MSMPR crystallizer together with a limited amount of information concerning nucleation behavior, the actual CSD from any of the above mentioned crystallizer modes could be estimated in terms of the generalized CSD from the MSMPR crystallizer.

NOTATION

a = constant in size-dependent growth rate equation
a' = integration constant in population equation
b = constant exponent in size-dependent growth rate equation
C = concentration of solute in mother liquor, lb./cu.ft.
C_i = concentration of solute in i'th stream of input feed concentration, lb./cu.ft.

C_o = equilibrium concentration of solute in mother liquor, equal to exit concentration for class II system, lb./cu.ft.

i = nucleation-growth rate sensitivity parameter in kinetic nucleation equation

j = kinetic order of growth rate in terms of supersaturation

k_g = specific rate constant in kinetic growth rate equation

k_L = crystal shape factor, volume/(crystal)(length)^3

k_N = specific rate constant in kinetic nucleation rate equation

L = linear crystal size, ft.

L_D = dominant crystal size (weight basis) in exponential population distribution, ft.

M_i = solids concentration in i'th stream, lb./cu.ft. of mother liquor

M_T = solids concentration in crystal suspension, lb./cu.ft. of mother liquor

n = crystal population density, number/ft.-cu.ft. of mother liquor

n_i = crystal population density, in i'th stream, number/ft-cu.ft. of mother liquor

n^o = nuclei population density, number/ft.-cu.ft. of mother liquor

$n\delta L$ = number of particles of original size range L to $L + \delta L$ remaining in suspension at time t

$n^o\delta L$ = original number of particles in size range L to $L + \delta L$

$\dfrac{dN^o}{dt}$ = nucleation rate, number/sec.-cu.ft. of mother liquor

p = dummy variable of integration

$\overrightarrow{Q_i}$ = flow rate of i'th stream, positive for flow into suspension and negative for flow out, cu.ft. of mother liquor/sec.

Q_i = feed stream flow rate, cu.ft./sec.

Q_o = suspension discharge flow rate, cu.ft. of mother liquor/sec.

r = linear crystal growth rate, ft./sec.

s_i = apparent supersaturation in feed, lb./cu.ft.

T = suspension holding time, V/Q_o, sec.

V = crystallizer volume, cu. ft. of mother liquor

$W(L)$ = cumulative mass fraction size distribution

W_p = cumulative mass fraction size distribution of product crystals

W_s = cumulative mass fraction size distribution of crystals in suspension

$w(x)$ = theoretical cumulative mass fraction size distribution for MSMPR crystallizer

x = dimensionless crystal size, L/rT

z = ratio of residence time probability of small crystals to large crystals in classified product crystallizer, or ratio of overflow to underflow mother liquor in growth type of crystallizer

ρ_c = crystal density, lb./cu.ft.

α = fraction of total crystallization occurring in first stage of two-stage crystallizer

μ = fraction of seed crystals left of grow in crystallizer with seed crystal removal system

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APPENDIX

The population balance (*6*) for a mixed crystal suspension may be written as

$$V\left[\frac{\partial n}{\partial t}+\frac{\partial}{\partial L}\left(n\frac{\partial L}{\partial t}\right)\right]+Q_o n=O \tag{46}$$

At steady state $\dfrac{\partial n}{\partial t} = O$, leaving the ordinary differential equation

$$\frac{d}{dL}\left(\frac{dL}{dt}n\right)=-n/T \tag{47}$$

where in general the growth rate

$$r=\frac{dL}{dt}=r(L) \tag{48}$$

may be thought of as a function of size. Thus if McCabe's ΔL law does not hold, the growth rate cannot be taken out of the differentiation. Bransom (*6*) uses a growth rate function of the type

$$r=aL^b \tag{49}$$

Thus the proper differential equation which must be integrated to obtain population density when size dependent growth rate is given as in Equation (49) is

$$\frac{d}{dL}(aL^b n)=\frac{-n}{T} \tag{50}$$

The development given by Bransom (after switching to nomenclature used in this paper) is

$$n\,\delta\,L=n^o\,\delta\,L\exp\left[\frac{-t}{T}\right] \tag{51}$$

where $n\,\delta\,L$ are the number of particles in an original group of number $n^o\,\delta\,L$ and of the size range L to $L + \delta L$, which remain in the suspension a time t; that is the original population $n^o\,\delta\,L$ decays exponentially with time. Bransom then integrates the size dependent growth rate, Equation (49), to obtain an age-size relationship which is then substituted for t in Equation (51), giving a final population equation of the form

$$n=a'\exp\left[\frac{-L^{1-b}}{aT(1-b)}\right] \tag{52}$$

However, if Equation (50) is integrated, the correct form of the population distribution is given as

$$n=\frac{a'}{L^b}\exp\left[\frac{-L^{1-b}}{aT(1-b)}\right] \tag{53}$$

The difference in the two derivations is that when growth rate is size dependent, the increment of size $\delta\,L$ is not fixed but changes with size as the particles grow. This stretching of an incremental size region with size is reflected by a corresponding decrease in population density, as given by Equation (53) but not in Equation (52).

For $b = O$ (McCabe's ΔL law holds) both equations reduce to the correct exponential distribution. Product CSD, which is obtained by integrating L^3dL over the entire distribution, would be qualitatively the same for both equations (that is, dominated by the exponential term), and the conclusions drawn by Bennett (*7*) remain valid.

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