Effect of Suspension Density on Crystal Size Distribution

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The concept of a continuous mixed suspension–mixed product removal crystallizer was used both as an analysis and experimental tool to study the effects of suspension density on crystal size distribution. If the crystals present in suspension are not a source of nuclei, larger crystals will be obtained in the presence of higher suspension densities. If the rate of new particle formation is proportional to the amount of crystals present, the crystal size obtained will not be changed by the suspension density level. There was evidence of nucleation rate dependency on the quantity of suspended crystals in the two systems studied experimentally.

In the study of crystal size distribution in continuous crystallizers, it is necessary to consider the important effect of the solids held in suspension on the size distribution obtained. It has been suggested by a number of investigators that the suspension density affects both (*3*, *4*) growth rate and nucleation rate. The relationship between these two phenomena, nucleation and growth, determines the size distribution obtained in continuous, mixed suspension crystallizers (*6*).

The concept of a mixed suspension–mixed product removal crystallizer has been advantageously used, both theoretically and experimentally, to study the variables affecting size distribution. Such a crystallizer is closely approximated by some industrial applications. Randolph (*4*) has suggested how data obtained from such crystallizers may be used in the study of a variety of other continuous crystallization schemes. His studies as well as others have been largely concerned with the effect of residence time and classified crystal removal on the particle size distribution. Consequently, the assumption of constant suspension density has been made. In most work the effect of suspension densities has been recognized but no quantitative analyses have been offered.

CONSERVATION OF POPULATION, MASS, AND ENERGY

In any crystallizer, particle population must be conserved as well as mass and energy. Randolph and Larson (*5*) have shown for continuous crystallization that the principle of conservation of crystal population leads to the development of the following equation at steady state:

$$n = n^o \exp(-L/rT) \tag{1}$$

The crystal suspension has been constrained in this development by the following simplifying assumptions and operating constraints: the suspension occupies a constant volume within the crystallizer, no external seed crystals are fed to the crystallizer, the crystal suspension is perfectly mixed, the crystal distribution withdrawn from the vessel is totally representative of the distribution within the vessel, growth rate, $r = dL/dt$, is not a function of crystal size, and crystals form a continuous distribution with respect to their size.

The coefficient n^o is the population density of the nuclei size fraction. Equation (1) is applicable if homogeneous nucleation occurs and if new particles are formed as a result of attrition (or because of some other solid dependent phenomena) so long as the new particles thus formed are of nuclei size and the parent crystals experience no measurable size degradation.

The principle of conservation of mass in conjunction with the principle of conservation of crystal population can be utilized to develop an expression which relates crystal growth rate, r, to solute concentration change, ΔC, and crystal size distribution. When changes in supersaturation are small compared to changes in suspended magma concentration, we obtain

$$r = \frac{V \Delta C}{3\, k_v\, T\, \rho \int_0^\infty nL^2 dL} \tag{2}$$

At steady state $\Delta C = M$, where suspension density is defined by

$$M = \frac{k_v \rho}{V} \int_0^\infty nL^3 dL \tag{3}$$

and suspension area by

$$A = \frac{k_A}{V} \int_0^\infty nL^2 dL \tag{4}$$

Thus, it should be noted that the integral in the denominator of Equation (2) is proportional to the total area of the suspension.

By maintaining isothermal operation conditions, the principle of conservation of energy may be satisfied.

NUCLEATION—INDEPENDENT OF SUSPENSION DENSITY

A kinetic expression defining the rate of formation of new crystals (nucleation) in a continuous crystallization process has been taken by previous authors (*1*, *5*) as a function only of supersaturation, such as:

$$\frac{dN^o}{dt} = f(s) \tag{5}$$

Such a model implies strongly that homogeneous nucleation is the dominant source of nuclei.

Let $f(s)$ be a simple power model; then

$$\frac{dN^o}{dt} = k\, s^i \tag{6}$$

For systems which exhibit growth rate as a power function of supersaturation, Equation (6) may be written as:

$$\frac{dN^o}{dt} = k_N\, r^i \tag{7}$$

It has been shown (*5*) that

$$\frac{dN^o}{dt} = rn^o \tag{8}$$

therefore

$$n^o = k_N\, r^{i-1} \tag{9}$$

The effect of ΔC or M on the size distribution for the case where all other conditions are held constant may now be examined. For steady state conditions Equation (1) may be substituted into the integral in Equation (2). After integration, Equation (2) becomes

$$r = \frac{VM}{6kvn^o r^3 T^4 \rho} \tag{10}$$

Comparison of the growth rates at two levels of M utilizing Equation (10) gives:

$$\left(\frac{r_1}{r_2}\right)^4 = \frac{M_1}{M_2}\,\frac{n^o{}_2}{n^o{}_1} \tag{11}$$

Combining Equation (11) with Equation (9) gives:

$$\frac{r_1}{r_2} = \left(\frac{M_1}{M_2}\right)^{\frac{1}{i+3}} \tag{12}$$

and

$$\frac{n^o{}_1}{n^o{}_2} = \left(\frac{M_1}{M_2}\right)^{\frac{i+1}{i+3}} \tag{13}$$

It can be shown that the dominant particle size on a weight basis is

$$L_d = 3rT \tag{14}$$

Therefore, the relationship of the expected L_d for the two cases is

$$\frac{L_{d_1}}{L_{d_2}} = \left(\frac{M_1}{M_2}\right)^{\frac{1}{i+3}} \tag{15}$$

Utilizing Equation (1) and the relationship given by Equations (12) and (13), the size distributions for two levels of ΔC and, consequently, two levels of M, may be compared. Figure 1 shows two plots of Equation (1) for two levels of ΔC where $\Delta C_2 = 3\Delta C_1$ and $i = 2$.

As can be seen from the plot, the crystal size is enhanced when the magma density is increased, if Equation (7) is an adequate model for nucleation rate. The lower the order of the kinetic order i, the greater will be this enhancement.

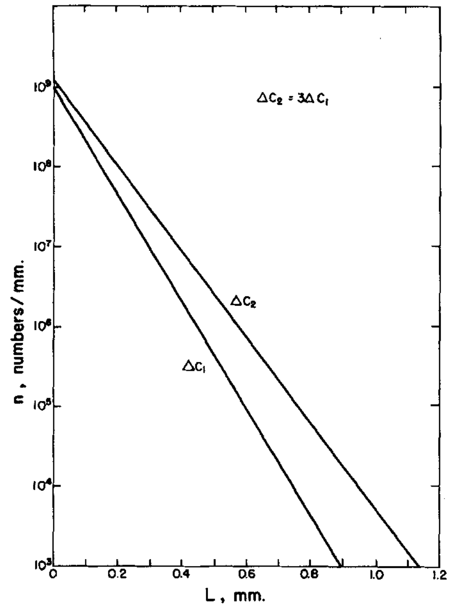

Fig. 1. Crystal size distribution: homogeneous nucleation.

NUCLEATION—DEPENDENT ON SUSPENSION DENSITY

The phenomena described in the previous paragraphs are not always observed. In fact, degradation in particle size sometimes results from increased suspension density. Murray (*2*) found in a limited experimental effort that a threefold change in suspension density gave no detectable change in size distribution, and, consequently, the growth rate, for the ammonium alum-enthanol-water system. This system is of low kinetic order, the order i being between 1 and 2 (*2*, *7*).

A number of authors have given various explanations for the effect of solids in suspension on nucleation. Among these are fracture of dendritic growth, the sweeping away from the neighborhood of the individual crystals a reservoir layer of high solute concentration (*3*), and attrition and catalysis. Any of these phenomena would be crystal area or crystal mass dependent and a correlation would be possible if two criteria are met: mixing must be maintained at constant intensity but adequate to keep the suspension well mixed, and if attrition is a factor, new particles thus formed must be small and near nuclei size and the parent crystal must not suffer measurable size degradation.

A kinetic model including the effect of suspension density must also recognize that supersaturation is still a factor in the formation of new particles. Supersaturation would not only affect the rate of dendritic growth, the magnitude of the reservoir layer previously mentioned and the rate of nucleation due to catalysis, but would also affect the probability of survival of the new particles thus formed.

A model which includes the effect of both supersaturation and solids present must result from the tacit assumption that supersaturation is at a level at which nucleation occurs only in the presence of suspended solids.

The following model relates the nucleation rate as a simple power functions of both supersaturation, s, and suspension density, M:

$$\frac{dN^o}{dt} = k_N\, M^j\, s^i \tag{16}$$

Incorporation linear growth rate as before we get

$$\frac{dN^o}{dt} = k_M\, M^j\, r^i \tag{17}$$

Thus, by Equation (8) we get

$$n^o = k_M\, M^j\, r^{i-1} \tag{18}$$

Substituting Equation (18) into Equation (11) and recalling that $\Delta C = M$ gives:

$$\left(\frac{r_1}{r_2}\right)^{i+3} = \left(\frac{M_1}{M_2}\right)^{1-j} \tag{19}$$

and

$$\left(\frac{n_1{}^o}{n_2{}^o}\right)^{i+3} = \left(\frac{M_1}{M_2}\right)^{i+4j-1} \tag{20}$$

Similarly, if nucleation is taken to be a power function of the suspended magma area instead of mass, the following results are obtained

$$n^o = k_A\, A^j\, r^{i-1} \tag{21}$$

$$\left(\frac{r_1}{r_2}\right)^{i+3} = \frac{\Delta C_1}{\Delta C_2}\left(\frac{A_2}{A_1}\right)^j \tag{22}$$

At steady state

$$\Delta C = M = 6\, K_v\, \rho\, n^o\, (rT)^4/V \tag{23}$$

$$A = 2\, K_A\, n^o\, (rT)^3/V \tag{24}$$

Thus

$$\left(\frac{r_1}{r_2}\right)^{i+2} = \left(\frac{A_1}{A_2}\right)^{1-j} \tag{25}$$

$$\left(\frac{n_1{}^o}{n_2{}^o}\right)^{i+2} = \left(\frac{A_1}{A_2}\right)^{i+3\,j-1} \qquad (26)$$

Therefore, Equations (19) and (20) [or Equation (25) and (26)] predict the steady state dependency of the growth rate and of the nuclei population density for those crystal systems which satisfy the constraints of the proposed model.

It is of interest to elaborate on the effect of the numerical value of j on the corresponding expected steady state crystal distribution described by Equation (1). If $j = 0$, then by Equation (16), the basic nucleation mechanism would be that of homogeneous nucleation and the analysis of the preceding section applies.

If $j = 1.0$, then the nucleation rate, Equation (16), is a linear function of suspension density. Furthermore, Equation (19) predicts that

$$r_1 = r_2 \qquad j = 1.0 \qquad (27)$$

and by Equation (20) we obtain

$$n_1{}^o = n_2{}^o\,(M_1/M_2) \qquad j = 1.0 \qquad (28)$$

Using the relationships described by Equation (27) and (28), Equation (1) is plotted in Figure 2 for the case where $M_2 = 3M_1$ and $i = 2$. Thus when suspension density is a linear factor in the nucleation rate, the same crystal size distribution results for different suspension densities regardless of the kinetic order of its dependency on supersaturation. This fact is illustrated by the parallel lines in Figure 2.

For the case of $0 < j < 1.0$ and for $M_1 < M_2$, Equation (1), (19), and (20) predict that the overall crystal size distribution will be enhanced by increases in suspension density. That is, the dominant particle size on a mass basis will increase as a result of an increase in M. The maximum enhancement will occur as j approaches zero.

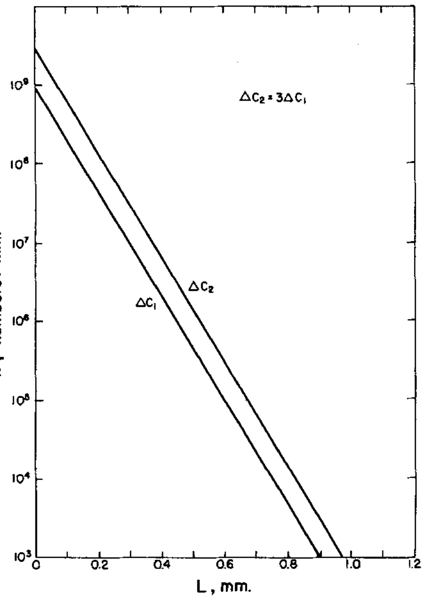

Fig. 2. Crystal size distribution: nucleation linear function of suspension.

For the case of $j > 1.0$ and for $M_1 < M_2$, Equation (1), (19), and (20) indicate that the overall crystal size distribution will be degraded as a result of an increase in M. That is, the dominant particle size will decrease. The larger the power j, the more severe will be the observed degradation. This phenomenon has been observed, but it does not seem likely from physical considerations that such behavior would be evident unless the increased probability of particle collision caused macroscopic attrition in such a way that the new particles formed are large and the parent particles are measurably reduced in size because of attrition. Such a phenomenon would no longer conform to the constraints of Equation (1), however; and consequently, the above treatment would not apply.

EXPERIMENTAL DATA: STEADY STATE

The crystallization system and the data reduction procedure used for this investigation have previously been described in detail by Timm and Larson (8) and Murray (2). In addition, their work has defined and demonstrated a procedure for determining the nucleation rate dependency with respect to supersaturation [i of Equation (16)] for several systems in a continuous, mixed suspension–mixed product removal, salting out crystallizer. For the alum (ammonium aluminum sulfate)-ethanol-water system, i was found to lie between 1 and 2. For the ammonium sulfate-methanol-water system, i was found to lie between 3 and 4. Using this kinetic information for these two crystal systems, the following procedure was used to define the nucleation rate dependency with respect to suspension density, j, of Equation (16).

According to Equation (1), a steady state plot of the log of the nuclei population density vs. crystal size will result in a linear relationship, the slope of which is proportional to $-1/rT$ and an intercept equal to the log of the nuclei population density. Similar data collected at different levels of suspension density, should provide a means by which the nucleation rate dependency on suspension density can be defined. In particular, Equation (19) indicates that a plot of the log of the growth rate, r, vs. the log of the suspension density, M, will be a linear relationship with a slope equal to $(1 - j)/(i + 3)$. Knowing the numerical value for i from previous results, j can be evaluated. Similarly, by Equation (20), a log-log plot of the nuclei population density versus suspension area will result in a linear relationship, the slope of which is equal to $(1 + 4\,j - 1)/(i + 3)$.

Representative steady state crystal size distribution data [Equation (1)] for the alum system are presented in Figure 3. For both ammonium alum and ammonium sulfate crystallization, operating conditions and other pertinent information are tabulated in Table 1. It should be noted

TABLE 1. EXPERIMENTAL OPERATING CONDITIONS AND OBSERVATIONS

System	T hr.	M g. solid 100 ml. slurry	Temp. °F	Feed Conc. g. solute 100 ml. H_2O	Feed Alcohol ratio	r, mm. hr.	n^o, No. mm.
Alum	0.25	0.020	80	6.0	3/1	0.279	1.0×10^9
	0.25	0.033	80	8.0	3/1	0.293	1.4×10^9
	0.25	0.054	80	10.0	3/1	0.287	2.3×10^9
Ammonium sulfate	0.25	0.047	80	50.0	10/3	0.088	1.0×10^{11}
	0.25	0.112	80	57.4	10/3	0.100	1.3×10^{11}
	0.25	0.179	80	72.5	10/3	0.101	2.3×10^{11}

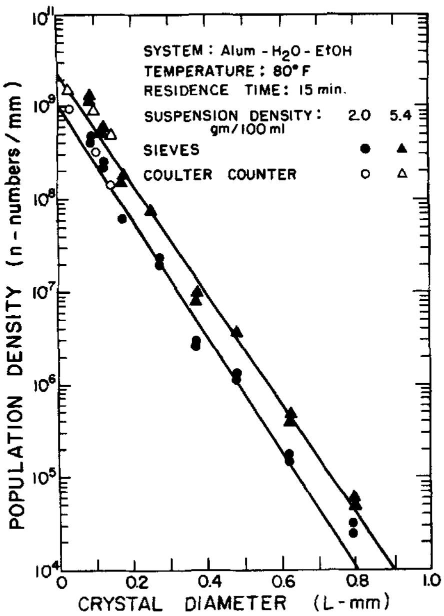

Fig. 3. Experimental crystal size distribution: ammonium alum.

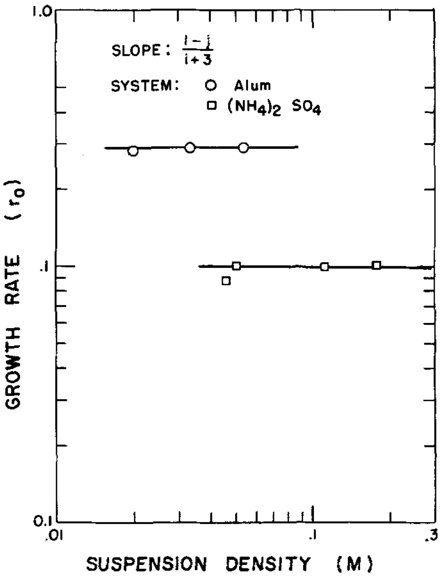

Fig. 4. Determination of nucleation dependency on suspension: growth rate measurements.

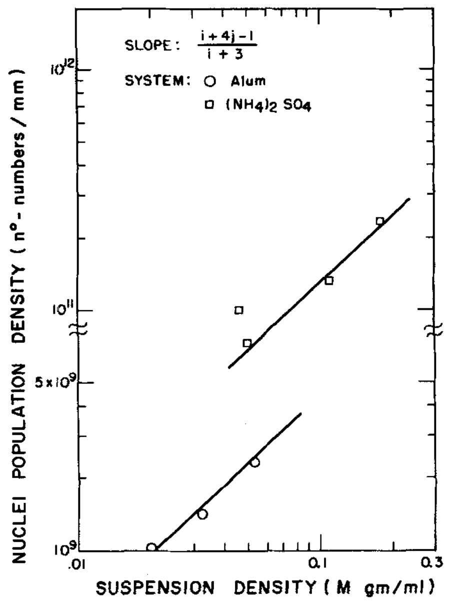

Fig. 5. Determination of nucleation dependency on suspension: nuclei density measurements.

that these crystal size distribution data are indeed linear as previously predicted by theoretical considerations.

The intercepts, log n^o, and the growth rates, r, determined from plots similar to Figure 3 are tabulated in Table 1. A plot of Equation (19) for both systems is shown in Figure 4 and a plot of Equation (20) is shown in Figure 5. With i set equal to 1.25, results of this steady state analysis indicate that for the alum system, $j = 1.0$; and with i set equal to 4.0 for the ammonium sulfate system, $j = 1.0$. Thus the results strongly suggest that the nucleation mechanism is that of a heterogeneous type and is dependent on the quantity and size of the crystals present.

DISCUSSION

A mathematical model is proposed to relate the size distribution of a mixed crystal suspension resulting from a continuous, mixed suspension crystallizer to system parameters and nucleation and growth kinetics. The limitations on this model are such that nucleation may result from homogeneous nucleation, attrition of the magma, or other physical phenomena which are closely related to the mass or surface area of the crystal suspension, so long as attrition, if present, causes only new particle formation and not measurable parent particle size degradation.

The steady state model predicts the effect of feed liquor concentration change, ΔC, on the suspension density and the size distribution. The model further relates the size distribution to the nucleation and growth kinetics. If the suspended crystals are not a factor in nucleation rate, an increase in suspension mass or crystal surface area results in the enhancement of the size distribution, the magnitude of which is related to the kinetic order of the nucleation rate i. When a linear relationship is assumed between suspension density and nucleation rate, an increase in suspension mass or surface area results in an unchanged size distribution. If nucleation rate is taken as a power function of crystal mass or area such that $j > 1$, the model predicts a degradation in size as a result of an increase in magma density.

The three phenomena mentioned above have all been observed by other investigators in experimental or production equipment. It is quite reasonable to assume that under some conditions nucleation resulting from the presence of other situations nucleation resulting from the presence of solids dominates. In cases where size degradation is observed when suspension density is increased, the controlling factor may be macroscopic attrition and, consequently, the treatment presented here does not necessarily apply.

Although a data analysis of heterogeneous effects based directly on the crystal suspension area has not been reported in this paper, such an analysis yielded similar results. That is, j of Equation (21) was found to be equal to 1.0 for both crystal systems. The mass dependency model was selected for illustrative purposes because suspension density can be independently determined by the experimental procedure (2) used in the study; whereas, suspension area must be calculated from the experimentally observed size distribution data by evaluating the second moment of the distribution. It is equally probable, however, that heterogeneous nucleation is closely dependent upon suspension area. If the fundamental heterogenous nucleation mechanism is that of attrition, catalysis, surface nucleation, or fracture of dendritic growth, the interfacial area between the crystalline and mother liquor phases will be of paramount importance. However, the observed crystal size distributions for the alum and ammonium sulfate systems are such that these factors were not distinguishable. Both suspension density and area nucleation models adequately correlated the observed distributions.

ACKNOWLEDGMENT

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NOTATION

A = crystal area
C = solute concentration, mass/unit volume
i = kinetic order of nucleation
k = proportionality constant
K_A = area shape factor
k_A = proportionality constant for nucleation rate
k_M = proportionality constant for nucleation rate
k_N = proportionality constant for nucleation rate

K_v = volume shape factor
L = particle size, linear
M = mass of solids in suspension, mass/unit volume
N^o = number of nuclei
n = population density, numbers/unit length
n^o = population density of nuclei
Q = feed or product rate, volume/unit time
r = linear growth rate
s = supersaturation
T = residence time
t = time
V = crystallizer volume
ρ = crystal density

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Effect of Nucleation Kinetics on the Dynamic Behavior of a Continuous Crystallizer

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The nucleation kinetics of three materials were related to the growth kinetics using steady state data obtained at various degrees of supersaturation. The power models obtained from the three crystallizations exhibited widely different kinetic orders. These materials were then crystallized under unsteady state conditions in a mixed suspension–mixed product removal crystallizer and the transient size distributions were determined. The unsteady state model previously developed by Randolph and Larson was solved on a digital computer for the three systems. Good agreement was obtained. It was found that unsteady state experiments have some advantages over steady state experiments in determining the kinetic order of nucleation.

Experimental growth and nucleation rate data that are relevant to the behavior of crystal size distribution in industrial continuous crystallizers, and descriptions of methods for obtaining such data are woefully lacking in the literature. Classical methods for measuring growth rates usually utilize an experiment only where growth occurs on a single crystal or on a suspension of monosized crystals. Conditions selected are such that little or no nucleation occurs. Nucleation experiments are conducted in a way that is even further removed from reality. They are usually carried on by inducing nucleation in a previously clear nuclei free solution under conditions of supersaturation that vary during the experiment. In a continuous industrial crystallizer, nucleation and growth are taking place hopefully under constant conditions of temperature, pressure, and supersaturation.

An extensive analysis of mixed suspension, mixed product removal, and continuous crystallization has been performed by Randolph and Larson (*8*). A model was developed from a basic numbers balance, to predict and analyze transient as well as steady state behavior for such a crystallization system. The following equation predicts the transient response for unsteady state operating conditions:

$$\frac{\partial n}{\partial t} = -r\frac{\partial n}{\partial L} - \frac{n}{T} \tag{1}$$

The characterizing parameter is population density, n, which is defined by

$$\Delta N = \int_{L_1}^{L_2} n \, dL \tag{2}$$

At steady state, Equation (1) simplifies to

$$n_o = n_o^o \exp\left(-L/r_oT_o\right) \tag{3}$$

Equation (3) has been used by several authors (*1, 6, 9*) in the analysis of factors that affect size distribution in continuous crystallizers.

In the development of the model, it was assumed that the following constraints were imposed on the system: no crystal seeding, perfectly mixed crystal suspension, mixed product removal, and isothermal environment. It was further assumed that McCabe's ΔL Law applied and the fluid properties were constant.