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Transient and Steady State Size Distributions in Continuous Mixed Suspension Crystallizers

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Miller and Saeman (*4*) experimentally demonstrated that at a given production rate superior ammonium nitrate crystals could be produced in an Oslo type of crystallizer when one worked with a mixed rather than a classified crystal suspension. This difference in crystal quality was due to the differences in crystal growth rate which occurred in the two types of crystal suspensions. In a classified crystal suspension there is a gradient of supersaturation from bottom to top, with the highly supersaturated solution entering the bottom and a solution relieved of most of its supersaturation leaving the top. Most inorganic crystals have an upper limit of supersaturation which produces too high a growth rate and results in poorly formed, weak, and friable crystals, as well as crystals with a considerable amount of occluded crystallizing solution. In the case of a mixed suspension the average growth rate is much less than the maximum growth rate at the bottom of a classified crystal suspension. It was this high initial value in the latter case that was reported to cause the difference in crystal quality between the two systems.

In actual practice many industrial crystallizers are operated at higher than design throughput and result in a crystal suspension approaching perfect mixing. Saeman (*7*) has derived relationships for the size distribution, expressed as cumulative weight of crystals vs. size, for a single-tank continuous mixed suspension crystallizer operating at steady state and for the separate cases of mixed and classified product removal. It was observed that the size distribution from a large commercial crystallizing unit was a reasonable approximation of the theoretically predicted distribution. A major point that was brought out in this work was the extreme influence of nucleation rate on resultant size distribution. Methods of controlling size distribution by dissolving excess nuclei were discussed.

Newman and Bennett (*5*) also emphasize the importance of nucleation rate in determining the size of crystals. Net nucleation rate is the sum of nuclei formed at the boiling surface, homogeneously in solution, from attrition of the crystal bed, and by seeding. These authors conclude that the former two sources of nuclei can be reduced by proper crystallizer design. It was also stated that the nucleation rate present in any industrial equipment tends to limit the average product crystal size to a range characteristic of that particular crystal system.

Robinson and Roberts (*6*) made a mathematical study of the size distribution which leaves the k'th stage of k agitator-crystallizers operated in series with nucleation in only the first stage. They compared their equation for the case of a single tank with the size distribution from a commercial unit producing ammonium sulphate. The results from the theory agreed quite well with data from this unit. This work also emphasized the role of nucleation in determining crystal size distribution. Logically all sources of crystal nuclei except deliberate seeding and crystal attrition should be some function of the supersaturation in solution. These authors presented a possible kinetic nucleation equation for the ammonium sulphate system of the form

$$dN^\circ/dt = k_1 (s - s_o)^{k_2} \qquad (1)$$

The value of k_2 was given as ≥ 4, but no data were given to support this equation.

The purpose of the present work was to derive a general size distribution equation which describes the transient behavior of particles in an arbitrary suspension. It was shown that long term transients in product size distribution from a continuous crystallizer can occur in spite of steady state heat and material inputs which can be enforced on the system. This equation

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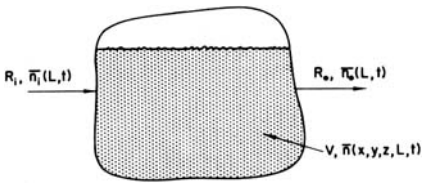

Fig. 1. Arbitrary particle suspension.

was solved to illustrate the dynamic behavior of a continuous, mixed suspension crystallizer.

DEVELOPMENT OF THEORY

There are at least four different ways to express the size distribution of an aggregate of particles distributed along a size axis: cumulative weight percent, weight percent distribution, cumulative number of particles, and population density or number distribution. The second and fourth are respectively the derivatives of the first and third cumulative functions. The cumulative weight plot is perhaps the most common because it is directly obtainable from a screen analysis, but the population density is the distribution which has the most direct theoretical significance with respect to the factors which control size distribution. Thus the number of crystals present in a small size range ΔL is given by

$$\Delta N = n\Delta L \qquad (2)$$

The following derivation utilizes an overall population balance for an arbitrary suspension of particles under unsteady state conditions. The system is not restricted to a crystallizer but is an arbitrary suspension as shown in Figure 1 and is defined by the following assumptions.:

1. The suspension occupies a variable volume V enclosed by fixed boundaries except for a free gravity surface.
2. This volume has inputs and outputs which may be considered mixed across their respective pipe diameters, but the suspension itself is not necessarily mixed.
3. The particles in the suspension are small enough and numerous enough to be considered a continuous distribution over a given size range of particles and over a given volume element of the suspension.
4. No particle breakage occurs except possibly the chipping of a particle into unequal pieces such that one piece is essentially unchanged in size while the other is small enough to be considered a nuclei.

Considering the total number of particles in the suspension within the size range L_1 to L_2 one may write

Accumulation = Input − Output

or may express this statement mathematically in terms of the local population density:

$$\frac{d}{dt}\int_V \int_{L_1}^{L_2} \bar{n}\,dL\,dV = \int_{L_1}^{L_2} \left[\frac{R_i\bar{n}_i}{\rho_i} - \frac{R_o\bar{n}_o}{\rho_o}\right] dL \qquad (3)$$

The left-hand side of Equation (3) can be differentiated inside both integrals by a repeated use of Leibnitz's Rule to get

$$\frac{d}{dt}\int_V \int_{L_1}^{L_2} \bar{n}\,dL\,dV = \int_V \int_{L_1}^{L_2} \left[\frac{\partial \bar{n}}{\partial t} + \frac{\partial}{\partial L}\left(\bar{n}\frac{\partial L}{\partial t}\right)\right] dL\,dV + \int_{L_1}^{L_2} \frac{dV}{dt}\,\bar{n}_s\,dL \qquad (4)$$

$\bar{n}_s$ is assumed constant across the surface. If one interchanges order of integration and transposes, Equation (3) becomes

$$\int_{L_1}^{L_2}\left\{\int_V \left[\frac{\partial \bar{n}}{\partial t} + \frac{\partial}{\partial L}\left(\bar{n}\frac{\partial L}{\partial t}\right)\right] dV + \bar{n}_s\frac{dV}{dt} - \frac{R_i\bar{n}_i}{\rho_i} + \frac{R_o\bar{n}_o}{\rho_o}\right\} dL = 0 \qquad (5)$$

For Equation (5) to be identically zero for an arbitrary size range of particles L_1 to L_2 it is necessary that

$$\int_V \left[\frac{\partial \bar{n}}{\partial t} + \frac{\partial}{\partial L}\left(\bar{n}\frac{\partial L}{\partial t}\right)\right] dV + \bar{n}_s\frac{dV}{dt} - \frac{R_i\bar{n}_i}{\rho_i} + \frac{R_o\bar{n}_o}{\rho_o} = 0 \qquad (6)$$

Equation (6) is a general population balance for an arbitrary suspension of particles subject to the original four assumptions and includes the effects of unsteady state production rate and unsteady suspension volume and density.

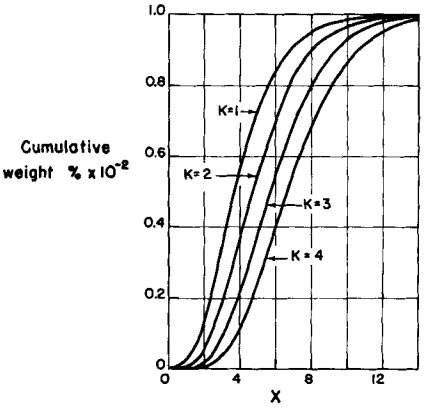

Fig. 2. Cumulative weight per cent vs. dimensionless size for multitank operation and nucleation only in first tank.

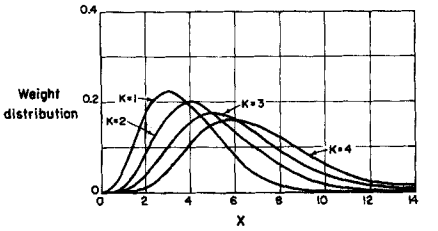

Fig. 3. Weight distribution vs. dimensionless size for multitank operation and nucleation only in first tank.

STEADY STATE SIZE DISTRIBUTIONS IN MIXED SUSPENSIONS

Consider the problem posed by Robinson and Roberts (6) of k agitator-crystallizers operating in series but with the more realistic condition of nucleation in each tank. For steady state operation with perfect mixing in each tank Equation (6) reduces to

$$\frac{d}{dL}\left(\frac{\partial L}{\partial t}n_j\right) = \frac{R_{j-1}n_{j-1}}{W_{j-1}} - \frac{R_jn_j}{W_j} \qquad (7)$$

for the j'th crystallizer tank in the series. If McCabe's ΔL law is assumed to hold, the growth rate $r = \partial L/\partial t$ is independent of L and can be taken out of the differentiation. It will be assumed that the ratio $W/R = T$ is the same in each tank. Equation (7) can then be written for each tank to give the series of equations

$$\begin{aligned} dn_1/dL &= -n_1/rT \\ dn_2/dL &= (n_1 - n_2)/rT \\ &\vdots \\ dn_k/dL &= (n_{k-1} - n_k)/rT \end{aligned} \qquad (8)$$

This assumes that the growth rate remains constant from tank to tank. At this point it is convenient to make the dimensionless substitutions $x = L/r_oT_o$ which yields the set of equations

$$\begin{aligned} dn_1/dx &= -n_1 \\ dn_2/dx &= n_1 - n_2 \\ &\vdots \\ dn_k/dx &= n_{k-1} - n_k \end{aligned} \qquad (9)$$

This set of k first-order differential equations can be solved algebraically to give a single k'th order differential equation for the population density leaving the k'th stage. Thus

$$(D+1)^k n_k = 0 \qquad (10)$$

where D is the differential operator. Equation (10) has a solution of the form

$$n_k = c_1e^{-x} + c_2xe^{-x} + \ldots c_kx^{k-1}e^{-x} \qquad (11)$$

The constants in Equation (11) are determined by the nuclei density in each tank. These coefficients are obtained by equating the derivatives of

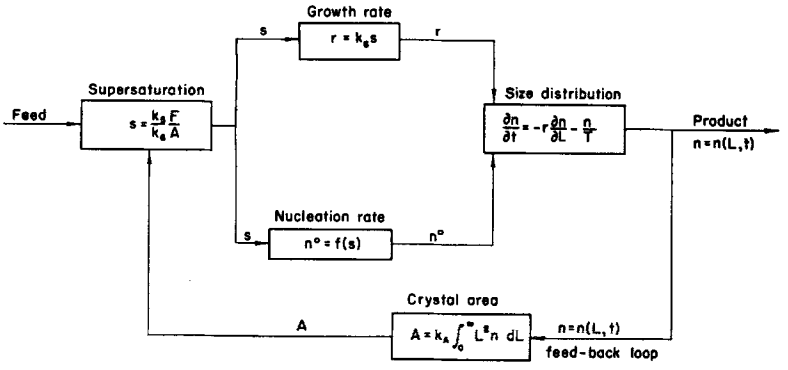

Fig. 4. Information diagram showing factors affecting size distribution.

n_k evaluated at $x = 0$ from Equation (11) and from Equation (9). Thus

$$\text{Cumulative weight fraction below size } x = \frac{\int_0^x x^3 e^{-x}\left[n^\circ_k + \frac{n^\circ_{k-1}x}{1!} + \ldots \frac{n^\circ_1 x^{k-1}}{(k-1)!}\right]dx}{\int_0^\infty x^3 e^{-x}\left[n^\circ_k + \frac{n^\circ_{k-1}x}{1!} + \ldots \frac{n^\circ_1 x^{k-1}}{(k-1)!}\right]dx} \quad (17)$$

and

$$\text{weight \% distribution} = \frac{x^3 e^{-x}\left[n^\circ_k + \frac{n^\circ_{k-1}x}{1!} + \ldots \frac{n^\circ_1 x^{k-1}}{(k-1)!}\right]}{\int_0^\infty x^3 e^{-x}\left[n^\circ_k + \frac{n^\circ_{k-1}x}{1!} + \ldots \frac{n^\circ_1 x^{k-1}}{(k-1)!}\right]dx} \quad (18)$$

$$\begin{aligned} c_1 &= n^\circ_k \\ -c_1 + c_2 &= n^\circ_{k-1} - n^\circ_k \\ c_1 - 2c_2 + (2)(1)c_3 &= n^\circ_{k-2} - 2n^\circ_{k-1} + n^\circ_k \\ &\cdots \end{aligned} \quad (12)$$

where the superscript ($^\circ$) refers to the nuclei population density. Or in general

$$c_j = \frac{n^\circ_{k+1-j}}{(j-1)!} \quad (13)$$

Thus for the general case of k agitator-crystallizers operating in series at steady state with perfect mixing in each tank the exit population density leaving the tank is given in terms of crystal size and nucleation rate in each tank by the equation

$$n_k = e^{-x}\left[n^\circ_k + \frac{n^\circ_{k-1}x}{1!} + \frac{n^\circ_{k-2}x^2}{2!} + \ldots \frac{n^\circ_1 x^{k-1}}{(k-1)!}\right] \quad (14)$$

For nucleation only in the first tank

$$n_k = \frac{n^\circ_1 x^{k-1} e^{-x}}{(k-1)!} \quad (15)$$

which is equivalent to the equations developed by Robinson and Roberts (6), and for a single tank

$$n = n^\circ e^{-x} \quad (16)$$

which is the theoretical population density in a mixed suspension, mixed product removal crystallizer as given by Saeman (7).

Both the cumulative weight and weight distribution functions can be obtained directly from Equation (14) by integration. Thus

Equations (17) and (18) can easily be integrated for a given number of tanks k. Figures 2 and 3 are plots of Equations (17) and (18) for the case of nucleation only in the first tank and $k = 1, 2, 3$, and 4. Referring to Figure 3 one sees that the size for maximum weight distribution increases with the number of tanks in series. This dominant crystal size is given by

$$x_m = k + 2 \quad (19)$$

Equation (18) suggests the interesting possibility of producing crystals of a nearly arbitrary weight distribution, for instance bimodal, by means of a series of crystallizing tanks with controlled nucleation or seeding in each tank. The desirability of such an operation would have to be evaluated economically taking into account also the loss of versatility over such alternate methods as blending product from individual units.

DYNAMICS OF A CONTINUOUS MIXED SUSPENSION MIXED PRODUCT REMOVAL CRYSTALLIZER

The problem of size distribution in a continuous crystallizer is a problem of kinetics and not of thermodynamics. Thus by fixing the energy and material inputs one can guarantee the production of a pound of crystalline material, but whether this pound of material is distributed over a few large sized crystals or many small ones is determined by the kinetic nucleation rate. Thus the control of size distribution in a continuous crystallizer cannot be guaranteed no matter how well the external operating variables are controlled unless nucleation is controlled. Furthermore the problem of transient size distribution in a crystallizer is not trivial owing to the large time lag from nucleation to full crystal size and to a feedback relationship between nucleation rate, growth rate, and size distribution. This feedback relationship will be developed in the following discussion.

Consider a continuous, mixed suspension, mixed product removal crystallizer operating under the following controls:

1. Feed rate is set at constant rate.
2. Energy input is controlled to maintain constant suspension.
3. Constant suspension volume is maintained.

Equation (6) reduces to

$$\frac{dn}{dt} = -r\frac{\partial n}{\partial L} - \frac{n}{T} \quad (20)$$

where $n = \bar{n}V$ because of mixed suspension, $\partial L/\partial t = r \neq f(L)$ if McCabe's ΔL law holds, $\bar{n}_i \equiv$ zero for liquid feeds, $\bar{n}_o = \bar{n}$ because of mixed product removal, $dV/dt =$ zero for constant suspension volume, and $1/T = R_o/\rho_o V$ the reciprocal of the draw down time. The operation of the control system to maintain restraints 1 through 3 is assumed to be ideal, that is instantaneous response with no time lag. In any case it will be shown that the characteristic time response of the crystal size distribution is several orders of magnitude greater than any reasonable time constants for the control system, and hence fluctuations in the latter will average out and can be neglected. Equation (20) demonstrates that even under conditions of perfect energy and material balance control the possibility for transient size distribution still exists. The next step is to determine the variation of the crystal growth rate under the above conditions. From conditions 2) and 3) the total mass of crystals in suspension remains constant, where

$$M = k_s \rho_o \int_0^\infty nL^3\, dL \quad (21)$$

Crystals of all sizes are assumed similar in shape (habit). Differentiating (21) one gets

$$\frac{dM}{dt} = 0$$

$$\frac{d}{dt}\int_0^\infty nL^3\, dL = 0 \quad (22)$$

Thus

$$\int_0^\infty L^3 \frac{\partial n}{\partial t}\, dL = 0 \quad (23)$$

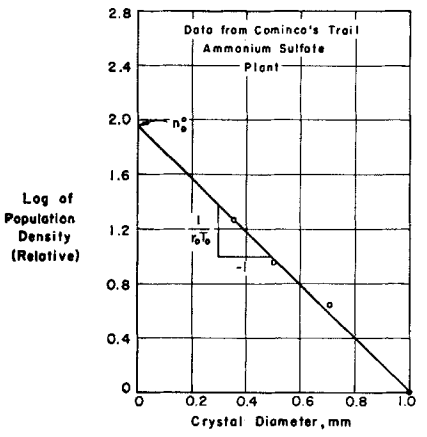

Fig. 5. Comparison of theoretical and actual size distribution from mixed suspension, mixed product removal crystallizer.

Substituting for $\partial n/\partial t$ from Equation (20) in the left-hand member of Equation (23) and integrating by parts one finds

$$\frac{\partial L}{\partial t} = r = \frac{\int_o^\infty nL^3\,dL}{3T\int_o^\infty nL^2\,dL} \qquad (24)$$

But from Equation (21) the numerator of Equation (24) is constant, and hence the growth rate is given by

$$r = \frac{k_4}{T\int_o^\infty nL^2\,dL} \qquad (25)$$

or

$$r = \frac{k_5 P}{k_4\int_o^\infty nL^2\,dL} = \frac{k_5 F}{k_4\int_o^\infty nL^2\,dL} \qquad (26)$$

Equation (26) shows that under conditions of constant total mass of crystals in a constant volume crystallizer the growth rate is proportional to the feed rate (or production rate) and inversely proportional to the total crystal area in suspension. Equation (26) can be arrived at independently from completely physical arguments by relating the gain of mass on a single crystal to the growth rate and then summing over the entire crystal suspension to obtain the total production rate.

The final step to describe transients in size distribution in a continuous crystallizer is to determine the behavior of the nucleation rate. A first-order kinetic rate law has been used (7) to describe the relationship between growth rate and supersaturation. Thus

$$r = k_6 s \qquad (27)$$

There is experimental evidence (3) for this type of equation, but in any case the growth rate can be assumed to be only a function of supersaturation if there is no variation of growth rate with crystal size, that is if McCabe's ΔL law holds. The fact that nucleation rate can logically be assumed to be a kinetic function of supersaturation has previously been discussed. Thus in the light of Equation (27) one may write

$$\frac{dN^\circ}{dt} = h(s) = g(r) \qquad (28)$$

where dN°/dt is the net rate of nuclei formed and the function $g(r)$ would have to be determined experimentally by correlating dN°/dt and r for a series of steady state runs at different production rates. The nuclei density is related to the nucleation rate in the following equation:

$$dN^\circ/dt = \frac{\partial L}{\partial t}\left(\frac{dN}{dL}\right)_{L=0} = rn^\circ \qquad (29)$$

which indicates that the nuclei density can also be directly correlated with the growth rate. Figure 4 is an information flow diagram which illustrates the dynamic interrelationship between variables affecting the product size distribution. Starting from the left of Figure 4 one sees that the level of supersaturation in the suspension is determined by the feed rate and the total surface area of the crystal suspension. The level of supersaturation then simultaneously determines the growth and nucleation rates. These rates are given by the appropriate kinetic equations. The growth and nuclei density then appear as a factor and as a boundary value of Equation (20) which relates population density to size and must be solved to determine the size distribution at any time. However the total surface area in the crystal suspension is determined by the size distribution as shown by the block in the feedback loop. Thus it is apparent that disturbances can feed back into the system and cause transients which make control of product size distribution difficult.

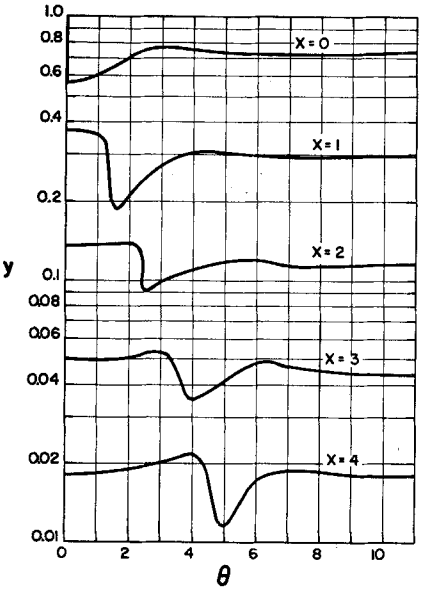

Fig. 6. Transients in population density for a step decrease in production rate, T_o/T = 0.8333.

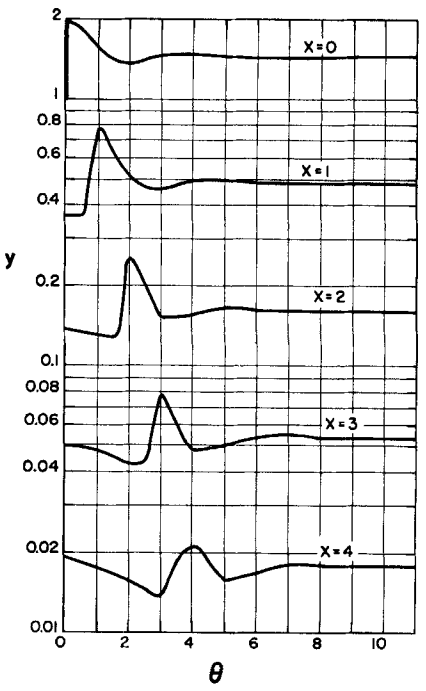

Fig. 7. Transients in population density for a step increase in production rate, T_o/T = 1.250.

SOLUTION OF TRANSIENT SIZE DISTRIBUTION EQUATION

Step Change in Production Rate

The transient size distribution equation can be solved for a step change in production rate for an ammonium sulfate crystallizer operating with mixed suspension and mixed product removal if the kinetic nucleation equation of Robinson and Roberts is assumed to hold. Unpublished nucleation experiments (2) on the ammonium sulfate system indicated that in a stirred seeded solution, nucleation occurred immediately when the solution was cooled to its saturation temperature. This indicated that there was no measurable supersaturation below which the solution was metastable. Thus the kinetic nucleation rate Equation (1) becomes

$$dN^\circ/dt = k_1 s^4 = k'_1 r^4 \qquad (30)$$

or from Equation (29)

$$n^\circ = k'_1 r^3 \qquad (31)$$

At this point it is convenient to introduce the following dimensionless substitutions in Equation (20). Let

$$\begin{aligned} x &= L/r_o T_o \\ y &= n/n^\circ_o \\ \theta &= t/T_o \\ \phi &= r/r_o \end{aligned} \qquad (32)$$

where the subscripts $(_o)$ refer to steady state values at a reference pro-

duction rate. Under these substitutions Equation (20) becomes

$$\frac{\partial y}{\partial \theta} = -\phi \frac{\partial y}{\partial x} - y \frac{T_o}{T} \qquad (33)$$

The steady state solution which satisfies this equation at a production rate equal to the reference production rate is

$$y = e^{-x} \qquad (34)$$

which becomes an initial condition in describing adjustment of the size distribution to a step change in production rate. (To conform with constraints 2 and 3 a simultaneous change in energy inputs would have to accompany a change in feed rate.) The dimensionless growth and nucleation rate functions are obtained directly by performing the corresponding dimensionless substitutions. Thus

$$y^o = n^o/n^o_o = (r/r_o)^3 = \phi^3 \qquad (35)$$

and

$$\phi = \frac{T_o \int_o^\infty x^2 e^{-x} dx}{T \int_o^\infty x^3 y dx} = \frac{2T_o/T}{\int_o^\infty x^3 y dx} \qquad (36)$$

Equation (33) solved with the initial and boundary conditions (34) and (35) and with the constraint on the growth rate, Equation (36), gives the transient response of the crystal population density as the suspension adjusts from one steady state production rate to another. Equations (33) through (36) were solved numerically on an IBM-704 digital computer with standard finite difference techniques for the two cases of $T_o/T = 1.25$ and 0.8333. The range of x was taken in the interval (0, 15) to insure the convergence of the numerical solution. It is recognized that in an actual crystallizer few if any crystals greater than about 8 mesh would be found in suspension. Crystals of this size would not obey the original assumptions used in developing the equations, but they only constitute a small portion of the total crystal area. Equations (33) and (36) involve only the ratio of production rates and hence are independent of the magnitude of production rate. There are physical limitations however which limit production from a crystallizer unit to some range, as well as an upper limit on growth rate beyond which poor quality crystals result. These equations would not be expected to pertain for a step change outside the allowable operating range. Industrial ammonium sulfate crystallizers usually operate with drawdown times of the order of 6 to 12 hr. Robinson and Roberts (6) give the size distribution from a vacuum ammonium sulfate crystallizer operating with a drawdown time of 11.5 hr. and with an estimated growth rate of 2.0 by 10^{-6} ft./min. These data provide an illustration of the method of obtaining values of y^o_o and r_o from steady state screen analyses and also provide an estimate of the growth rate so that the numerical solution of Equations (33) through (36) can be converted to screen sizes. Figure 5 plots ln n vs. L from data of Robinson and Roberts which illustrate the agreement between the theoretical distribution and actual size distributions from a large industrial crystallizer. The values of n^o_o and r_o can be obtained from the intercept and slope of this plot.

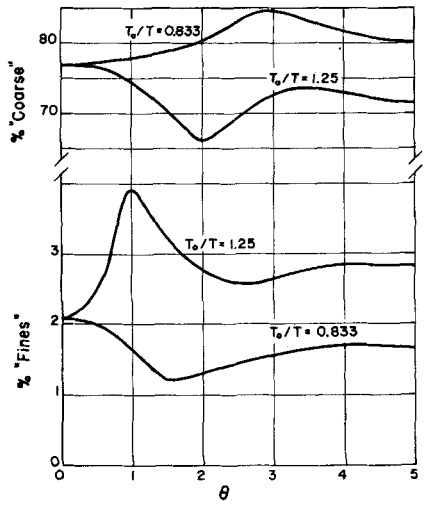

Fig. 8. Transient response of fines and coarse to step production rate changes.

Figure 6 gives the transient behavior of population density vs. θ for various dimensionless size ratios for a step decrease of production rate of $T_o/T = 0.8333$. Figure 7 gives the same information for a step increase of $T_o/T = 1.250$. From inspection of these curves it is seen that the change in production rate causes an abrupt change in nucleation rate. This change in nuclei density propagates as a wavelike disturbance traveling at the instantaneous dimensionless growth velocity, approximately unity. As this wave disturbance travels along the x-axis the total crystal area changes, thereby changing the growth and nucleation rates in a direction opposite from the initial step changes. With the kinetics which were used this feedback change in growth and nucleation rates is smooth and quite damped and causes the propagation of a second smoother wave disturbance which is practically negligible compared with the first. This second wave generates a third and so on, with each disturbance less than the previous one. Only the first abrupt disturbance is of great enough magnitude to cause a significant change in product weight distribution. Even though only the original step disturbance causes significant fluctuations in product weight distribution, these transients are of long-term duration owing to the relatively long length of time required to grow a product-sized crystal. Figure 8 plots the transient behavior of fines (−35 mesh) and coarse (+16 mesh) for both a step increase and decrease in production rate. These curves were obtained by the use of the value of $r_oT_o = 0.421$ mm. and the definition of weight percent in an interval:

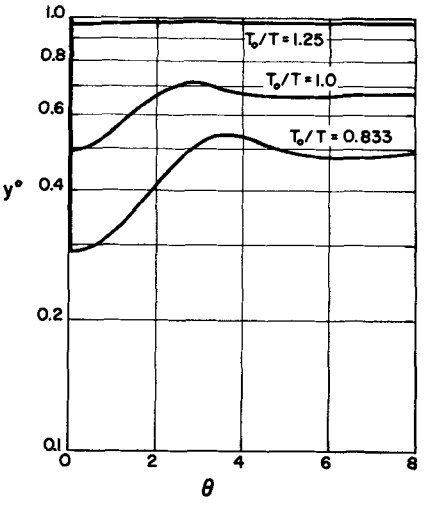

Fig. 9. Transient response of nuclei density to simultaneous step changes in nuclei dissolving rate and production rate.

$$\text{weight } \% = \frac{\int_{x_1}^{x_2} x^3 y dx}{\int_o^\infty x^3 y dx} = \frac{\int_{x_1}^{x_2} x^3 y dx}{1/6} \qquad (37)$$

From Figure 8 it is seen that for a crystallizer operating with a drawdown time of 10 hr., a period of approximately 40 hr. is required for the size distribution to adjust to a new level after a 20% change in production rate. In view of this long period of adjustment and in view of the frequency of upsets encountered with such operations as washing, etc., it is unlikely that a steady state size distribution is ever achieved.

Nuclei Dissolving

It is apparent from earlier work reported in the literature and from the equations developed in this work that control of nucleation is the key to control of crystal size distribution. One way to affect the net nucleation rate (but not necessarily to control it in a closed-loop sense) is to separate nuclei from the crystal suspension and steam dissolve them. If assumptions are made concerning the operation of the nuclei dissolving system, then the previously derived equations may be used to describe the transient response to changes

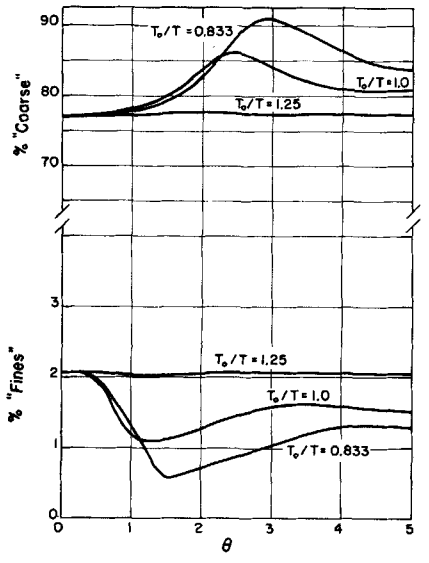

Fig. 10. Transient response of per cent weight coarse or fines to simultaneous step changes in nuclei dissolving rate and production rate.

in nuclei dissolving rate. It is rather open to question what the operating characteristics of a nuclei dissolving system would be (8), but in the case of a dissolving region with a fixed degree of unsaturation and constant residence time of nuclei, a proportional model seems reasonable in which the number of nuclei destroyed are proportional to the nuclei density. If this proportional model is assumed, then the nucleation equation becomes

$$y^\circ = \mu\phi^3 \qquad (38)$$

Equations (33), (34), and (36) still pertain. To illustrate the effect of a step change in dissolving rate and also the possibility of controlling size distribution with proper steam dissolving, Equations (33), (34), (38), and (35) were numerically solved for the three cases of a step change $\mu = 0.5$ and T_o/T respectively 0.8333, 1.0, and 1.250. Figure 9 gives the behavior of the population density for these three cases. It is seen that for the decrease in production rate ($T_o/T = 0.8333$) the application of nuclei dissolving is in the wrong direction. This accentuates the sudden decrease in nuclei density and magnifies the transient behavior of the system. For the case of an increase in production rate($T_o/T = 1.250$) the effect of nuclei dissolving essentially cancels the effect due to the production rate change. Figure 10 gives the weight per cent of coarse and fine crystals in the product as a function of θ for the same three cases as shown in Figure 9. It is apparent that for an increase in production rate a steam dissolving system for nuclei can be used not only to eliminate transients in size distribution but to maintain the original crystal quality of the lower production rate.

Response to Periodic Upsets

The distribution of total crystal area in a continuous crystallizer at steady state under operating conditions as described previously is given by

$$da/dx = x^2 e^{-x} \qquad (39)$$

This function has a maximum at $x = 2$. Thus as the transient population density behaves in general like e^{-x}, disturbances fed into the system in the form of nuclei changes should have their maximum effect on growth rate at approximately $\theta = 2$. Actually in the previous example of nuclei dissolving this maximum of growth rate was very broad and occurred closer to $\theta = 3$ than $\theta = 2$ because of a shift of the size distribution curve. One would then expect the system to be sensitive to step disturbances of approximate duration $3T$. Whether or not such disturbances feed back into the system to give an amplitude ratio (based on fluctuations in the growth rate) greater than unity would depend on the kinetics of nucleation. However the system should achieve its greatest sensitivity to cyclic disturbances of this approximate frequency. To test the response to periodic upsets of a continuous crystallizer the nucleation equation was modified to be

$$y^\circ = C(\theta)\,\phi^3 \qquad (40)$$

where the function $C(\theta)$ was a square wave function of half period B and amplitude either 0.9 or 1.0. Equation (40) was solved numerically with Equations (33), (34), and (36). The disturbance described by Equation (40) corresponds directly to periodic step changes in steam dissolving rate but indirectly would approximate the effects of step disturbances in vacuum control (temperature), suspension, production rate, or any other variable having an effect on nucleation rate. The amplitude ratio for these disturbances was arbitrarily defined as the ratio of maximum steady state growth rate amplitude to the maximum amplitude based on a single aperiodic step change of equal magnitude. It can easily be shown that for the assumed kinetics the steady state growth rate resulting from a step change in dissolving rate is

$$\phi = \mu^{-1/7} \qquad (41)$$

Thus the amplitude ratio is defined as

$$A.R. = \frac{\theta_{max} - 0.95^{-1/7}}{\theta_{max,\infty} - 0.95^{-1/7}} \qquad (42)$$

The amplitude ratio as defined in Equation (42) equals unity for an aperiodic step and approaches zero for an input disturbance of infinite frequency. Figure 11 gives the amplitude ratio of the growth rate vs. the frequency of disturbance. It is apparent from this plot that the maximum disturbance in the system does occur with a step disturbance with duration of about $3T$ hr. However the kinetic nucleation equation which was used does not appear to feed back much instability into the system. The amplitude ratio around the critical frequency should be quite sensitive to the kinetic nucleation function, and it is possible that extreme variations would occur if a higher order nucleation equation were used. It is interesting to speculate that some of the instability and long-term transients in size distribution observed in ammonium sulfate crystallizers could be generated by small daily changes in operation over three shift periods for units operating with drawdown times in the range of 8 hr. Figure 11 shows conclusively that the short-term fluctuations in instrument control systems should not cause transients in product size distribution. However these fluctuations could result in substantial degradation of product size if nucleation rate were adversely effected.

CONCLUSIONS

A general population balance for particles in an arbitrary suspension has been presented. This equation holds for any system subject to the original assumptions in the derivation, but it is particularly interesting for a growing system, that is where $\partial L/\partial t \neq 0$, of which crystallization is the best example. This equation can be solved for steady state single and multitank crystallizers with mixed suspension to give size distributions given previously (6, 7) in the literature. These equations were solved for the more general case of nucleation in each tank. The resulting size distribution equation contains coefficients for individual terms which are equal to the nuclei density in the various tanks. This equation suggests the interesting possibility of producing nearly arbitrary size distributions by means of multitank operation with controlled nucleation or seeding in

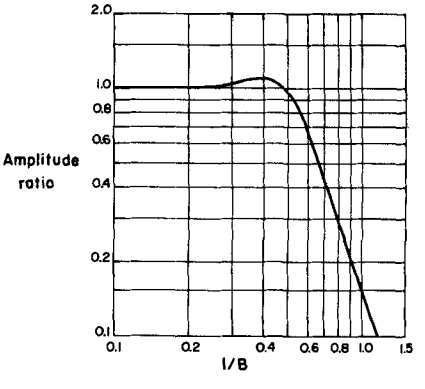

Fig. 11. Frequency response of growth rate to disturbance of half-period B.

each tank. The analytic solutions presented in this and earlier works emphasize that whereas control of operating variables and close attention to design details can result in improvement in crystal quality from a unit, the basic type of size distribution obtainable is set by the type of crystallizer used, that is mixed suspension, classified product removal, multitank, etc.

With the general population balance equation it was shown that even with all controllable operating variables held constant, the possibility of transient behavior of the size distribution still exists. This transient behavior of crystal size distribution under the constraint of constant total crystal suspension was studied for the cases of step changes in production rate and nuclei dissolving by means of assumed kinetics of nucleation which have been suggested for the ammonium sulfate system. The transient behavior in detail is a function of the sensitivity of the nucleation equation, but gross behavior should be independent of nucleation sensitivity and is illustrated by these solutions. The equations were solved in dimensionless form and should be applicable for any crystal system having the same functional relationship between nucleation and growth rates. This work points up the need for more information on the kinetics of nucleation rate under conditions resembling those in a mixed crystal suspension. Until a method of counting nuclei in a mixed suspension is devised, the only feasible method for such a study appears to be the rather crude method of inferring net nuclei density from steady state size distributions as illustrated in this paper and first suggested by Bransom et al. (*1*).

A frequency analysis was made for a continuous crystallizer in which the effect on the system of a periodic, small amplitude disturbance of the nuclei dissolving rate was measured in terms of its effect on growth rate. It was found that a crystallizer is sensitive to step upsets of duration $3T$ (that is total cyclic period $6T$), but the amount of instability resulting from such disturbances depends on the sensitivity of the nucleation rate. This suggests the alternate possibility of obtaining nucleation data from an experimental frequency analysis of an operating crystallizer. However the uncertainties in the operating behavior of the nuclei dissolving system would make this possibility appear dubious.

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NOTATION

A = total surface area of crystals in suspension

$A.R.$ = amplitude ratio of fluctuations in growth rate caused by periodic upset of nucleation rate

a = dimensionless crystal area function defined as $a = \int_0^x x^2\, y dx$

B = half period of square wave disturbance imposed on nucleation rate, dimensionless

$C(\theta)$ = dimensionless square wave function imposed as coefficient of nucleation function

F = total crystallizer feed rate, lb./hr., based on solids content

$g(r)$ = functional relationship between nucleation rate and crystal growth rate

$h(s)$ = functional relationship between nucleation rate and supersaturation

k_1 = constant relating nucleation rate to power of supersaturation

k'_1 = constant relating nucleation rate to power of growth rate

k_2 = exponent constant equal to the order of the kinetic nucleation equation

k_3 = crystal volume shape factor, volume/crystal/(length)^3

k_4 = constant relating crystal growth rate to drawdown time and suspension area function

k_5 = constant relating crystal growth rate to product or feed rate and suspension area function

k_6 = proportionality constant between growth rate and supersaturation

k_A = crystal area shape factor, area/crystal/(length)^2

L = crystal length, ft., measured along a characteristic axis

M = total mass of crystals in suspension, lb.

ΔN = total number of crystals in size range ΔL

N^o = total number of nuclei

n = total crystal population density, number/ft.

$\bar{n}$ = point crystal population density, number/ft./cu.ft.

$\bar{n}_i$ = suspension input population density, number/ft./cu.ft.

$\bar{n}_o$ = suspension output population density, number/ft./cu.ft.

$\bar{n}_s$ = crystal population density at suspension surface, number/ft./cu.ft.

n^o = total nuclei population density, number/ft.

n^o_o = steady state reference total nuclei population density, number/ft.

P = crystal product rate, lb./hr., of solid product

r = crystal growth rate along characteristic crystal axis, ft./hr.

r_o = steady state reference crystal growth rate, ft./hr.

R_i = suspension input rate, lb./hr.

R_o = suspension output rate, lb./hr.

s = supersaturation in solution, lb./cu.ft.

s_o = critical supersaturation below which solution is metastable, lb./cu.ft.

T = drawdown time, hr.

T_o = reference drawdown time, hr.

t = time, hr.

V = total suspension volume, cu.ft.

W_j = total mass of suspension, lb.

x = dimensionless crystal size, L/r_oT_o

x_m = dominant crystal size on weight basis, dimensionless

y = dimensionless population density, n/n^o_o

y^o = dimensionless nuclei population density, n^o/n^o_o

Greek Letters

ϕ = dimensionless crystal growth rate, r/r_o

ϕ_{max} = maximum dimensionless growth rate under influence of periodic perturbation of nucleation rate

$\phi_{max,\infty}$ = maximum dimensionless growth rate occurring after aperiodic step perturbation of nucleation rate

μ = fraction of nuclei left undissolved

ρ_c = crystal density, lb./cu.ft.

ρ_i = input average suspension density, lb./cu.ft.

ρ_o = output average suspension density, lb./cu.ft.

θ = dimensionless time co-ordinate, t/T_o

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