Effect of residence time and suspension density on crystal size distributions in continuous crystallization

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EFFECT OF RESIDENCE TIME AND SUSPENSION DENSITY ON CRYSTAL SIZE DISTRIBUTIONS IN CONTINUOUS CRYSTALLIZATION

by

Delmar Clarence Timm

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

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ABSTRACT

A recently developed model relating crystal size distribution, nucleation and growth kinetics and operating parameters was compared with experimental crystal size distribution data obtained from a continuous, mixed suspension, mixed product removal, salting-out crystallization system. The effects of residence time (or production rate) and suspension density upon the resulting size distributions were extensively investigated for several crystal systems. The results demonstrated that the nucleation rate can be related to crystal growth rate and suspension density as a simple power function over a wide range of levels of supersaturation.

Steady state correlations were developed to explain observed phenomena relating nuclei population density, growth rate and nucleation rate to residence time and suspension density. It was observed that decreasing residence time resulted in a significant overall size distribution degradation; whereas, suspension density had little or no effect on the overall size distributions. These observations indicate that heterogeneous nucleation is a significant factor in new crystal formation.

The model was used to simulate crystal size distribution dynamics for step changes in solute feed concentration and in residence time from initial steady state conditions. Qualitative agreement between theory and experimental observations
was obtained by using the previously stated nucleation rate relationship.
INTRODUCTION

Crystallization processes have been extensively utilized in the chemical industries. In the past much work has been done in calculating theoretical yields from phase relationships and in improving operating conditions in order to increase actual crystalline yields. However, until recently, little work has been published dealing with the complex problem of predicting and controlling the size distribution of crystalline products. In the study of factors which determine crystal distribution, quantitative descriptions of the rate of formation of new crystals, nucleation, and their subsequent rate of enlargement, growth, must be related to the degree of supersaturation existent in the crystallizing system.

A solution is said to be saturated at a given constant environment if the liquid phase is in equilibrium with the solid phase. Solute concentrations above the saturated concentration are defined as levels of supersaturation. Supersaturation, the driving force for phase change, acts to establish equilibrium between the solid and liquid phases. Supersaturation may be generated by several techniques, including the removal of solvent by evaporation, reducing the solute's solubility through cooling or adding a precipitant and using a chemical reaction which occurs in a homogeneous phase, resulting in a compound with a reduced solubility compared to that of the reactant.
Kinetic growth and nucleation rate relationships which have relevance to the behavior of crystal size distributions in industrial continuous crystallizers and descriptions of methods for obtaining such relationships are woefully lacking in the literature. Classical methods for measuring growth rates usually utilize an experiment where only growth occurs on a single crystal or on a suspension of monosized crystals. Conditions are selected such that little nucleation occurs. Nucleation experiments are conducted in a way which is even farther removed from reality. They are usually carried on by inducing nucleation in a previously clear, nuclei-free solution under conditions of supersaturation which vary during the experiment. In a continuous industrial crystallizer, nucleation and growth are both taking place, hopefully under constant conditions of temperature, pressure and supersaturation. Thus, these two phenomena, nucleation and growth, actively compete to relieve the level of supersaturation of the metastable state. Their respective kinetic dependencies with supersaturation are, therefore, the primary functions which determine the resulting phase change and, consequently, determine the size distribution.

Crystallization, on a macroscopic scale, is a mass transfer process controlled by fundamental laws. For a heterogeneous reaction, such as crystal growth, Van Hook (31) discusses the following sequence of kinetic reactions:
Transport of solute from the surroundings to the surface of the crystal
Surface adsorption
Molecular orientation into crystalline lattice
Desorption of by-products, including transfer of energy
Dissipation of by-products into surrounding liquid phase

Early theories placed particular emphasis on models assuming that diffusion was the rate-controlling step. However, frequently the rate of crystal growth and the rate of dissolution are not reciprocal processes. Thus, such a model is an oversimplification of the actual sequence of steps.

Similarly, extensive investigations concerning nucleation have been reported in the literature. LaMer (10) defined a nucleus as the minimum sized embryo capable of spontaneous growth. Ostwald (18) defined metastable and labile regions for supersaturated solutions. He observed that as the level of supersaturation is increased, a point is reached at which spontaneous mass nucleation occurs; but at lower levels of supersaturation, supersaturation is relieved only by growth on existing crystals. Although an oversimplification for many crystal systems, these observations do stress the importance which supersaturation places on nucleation and subsequent growth.
Volmer and Weber (32) developed from thermodynamics an Arrhenius-type relationship for the rate of nucleation, 
\[ \exp(-\Delta G/kT), \]
where \( \Delta G \) is the Gibbs free energy of formation. Becker and Döring (2) identified a pre-exponential factor based on evaporation and condensation velocities, deduced from molecular collision frequencies. Nielsen (17) has estimated the numerical value of this coefficient and also has expressed Gibbs free energy in terms of a supersaturation ratio. He emphasized that a simple power model approximately predicts nucleation rates. Uhlmann and Chalmers (30) reviewed some of the more important areas of the nucleation process based primarily on thermodynamic considerations.

An extensive theoretical study of mixed suspension, mixed product removal, continuous crystallization was developed by Randolph and Larson (22). Murray and Larson (16) and Timm and Larson (29) have applied this analysis technique to a particular crystallization system in an attempt to verify the model through experimental results. These experiments have placed particular emphasis on crystal size distributions as influenced by crystallizer residence time. Their conclusions substantiated the adequacy of the model for predicting steady state size distributions and transient distributions for step changes in residence time for an aluminum ammonium sulfate-water-ethanol system.

The kinetic order of the nucleation rate of the alum-
water-ethanol system was found to lie between 1.0 and 2.0 (16, 28). However, such a system's population distribution is relatively insensitive to changes in crystallizer residence time. Thus, a need to investigate crystal systems more sensitive to residence time was revealed. Also during the course of these investigations, the kinetic equation representing nucleation rate was found to be inadequate for changes in suspension density (weight of suspended crystalline phase/volume of magma slurry). Thus, the purpose of this dissertation was to investigate crystal systems with higher kinetic orders for their respective nucleation rates and to define the relationships between suspension density and nucleation rates as specifically applied to the analysis of a continuous, mixed suspension, mixed product removal crystallizer.
Lord Kelvin first considered the variation of vapor pressure with particle size for a liquid droplet at constant temperature. If a differential molar quantity of liquid, \( dm \), is transferred from a plane surface to a droplet, the free energy associated with the transfer may be calculated from the definition of internal energy and Gibbs free energy. For such an occurrence, Gibbs free energy is \( RT \ln(P/P_\infty) \ dm \), where \( P \) is the vapor pressure of the droplet and \( P_\infty \) is that of the plane surface. If the addition of \( dm \) moles to a spherical droplet increases the radius by \( dr \), the corresponding area change is \( 8\pi r \ dr \). The corresponding change in surface free energy is, therefore, \( 8\pi \sigma \ dr \) where \( \sigma \) is the surface tension. At equilibrium, these two free energy changes are equal:

\[
8\pi \sigma \ dr = RT \ln(P/P_\infty) \ dm
\]  

(1)

Now

\[
dm = 4\pi r^2 \ dr/v
\]

(2)

where \( v \) is the molar volume. Thus

\[
RT \ln(P/P_\infty) = 2\sigma v/r
\]

(3)
in summarizing the work of Ostwald, Van Hook (31) has shown by analogy for very fine precipitates:

\[ RT \ln(C/C^*) = 2\sigma'v/r \]  

(4)

where \( C \) and \( C^* \) are the solubilities of the material of radii \( r \) and of a plane surface, respectively, and \( \sigma' \) is the interfacial tension.

Equations 3 and 4 show that embryos will exhibit a greatly enhanced solubility. At a critical size, this enhanced solubility will be equal to the concentration of the environment. Thus, embryos smaller than this critical size will dissolve and those larger will grow. A nucleus may then be defined as an embryo having a size larger than that associated with the critical size.

Now

\[ r = \frac{2\sigma'v}{RT \ln S} \]  

(5)

where \( S \) is the pressure or concentration ratio. Assuming an Arrhenius-type expression for the spontaneous rate of nucleation at constant temperature:

\[ \frac{dN^0}{dt} = k_a \exp(-W/RT) \]  

(6)

where \( k_a \) is a frequency factor and \( W \) is the minimum energy required to form the nucleus. This energy is the net work of
forming the bulk of the embryo and its surface:

\[ W = W_s - W_v \]  

(7)

The contribution of a surface is \( \sigma' A \), where \( A \) is surface area. Thus, the net surface work of transferring an infinitesimal amount of solute from the homogeneous solvent phase to the surface requires a free energy change of \( \sigma' dA \), which at equilibrium is equal to the product of the volume transferred across the pressure gradient \( P \); therefore, \( P dV = \sigma' dA \). For a spherical particle it follows that \( P = 2\sigma'/r \) and the total work is

\[ W = \sigma' A - \frac{2\sigma' rA}{r} = \frac{\sigma' A}{3} = W_s/3 \]  

(8)

The work of nucleation for a critical sized spherical particle is thus one-third the work required to form its own surface.

\[ W = \frac{4\pi r^2 \sigma'}{3} = \frac{16\pi \sigma^3 v^2}{3 R^2 T^2 \ln^2 S} \]  

(9)

Hence, Equation 6 becomes for a spherical nucleus

\[ \frac{dN^0}{dt} = k_a \exp\left(- \frac{16\pi \sigma^3 v^2}{3 R^3 T^3 \ln^2 S} \right) \]  

(10)

Nielsen (17) considers the form of Equation 10 and stresses that a power function of concentration is a good approximation
for the nucleation rate for sparingly soluble salts:

\[
\frac{dN^0}{dt} = k_n C^n
\]  

Previous experimental work has extensively dealt with nucleation from clear, nuclei-free solutions. Frequently, experimenters report the level of supersaturation at which the first crystals are observable. Ostwald (18) thus identified three classic regions of supersaturation - the labile region in which spontaneous nucleation occurs, the metastable region in which only growth on existing crystals occurs and the stable region in which neither growth nor nucleation occurs. However, Equation 10 indicates that spontaneous nucleation may occur at all levels of supersaturation. If the solution is just saturated with respect to a critical size particle, \( S = 1 \) and an infinite amount of work will be required. But for levels of concentration exceeding this limiting value, a finite energy expenditure will result in spontaneous nucleation. The greater the level of solute concentration \( C \), the smaller will be the magnitude of the work required for this occurrence. Thus, levels of supersaturation may be achieved at which spontaneous nucleation occurs in an explosive manner, defining the labile region observed by Ostwald.

Critical sized embryos are reported to have structures containing from ten to several thousand building units, ions
or molecules. A spontaneous occurrence which requires the constituent units to first coagulate in such a manner as to resist redissolving and, furthermore, requires a meticulous orientation of different species into a rigid crystalline lattice is highly unlikely to occur as a result of a single, simultaneous collision. But a more probable macroscopic chain of events would be that of a sequence of small, repeatable steps. This rapid construction process can only continue in local regions of high solute concentrations and many of the embryos fail to reach the critical size, but dissolve. The homogeneous theory of nucleation suggests that such a sequence of multiple collisions results in a nucleus which then continues to enlarge by growth. The centers of growth are entirely a matter of chance and thus any supersaturated solution will eventually adjust to its equilibrium level.

The rate of nucleation is also known to be influenced by factors other than supersaturation and temperature. Many techniques and rituals may be performed on an unwilling system. Agitation or bubbling of a gas through a solution will often induce nucleation. Van Hook (31) reports in his investigations concerning sugar solutions that accidental contact of a glass stirrer with the sides of the vessel promptly caused nucleation. Mechanical shock, friction, attrition and solid contaminants, including dust, can also readily initiate the nucleation process. Strickland-Constable
and Mason (27) observed showers of nuclei near areas of irregular growth on suspended crystals. Similar observations have lead to theories concerning heterogeneous nucleation. Thus, in a continuous crystallization process, the presence of a solid, crystalline phase, accompanied by agitation and attrition, may result in a mechanism which is significantly different than that of homogeneous nucleation.

If one considers a system which contains fragments of less soluble matter in suspension, the following discussion may explain in part the nucleation tendencies of the preceding paragraph. A theory of heteronucleation can be formulated by means of the concept of interfacial tensions between the crystal to be formed, the heteronucleus and the solution (17). Let \( \sigma'_c \) denote the surface tension between the crystal and solution, \( \sigma'_n \) between the heteronucleus and solution and \( \sigma'_s \) between the two solids. The free energy change of formation of a square surface nucleus with edge \( l \) and height \( h \) on a heteronucleus is

\[
\Delta G = -(\mu_1 - \mu_2)m + \sigma'_c (l^2 + 4hl) + \sigma'_n l^2 - \sigma'_s l^2 \tag{12}
\]

where \( \mu_2 \) is the chemical potential of the solute in the crystalline phase, \( \mu_1 \) is that in the solution, \( m \) is the mass of material transferred and \( 2\sigma'_o = \sigma'_c - \sigma'_n + \sigma'_s \). For a fixed volume, \( V = l^2h \), the most probable ratio between \( h \) and \( l \) is
determined by minimizing the free energy:

\[ \frac{d}{dl} \left( 2 \sigma_0 l^2 + 4 \sigma_c v/l \right) = 0 \]  

(13)

Therefore

\[ \sigma_0 / \sigma_c = v/l^3 = h/l \]  

(14)

and

\[ l^2 = \left( v \sigma_c / \sigma_0 \right)^{2/3} \]  

(15)

Thus

\[ \Delta G = - (\mu_1 - \mu_2)m + 6 (\sigma_0 \sigma_c^2 v^2)^{1/3} \]  

(heteronucleation)  

(16)

Similarly, for spontaneous or homogeneous nucleation,

\[ \Delta G = - (\mu_1 - \mu_2)m + \sigma_c (2l^2 + 4hl) \]  

(17)

which leads to \( h = 1 \) and

\[ \Delta G = - (\mu_1 - \mu_2)m + 6 \sigma_c v^{2/3} \]  

(spontaneous nucleation)  

(18)

If \( \sigma_0' \) is less than \( \sigma_c' \), it follows that heteronucleation may predominate over spontaneous nucleation. In general \( \sigma_0' \) will be determined by the similarity of the atomic distance of the species and by the lattice structure of the crystals.
In a continuous process, the source of heteronuclei may be large crystals of the suspension. For such, $\gamma_s = 0$, $\gamma_c = \gamma_n$, $\gamma_0 = 0$ and only work associated with the chemical potentials will be required to form the surface nuclei. But in reality, atomic structures determine the minimum dimensions of $h$, not identically equal to zero. Thus, self-nucleation will contain a small surface free energy barrier. Such phenomena may also lead to surface nucleation controlled growth or to dendritic growth which may increase nucleation rates.

Growth Kinetics

For heterogeneous reactions such as crystal growth, a sequence of kinetic transformations occurs:

- Diffusion of solute to interface
- Surface adsorption
- Molecular orientation into crystalline lattice
- Desorption of by-products, including energy
- Dissipation of by-products

Early theories have placed particular emphasis on diffusion controlled growth:

$$\frac{dm}{dt} = (DA/l)(C-C_{eq}) \quad (19)$$

where $D$ is the solute diffusivity, $l$ the effective film thickness, $A$ the surface area, $C$ the solute concentration of
the environment and \( C_{eq} \) the solute concentration at saturation. This diffusion theory has several weaknesses, indicating that the rate of growth or dissolution should be reciprocal. Experimentally this is often not true. In addition, if the laminar film thickness is reduced by increasing the relative liquid-solid velocity, the rate of growth should increase. This, too, is not frequently observed.

The overall driving force has also been assumed to be related to the saturated concentration of the solute. However, Miers (14), by refractive index determinations, showed that the solution in contact with growing crystals of sodium chlorate was not saturated, but supersaturated. This observation strongly suggests that a second mechanism is important for an overall rate equation, namely a surface reaction or orientation.

If a first order reaction and diffusion combine to form the dominant resistance, then at equilibrium:

\[
\frac{dm}{dt} = \frac{(DA/l)(C-C_i)}{\text{diffusion}} \quad (20)
\]

\[
\frac{dm}{dt} = k_r A(C_i-C_{eq}) \quad \text{(surface reaction)} \quad (21)
\]

where \( C_i \) is the interfacial solute concentration and \( k_r \) the reaction rate constant. In general, the interfacial solute concentration will not be known. Thus, by combining Equations 20 and 21, an overall relationship may be obtained:
\[
dm/dt = \frac{1}{1/D+1/k_r} A(C-C_{eq}) = K A s
\]  

(22)

where supersaturation, \( s = C-C_{eq} \). As the film thickness decreases, the overall rate constant approaches \( k_r \), growth rate remains finite and is surface reaction controlled. Similarly, as \( k_r \) becomes infinite, the controlling resistance approaches that of diffusion. Thus, for a given crystallization application, surface reaction, diffusion or a combined resistance thereof may control the kinetics of growth.

Rumford and Bain (24) reported for the controlled growth of sodium chloride, that above 50°C, growth was controlled by diffusion, and at lower temperatures, by surface reaction. Cooke, as referred to by Mullin (15), however, is of the opinion that the crystallization of sodium chloride is controlled at all temperatures by a diffusion mechanism, even though the resistance of the surface reaction increases at lower temperatures and low degrees of supersaturation.

The mass and area of a crystal may be related to the particle size \( L \):

\[
m = \mathcal{C} K_v L^3 \\
A = K_A L^2
\]

(23)

where \( \mathcal{C} \) is the crystalline density, \( K_v \) and \( K_A \) geometric shape factors and \( L \) a characteristic particle dimension.
Thus

\[ \frac{dm}{dt} = 3 \, \Phi \, K_v L^2 \quad \frac{dL}{dt} = 3 \, \Phi \, K_v A_r / K_A \quad (24) \]

Linear crystal growth rate, \( r = \frac{dL}{dt} \), can be expressed in terms of supersaturation through the use of Equation 22:

\[ r = k_g \, s \quad (25) \]

Jenkins (9) found that growth rate was a linear function of supersaturation for a variety of crystals in both aqueous and organic solutions, agreeing qualitatively with the form of Equation 25.

Other theories have been proposed in the literature to represent observed growth phenomena. Frank (8) showed that if a crystal contains a dislocation which is self-perpetuating, a suitable model may be developed to explain observed growth phenomena for many materials. Nielsen (17) also considers the case where crystal growth is controlled by surface nucleation and by several compound growth mechanisms. He concludes that actually over a wide range of supersaturations growth rate data may be correlated by a power function of supersaturation similar to Equation 25.
CRYSTAL POPULATION DISTRIBUTIONS

Conservation of Numbers of Crystals

Randolph (20) and Randolph and Larson (22) developed a general theoretical description of crystallization based on the concept of population density, \( n \), which is defined by

\[
    n = \lim_{\Delta L \to 0} \frac{\Delta N}{\Delta L} \tag{26}
\]

or

\[
    N = \int_{L_1}^{L_2} n \, dL \tag{27}
\]

where \( N \) is the total number of crystals contained in a size fraction of width \( L_2 - L_1 \). Their derivations were based on the conservation of an arbitrary particle population, subjected to the following constraints:

. The suspension occupies a variable volume \( V \) enclosed by fixed boundaries, except for a free gravity surface.

. This volume has perfectly mixed inputs and outputs.

. The particles in the suspension are numerous enough to form a continuous distribution over a given size range and over a given element of suspension volume.
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 nucleus.

They considered the total number of particles in a suspension having an arbitrary size range $L_1$ to $L_2$ and developed the following equation:

$$
\frac{d}{dt} \int \int_0^{L_2} \bar{n} dL dV = \int \int_{L_1}^{L_2} \left[ Q_j \bar{n}_j - Q_0 \bar{n}_o \right] dL \tag{28}
$$

where $t$ is time, $\bar{n}$ is the point population density per unit volume, $V$ is the volume of the suspension and $Q$ is the volumetric suspension input or output flow rate.

The left hand side of Equation 3 represents the accumulation or the depletion of the number of particles within the suspension volume. The right hand term represents the number of particles contained in the inputs and the number removed by the outputs from the suspension volume.

Using the rule of Leibnitz on the left hand side of Equation 28, the equation is simplified to
\[
\int_V \left[ \frac{\partial \tilde{n}}{\partial t} + \frac{\partial}{\partial L} \left( \tilde{n} \frac{\partial L}{\partial t} \right) \right] \, dV + \frac{dV}{dt} \tilde{n}_s - Q_1 \tilde{n}_1 + Q_0 \tilde{n}_0 = 0 \quad (29)
\]

which is a general population balance for an arbitrary suspension of particles subjected to the original four constraints. The integral term represents the transients in population density of particles of a given size range and the transport of crystals into and out of this size range due to their rate of growth. The second term represents the changes in population due to changes in volume. The third and fourth terms represent the inputs and outputs of particles resulting from bulk flow.

Making the additional assumptions
- Perfectly mixed suspension
- Perfectly mixed product removal, \( \tilde{n}_0 = \tilde{n} \)
- Constant volume, \( \frac{dV}{dt} = 0 \)
- Liquid feed, \( \tilde{n}_1 = 0 \)
- McCabe's \( \Delta L \) Law (12), \( r \) is not a function of \( L \)

Equation 29 simplifies to

\[
\frac{d\tilde{n}}{dt} = -r \frac{\partial n}{\partial L} \tilde{n} \quad (30)
\]

where \( n = \tilde{n}V \) and \( T \) is the residence time or drawdown time.

Similar expressions have been developed by other authors (3, 26).
In order to solve this equation for transient behavior of crystal size distributions, growth rate, \( r \), must be defined in terms of system parameters and constraints; and an initial condition and a boundary condition are required.

Growth Rate

An unsteady state mass balance at constant environmental conditions results in the following relationship:

\[
\frac{d((C+M)V)}{dt} = C_i Q_i - (C_o + M_o) Q_o
\]  \( (31) \)

where \( C \) is solute concentration in the liquid phase, \( M \) is suspension density, and \( Q \) is a volumetric flow rate. Subscripts \( (i) \) and \( (o) \) correspond respectively to the inputs and outputs. When changes in supersaturation are small compared with changes in suspension density at constant volume, Equation 31 simplifies to

\[
\frac{dM}{dt} = \frac{1}{T} (C_i - C_o - M_o)
\]  \( (32) \)

where residence time \( T = V/Q \). At steady state, \( \Delta C = C_i - C_o = M \).

Suspension density is related to the particle size distribution by
When growth rate is not a function of crystal size, Equations 30, 32 and 33 may be combined using Liebnitz rule to obtain the desired expression for growth rate, \( r \), in terms of \( \Delta C \) and size distribution:

\[
M = \frac{K_v}{V} C \int_0^\infty nL^3 \, dL
\]  

(33)

This equation is particularly applicable for analyzing experimental data subjected to large changes in suspension density, accompanied by inappreciable changes in supersaturation. It should be noted that the integral in the denominator is proportional to the area of the crystal suspension.

When a crystallizer is subjected to a step change in residence time, at constant suspension density, the differentiation of Equation 33 yields the following expression:

\[
\frac{dM}{dt} = \frac{d}{dt} \int_0^\infty nL^3 \, dL = 0
\]  

(35)

Utilizing Equations 30 and 35, Randolph (21) developed the
following relationship for growth rate at constant suspension density:

\[ r = \frac{\int_{0}^{\infty} nL^3 \, dL}{3T \int_{0}^{\infty} nL^2 \, dL} = \frac{M \nu}{3K_v \nu T \int_{0}^{\infty} nL^2 \, dL} \quad (36) \]

The integral of the denominator is again proportional to the area of the suspension; the integral of the numerator is proportional to suspension density, a constant. Thus, Equation 3^4 is applicable also for step changes in residence time for which \( \Delta C = M \), a constant.

For a third class of disturbances, those for which both the rate of change of solute concentration and the rate of change of suspended solids are of the same magnitude, that is, a system which exhibits high supersaturation, the following relationships may be developed. By the defining relationship for suspension density, Equation 33, it follows that

\[ \frac{dW}{dt} = 3 K_v \nu r \int_{0}^{\infty} nL^2 \, dL - M/T \quad (37) \]

Defining growth rate as

\[ r = k_g (C - C_{eq})^a \quad (38) \]
and

\[ r^* = k_g (C_i - C_{eq})^a \]  

(39)

Equation 31 may be reduced to a relationship relating growth rate, population density and time:

\[ \frac{dr}{dt} + a \frac{k_g}{T} \ \left( 3K_v \int_0^\infty nL^2 dL \right) r^{2a-1} \]

\[ + \frac{ar}{T} = \left( \frac{a}{T} \right) r^{*a/a} r^{(a-1)/a} \]

(40)

This equation will reduce to the form of Equation 36 when M is constant or when the rate of change of M is large compared with that of C.

Steady State Size Distribution

If the additional constraint of steady state is applied, Equation 30 simplifies to

\[ n_0 = n_0^0 \exp(-L/r_0T_0) \]  

(41)

where \( n_0^0 \) is a constant and is defined as the nuclei population density at steady state and \( r_0 \) and \( T_0 \) refer to steady state growth rate and residence time respectively. Equation 41 provides a suitable initial steady state size distribution for the unsteady state solution of Equation 30, subjected to the original constraints of the latter equation. Several authors (4, 21, 25) have derived similar expressions to be used in the
analysis of crystal size distributions at steady state. The form of Equation 41 also assures the convergence of Equation 30.

Nucleation Rate

A kinetic expression for nucleation rate provides a suitable boundary condition. Nucleation rates have been taken by several authors (16, 21, 23) to be functions of supersaturation:

\[
\frac{dN^0}{dt} = f(s) = Ks^h
\]  

(42)

Such a model strongly suggests that the dominant source of nuclei is homogeneous nucleation. Larson et al. (11) showed that this model predicts an enhancement in crystal distribution for an increase in magma density. The lower the kinetic order \( h \), the greater will be this enhancement. However, this phenomenon is not always observed.

A number of authors have given various explanations for the effect of suspended solids on nucleation, including the sweeping away from the neighborhood of a crystal a reservoir layer of high concentration (19), fracture of dendritic growth, catalysis and attrition. If attrition is a factor, new particles thus formed must be near nuclei size for the application of Equation 30. However, any of these phenomena
would be dependent upon the total area or mass of the magma suspension. The following model relates nucleation rate, suspension density $M$ and supersaturation $s$:

$$\frac{dN_0}{dt} = K_1 M^j s^h$$  \hspace{1cm} (43)

For systems which exhibit growth rate as an exponential function of supersaturation, Equation 43 simplifies to

$$\frac{dN_0}{dt} = k_n M^j r^i$$  \hspace{1cm} (44)

If growth rate is a linear function of supersaturation, $i = h$. Now,

$$\frac{dN_0}{dt} = \left. \frac{dN_0}{dL} \frac{dL}{dt} \right|_{L_0} = n^0 r$$  \hspace{1cm} (45)

Therefore,

$$n^0 = k_n M^j r^{i-1}$$  \hspace{1cm} (46)

Equation 46 is a suitable time variant boundary condition for the solution of Equation 30. The proportionality constant is a function of operating conditions, including temperature, degree of agitation and fluid characteristics which affect the basic mass transfer process. Therefore, an additional constraint of a constant environment must be imposed on the
system.

For changes in residence time or in solute feed concentration, Equations 34, 41 and 46 form a suitable set of expressions for the solution of Equation 30.
The transient size distribution equation, Equation 30, has been solved by numerical methods by several authors (21, 28, 33). It was convenient to introduce the following dimensionless substitutions:

\[ x = \frac{L}{r_o^{T_o}} \]  
\[ y = \frac{n}{n_o^0} \]  
\[ \theta = \frac{t}{T_o} \]  
\[ \phi = \frac{r}{r_o^0} \]

where the subscript \(^0\) refers to initial steady state values at a reference production rate and the superscript \(^0\) refers to properties associated with nuclei. Thus, Equation 30 simplifies to

\[ \frac{\partial y}{\partial \theta} = - \phi \frac{\partial y}{\partial x} - y \frac{T_0}{T} \]

and the steady state equation, Equation 41, reduces to

\[ y_o = \exp(-x) \]

This equation is equivalent to an initial crystal distribution at a reference production rate before a disturbance in the size distribution is caused by a step change in production rate or solute feed concentration.

Dimensionless nucleation and growth rate functions are obtained from Equations 46 and 40:
\[ y^0 = n^0/n_o^0 = \left(\frac{M}{M_o}\right)^j \left(\frac{r}{r_0}\right)^{i-1} \] (53)

\[ \frac{\partial \phi}{\partial \theta} + \frac{a}{2} M_o \int_0^\infty yx^2 \, dx \left(\frac{k_g}{r_0}\right)^{1/a} \phi^{(2a-1)/a} \]
\[ + a \frac{T_o}{T} \phi = a \frac{T_o}{T} \left(\phi^*\right)^{1/a} \phi^{(a-1)/a} \] (54)

where

\[ M_o = 6 K_v \left(\frac{r_o T_o}{r_0}\right)^{1/4} / \nu \]

\[ \phi^* = \left(\frac{k_g}{r_0}\right)^{1/a} M_o + 1 \right)^a \left(\frac{M_T}{M_{T_o}}\right)^a \]

and

\[ \frac{M_T}{M_{T_o}} = \frac{C_i - C}{(C_i - C)} @ \text{final steady state condition} \]
\[ \frac{M_T}{M_{T_o}} = \frac{(C_i - C)}{(C_i - C)} @ \text{initial steady state condition} \]

Similarly, Equation 36 simplifies to

\[ \phi = \frac{\Delta C}{\Delta C_0} \frac{T_o}{T} \int_0^\infty x^2 e^{-x} \, dx = \frac{2}{\Delta C_0} \frac{T_o}{T} \int_0^\infty x^2 y \, dx \]
\[ = \frac{\Delta C}{\Delta C_0} \int_0^\infty x^2 y \, dx \] (55)

The transient response of the size distribution to a disturbance to the system was determined by solving Equation 51. The initial condition was expressed by Equation 52; the population density of the nuclei was defined by Equation 53.
and the expression for the growth rate, Equation 55, was obtained by solving a mass balance. Figures 1, 2, 3 and 4 show the theoretical response of the crystal population distribution from an initial steady state size distribution for a three-fold step change in T at constant ΔC. When i = 1.0, Figure 1 shows that the crystal distribution remains constant. This observation follows directly from Equations 41 and 46.

If i is greater than 1, the crystal population distribution is dependent upon residence time, as is shown by the Figures 2, 3 and 4. The larger the kinetic order, the greater will be the effect of residence time on the crystal size distribution. The step disturbance initially creates a shower of nuclei which commence to grow into the larger size fractions. The population density of larger size fractions is diminished due to the increased growth rate of the system and due to the fact that smaller crystals are removed in the crystallizer's effluent before they grow into the larger size fractions.

Similarly, the transient response of the crystal size distribution was obtained for a step change in solute feed concentration, using Equation 55 to define dimensionless growth rate. The results are presented in Figures 5, 6 and 7. The disturbances at an initial steady state size distribution again resulted in an increased nucleation rate. The new particles thus formed grew into the larger size fractions, thereby causing transients in the population densities of
Figure 1. Transient response to a step change in production rate

\[ i = 1.0 \]
\[ \frac{\Delta C}{\Delta C_0} = 1.0 \]
\[ \frac{T_0}{T} = 1.0, \quad \frac{t}{T_0} < 20 \]
\[ \frac{T_0}{T} = 3.0, \quad \frac{t}{T_0} > 20 \]
Figure 2. Transient response to a step change in production rate

\( i = 2.0 \)

\( \Delta C/\Delta C_0 = 1.0 \)

\( \frac{T_0}{T} = 1.0, \frac{t}{T_0} < 20 \)

\( \frac{T_0}{T} = 3.0, \frac{t}{T_0} > 20 \)
Figure 3. Transient response to a step change in production rate

\[ i = 3.0 \]
\[ \Delta C / \Delta C_0 = 1.0 \]

\[ T_0 / T = 1.0, \ t / T_0 < 20 \]
\[ T_0 / T = 3.0, \ t / T_0 > 20 \]
Figure 4. Transient response to a step change in production rate

\[ i = 4.0 \]

\[ \frac{\Delta C}{\Delta C_0} = 1.0 \]

\[ \frac{T_0}{T} = 1.0, \frac{t}{T_0} < 20 \]

\[ \frac{T_0}{T} = 3.0, \frac{t}{T_0} > 20 \]
DIMENSIONLESS POPULATION DENSITY \( \left( \frac{n}{n_0} \right) \)
Figure 5. Transient response to a step change in solute feed concentration

\[ i = 1.0 \]
\[ j = 1.0 \]
\[ T_0/T = 1.0 \]
\[ \Delta C/\Delta C_0 = 1.0, \quad t/T_0 < 20 \]
\[ \Delta C/\Delta C_0 = 2.0, \quad t/T_0 > 20 \]
Figure 6. Transient response to a step change in solute feed concentration

\[ i = 2.0 \]
\[ j = 1.0 \]
\[ T_0/T = 1.0 \]
\[ \Delta C/\Delta C_0 = 1.0, \ t/T_0 < 20 \]
\[ \Delta C/\Delta C_0 = 2.0, \ t/T_0 > 20 \]
Figure 7. Transient response to a step change in solute feed concentration

\( i = 3.0 \)

\( j = 1.0 \)

\( T_0 / T = 1.0 \)

\( \frac{\Delta C}{\Delta C_0} = 1.0, \ t/T_0 < 20 \)

\( \frac{\Delta r C}{\Delta r C_0} = 2.0, \ t/T_0 > 20 \)
these larger sized crystals. The final steady state distributions are similar to the initial, each being displaced by a constant multiple, conforming to the constraint of a nucleation rate linearly related to suspension density. If the dominant source of nuclei were assumed to be homogeneous nucleation, that is, a mechanism independent of suspension density, the step disturbance would result in a final distribution that would be degraded. In other words, the dominant particle size on a mass basis would be smaller at the final, larger, steady state magma concentration.
EXPERIMENTAL

Apparatus

An isothermal, mixed suspension, mixed product removal, salting out crystallizer was used for this investigation. The crystallizer was a 5½ liter, Plexiglass, cylindrical vessel equipped with a draft tube, three baffles and a propeller type agitator. Figure 8 is a schematic representation of this vessel. The design was such that the cross section circulating magma flow was equal at all points; that is, the cross section area inside the draft tube and inside the annulus and the area above and below the draft tube were equal. The direction of magma circulation was down the draft tube and up the annular region. Feed streams were introduced at the surface of the suspension.

The salting out system of crystallization was selected because of its simplicity of design and operation. This method is free from heat transfer and vacuum problems that are associated with cooling and evaporative type crystallizers. The use of unsaturated feed streams eliminated the problem of feed line plugging during operation. The maintenance of a constant crystal suspension during an upset in production rate did not require a simultaneous change of heat transfer rates or vacuum levels. A step change in solute concentration was readily performed by using two solute feeds.
Figure 8. Crystallizer
Auxiliary equipment, shown in Figure 9, consisted of two solute feed tanks, each a 55 gallon stainless steel drum, and an elevated alcohol feed tank, a 5 gallon polyethylene bottle. All tubing and valves were 3/8 inch stainless steel.

Solute-water solutions were pumped by an Eastern E-1 centrifugal pump to a constant head tank; the output of the pump was controlled electrically by a reostat. Calibrated rotameters were used in conjunction with control valves to regulate the feed rates.

An automatic level controller was used to maintain the liquid level in the crystallizer. The controller regulated a Jabsco, semipositive displacement pump which periodically removed a non-classified suspension from the annular region. This intermittent discharge was designed to operate at a relatively high frequency to minimize the departure from a constant volume crystallizer.

Suspension samples were removed through a sample line in the center of the annular space. A pressure difference, generated by a vacuum in a calibrated Erlenmeyer flask, was used to withdraw magma samples from the crystallizer.

Salts and Solvents

The alum used was aluminum ammonium sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, supplied by General Chemical Division, Allied Chemical Corporation, and sold as "Ammonium Alum,
Figure 9. Crystallization system
CONSTANT HEAD TANK

ALCOHOL FEED TANK

SOLUTE FEED TANK A

SOLUTE FEED TANK B

CRYSTALLIZER

ROTAMETER
Code 125, Rice Statuary." The ammonium sulfate, \((\text{NH}_4)_2\text{SO}_4\), was a commercial grade fertilizer and was produced by Harrisons and Crosfield, Montreal, Canada. The sodium chloride, NaCl, was also a commercial grade salt, labeled "Sterling Brine Crystals," International Salt Company, Clarks Summit, Pennsylvania. Absolute ethanol was used as the salting out agent for alum and sodium chloride; methanol was used for ammonium sulfate. The alcohol was selected so that a single liquid phase was present for all operating conditions. Distilled water was used to dissolve the solute.

Procedure

Feed solutions were prepared by the following procedure. A predetermined weight of solute was dissolved in a known volume of water in a mixing tank. Insoluble matter, such as sand, was allowed to settle. The solution was filtered and transferred to the feed tanks. In addition, for ammonium sulfate an oily coating material was removed from the liquid's surface before the solution was filtered and transferred. The solute concentration of the clear feed solution was checked by drying a liquid sample and weighing the solid residue.

The crystallization experiments were initiated as follows. A predetermined volume of feed was charged to the crystallizer, agitation was established and then the required volume of alcohol was rapidly added. The two feed streams
were started and controlled at their proper flow rates. Then the crystal suspension was allowed to approach steady state, about 20 residence times being required. A step change in residence time was made by step changing the feed rates while maintaining all other operating parameters constant. A step change in solute feed concentration simply involved a step change from one feed system to a second, the two feed solutions containing different solute concentrations.

Magma samples were removed from the crystallizer through a submerged sampling tube. The rate of withdrawal was rapid in order to prevent classification in the tube. The total volume of the slurry was recorded and the crystals were separated from the mother liquor by filtering through a fritted disc, Buchner type funnel. The pore size of the disc was 40-60 microns. Twenty milliliters of the clear mother liquor were placed in a tared, one ounce sample bottle and evaporated to dryness. The sodium chloride and ammonium sulfate crystals, after the mother liquor had been removed, were washed thoroughly with a drying agent, isopropanol, and dried in an oven at 80-100\(^\circ\) C. The alum crystals were washed with acetone and allowed to dry at ambient conditions.

The dried crystals were analyzed by a conventional sieve analysis, using U. S. Standard, 3 inch, testing sieves. The sieves were subjected to ten minutes of shaking by a Ro Tap testing sieve shaker. The following mesh sizes were used:
16, 18, 20, 25, 35, 40, 50, 70, 100, 140, 200, 325 and the pan. Each size fraction was separated and weighed.

Due to uncertain results from a sieve analysis of small particles, a technique (28) utilizing a Coulter Counter, Model A (7), was used, enabling one to measure the size and to count the number of crystals in the micron size range. The results of the analysis agreed with the data obtained from the sieves and extended the measurable particle sizes down to 10-20 microns.
RESULTS

Treatment of Data

The experimental data for this investigation were obtained from sieve analyses and from Coulter Counter analyses of crystal size distributions. The crystal distributions obtained from the sieves had a size range down to 0.089 millimeters in diameter. Crystals in the size range of 0.020 to 0.140 millimeters were analyzed by the counter.

Weight fractions obtained from sieve analyses were converted into population density by the following procedure:

- An arithmetic average diameter was determined for each size fraction.
- The total weight of a given size fraction was converted to the number of crystals by dividing by the cube of the average diameter, a volumetric shape factor, and the density of the crystalline material.
- The population density of the size fraction was obtained by dividing the total number of crystals in a size fraction by the width of the size fraction.

The population density, arbitrarily based on the volume of the crystallizer $V$, may be calculated from the following equation:

$$ n = \frac{G}{v} \frac{1}{C} \frac{1}{(K\sqrt{L^2})\Delta L} $$

(56)
where \( G \) is the mass of the size fraction obtained from a suspension sample volume \( v \), \( V \) the total volume of the crystallizer, \( \rho \) the density of the crystalline material, \( K_v \) the volumetric shape factor, \( L \) the average diameter of the particles in the size fraction and \( \Delta L \) the width of this size fraction.

The Coulter Counter utilizes the fact that when electrolyte is displaced in an orifice by a moving solid particle, the conductance through that orifice is altered in a known relationship with the particle volume. It thereby counts the number of particles suspended in an inert electrolyte which have a diameter larger than a predetermined size. Repeated analyses of a suspended crystal sample at various conductance thresholds resulted in data that were directly convertible to the number of crystals of average size \( L \) contained in a size fraction of width \( \Delta L \). Population density was obtained by dividing the number of crystals contained in a size fraction by the width of the size fraction. Thus,

\[
n = \frac{C}{v_c} \frac{v}{M_e} \frac{K}{\Delta L}
\]  

(57)

where \( C \) is the number of particles of average size \( L \) that were counted in a known volume of electrolyte that traversed the aperture, \( v_c \) this known volume of electrolyte, \( v_e \) the total volume of electrolyte in which \( M_e \) grams of crystals were
slurried, $M_t$ the total weight of crystals obtained from a sample of volume $v$ from the crystallizer, $V$ the volume of the crystallizer, $K$ a conversion factor and $\Delta L$ the width of the size fraction.

Effect of Residence Time on Steady State Crystal Size Distribution

Previously developed expressions relating population density to system parameters and constraints indicate that average residence time will normally influence the crystal size distribution. This follows because of the constraints on the system and crystallization kinetics. An increase in residence time in a continuous crystallizer will result in a lower level of solute concentration in the mother liquor. By maintaining a constant saturation composition, this reduction in solute composition results in a reduced level of supersaturation. This decrease in supersaturation will, consequently, decrease the nucleation and growth rates. Depending upon the respective nucleation and growth kinetics, the average particle size of the resulting crystals will be increased.

Equation 41 indicates that if a crystallizer is operating at steady state, a plot of the log of population density versus average crystal size will result in a linear relationship, with a slope proportional to $1/r_0^T_0$ and an intercept equal to the log of the nuclei population density $n_0^\circ$. A set of experiments performed at different residence times provides data
which can be used to correlate growth rate as a function of nuclei population density. If the quantity of solute in solution at equilibrium is large compared with the mass represented by the degree of supersaturation, such a disturbance will not appreciably affect suspension density. Thus, Equation 46 can be applied at constant suspension density to relate the kinetics of nucleation to the kinetics of growth, the primary relationship which determines size distribution. If a plot of the log of the nuclei population density versus the log of the growth rate results in a straight line, the nucleation kinetics may be represented by a simple power function of growth rate.

Figures 10 and 11 show steady state size distributions for the ammonium sulfate and sodium chloride systems respectively at 15, 30 and 45 minute residence times. These plots demonstrate the continuity of data obtained by the two analyzing techniques. Their size distributions also substantiate the applicability of the steady state exponential relationship, Equation 41. Pertinent experimental operating conditions and results are tabulated in Table 1.

Figure 12 shows the linear correlation of the log of the nuclei population density versus the log of the growth rate for each system. The straight lines indicate that the data may be represented by Equation 46. Thus, the kinetic order for the nucleation rate of ammonium sulfate is 4.0 and that of
Figure 10. Steady state population density distribution for ammonium sulfate

10/3 ratio ammonium sulfate-water solution to methanol

57 grams ammonium sulfate per 100 milliliters water
SYSTEM: \( (NH_4)_2SO_4-H_2O-MeOH \)
TEMPERATURE: 80°F
SUSPENSION DENSITY: 0.1 gm/ml

RESIDENCE TIME, min
15 □
30 △
45 ◊

SIEVES
COULTER COUNTER ◊

POPULATION DENSITY (numbers/mm)

CRYSTAL DIAMETER (L-mm)
Figure 11. Steady state population density distribution for sodium chloride

5/1 ratio sodium chloride-water solution to ethanol

34 grams sodium chloride per 100 milliliters water
SYSTEM (NaCl-EtOH-H$_2$O)
TEMPERATURE: 80° F
SUSPENSION DENSITY: 3.3x10^{-2} gm/ml

RESIDENCE TIME, min
15  □
30  △
45  ○

SIEVES
COULTER COUNTER  ○
Table 1. Experimental Operating Conditions and Results

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<th>M gm alcohol / 100 ml</th>
<th>r_o mm/hr</th>
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* Data reported by Timm (28).

** Transient runs.
Figure 12. Nuclei population density versus growth rate
NUCLEI POPULATION DENSITY ($n_0^o$ - numbers/mm)

GROWTH RATE ($r_e$ - mm/hr)
sodium chloride is 9.0 under the conditions of the experiment. Robinson and Roberts (23) suggested a kinetic order of 4.0 for the reaction crystallization of ammonium sulfate. The alum system has previously been discussed by Timm and Larson (29).

Recalling that the kinetic order of Equation 30 is numerically equal to the slope of the graph of the log of the nuclei population density versus the log of the growth rate plus one, a brief discussion of the evaluation method used to obtain these results is pertinent. Figures 10 and 11 are semi-logarithmic graphs, log population density as ordinate and average crystal size as abscissa. Growth rates for the respective systems at different residence times are proportional to the slopes of these graphs; the intercepts are equal to the log of the nuclei population density. Noting the slight scattering of data, the best straight line is not always obvious. Small variations in the construction of these lines have but a slight effect on the numerical value of the growth rates, but significantly affect the numerical value for the nuclei population density. Therefore, the following procedure was developed to determine the best straight line.

Suspension density is expressed in terms of population density by the following relationship:

\[ M = \frac{K_v \int_0^\infty nL^3 \, dL}{V} \]  

(58)
At steady state, Equation 41 is applicable. Thus, Equation 58 may be reduced to the following:

$$M = \frac{6 \mathcal{C} K_v (r_0 T_0)^{L/4} n_0}{V}$$  \hspace{1cm} (59)$$

Thus, the steady state lines were adjusted until the calculated suspension density from Equation 59 agreed with that observed experimentally.

The population densities for the larger size fractions often lie above these straight lines, as shown by the steady state graphs. Microscopic examination indicated that a significant part of these larger crystals were really agglomerations. Therefore, their numerical values would be expected to lie above the linear relationship. However, the weight of these large size fractions was but a few percent of the total weight of a given sample. Consequently, the significance of these points is in question.

The dominant particle size (20) based on the mass fraction of the size distribution, obtained under the conditions of these experiments, is given by

$$L_d = 3rT$$  \hspace{1cm} (60)$$

Dominant particle sizes, which may be used as measures of crystal size distribution enhancement caused by increasing residence times, are tabulated in Table 1 along with pertinent
experimental operating conditions. Figures 10 and 11 demonstrate this size distribution enhancement as a function of increasing residence time and also as a function of the kinetic order of the nucleation rate. The higher the kinetic order, the greater is the effect of residence time on the size distribution enhancement.

The theoretical effect of residence time $T$ on the steady state size distribution may be expressed as follows. If all of the other operating parameters are constant, then by Equation 59, for two different residence times, $T_0 \, 1$ and $T_0 \, 2$

\[
\left[ \frac{T_0 \, 1}{T_0 \, 2} \right]^4 = \frac{n_0 \, 2}{n_0 \, 1} \left[ \frac{T_0 \, 2}{T_0 \, 1} \right]^4
\]  \hspace{1cm} (61)

and by Equation 46

\[
\left[ \frac{T_0 \, 1}{T_0 \, 2} \right]^4 = \left[ \frac{T_0 \, 2}{T_0 \, 1} \right]^{4(i-1)/i+3}
\]  \hspace{1cm} (62)

\[
\frac{n_0 \, 1}{n_0 \, 2} = \left[ \frac{T_0 \, 2}{T_0 \, 1} \right]^{4(i-1)/i+3}
\]  \hspace{1cm} (63)

Also, for dominant particle size $L_d$

\[
\frac{L_d \, 1}{L_d \, 2} = \left[ \frac{T_0 \, 2}{T_0 \, 1} \right]^{1-i/(i+3)}
\]  \hspace{1cm} (64)
If data corresponding to residence time \( T_0 \) are arbitrary, but known, it then follows that \( r^0_1 \), \( n^0_1 \), \( L_d^1 \) and \( T_0^1 \) may be conveniently determined. The resultant logarithmic graphs will be linear, having slopes proportional to the respective exponents and passing through a known experimental point. The experimental data of Table 1 are thus plotted in Figure 13. The alum data have been reported previously by Timm and Larson (29).

It is of interest to note the variations of \( L_d \) with \( T \). For the alum-ethanol-water system, increasing or decreasing residence time has but a slight effect on \( L_d \); thus, \( i \) is approximately one as reported by these investigators. By increasing \( T \) to 1.5 hours, sodium chloride's \( L_d \) would be approximately that of alum; but ammonium sulfate's residence time would have to be increased to 3.0 hours for the same \( L_d \). Thus, it is apparent that the size distribution of a crystal system with a high kinetic order is more sensitive to residence time than that of a system having a lower kinetic order.

Figure 13 also demonstrates the importance of residence time on the stability of a crystallizer. For sodium chloride, a disturbance from 0.9 to 0.8 hours in \( T_0 \) results in a final value of \( n^0 \) that is approximately 30 percent larger than that value at 0.9 hours. The shower of nuclei formed by such a disturbance, even if corrected in a short period of time, requires from 15 to 20 drawdown times, or longer, to grow
Figure 13. Effect of residence time on nuclei population density, growth rate and dominant particle size

- ○ - alum-ethanol-water system
- □ - ammonium sulfate-methanol-water system
- △ - sodium chloride-ethanol-water system
Slope $\frac{i - 1}{1 + 3}$

Slope $\frac{4(1-i)}{1 + 3}$

Slope $\frac{-4}{1 + 3}$
through the crystal size distribution. Thus, for an approximately 10 percent change in flow rate, at least a 30 percent increase in nucleation results. This shower of nuclei causes a family of transients which will be in the crystallizer for 20 drawdown times, a considerable period of time if a crystallizer is operating at a several-hour residence time. Therefore, for a higher kinetic order crystal system, such as that for sodium chloride, the controlling of the crystal distribution is extremely sensitive to small disturbances in residence time.

It is of interest to note that if \( i = 1.0 \), both the nuclei population density and dominant particle size are independent of residence time. This observation has also been shown by the numerical solution of Equation 30. For such systems, growth rate will be a linear function of residence time. The alum-ethanol-water system investigated by Murray and Larson (16) and Timm and Larson (29) approximates such a system. The correlation of particle size and residence time, Equation 64, should prove to be a useful tool in the scale-up, design and control of commercial crystallizers.

**Transient Crystal Distribution Dynamics for a Step Change in Residence Time**

Data were collected for unsteady state operating conditions for the two crystal systems. A transient response was forced by a step decrease in residence time, or a step
increase in production rate. The crystallizer was first operated at 45 minute residence time for 20 drawdown times; then a step change to 15 minute residence time was made. Data were then collected for an additional twenty residence times.

Figures 14 and 15 show the resulting transients as functions of population density and numbers of residence times with parameters of crystal size. Experimental operating conditions are tabulated in Table 1.

The figures show that the step change introduced a definite disturbance in the size distribution. This disturbance first occurred as a shower of nuclei and then "grew" through the larger size fractions. Steady state was again approached in an additional 20 residence times. The respective locations of the various size fractions were displaced. The larger sized crystals were reduced in number; the number of smaller crystals was increased. Thus, the net effect was an overall degradation of the crystal size distribution. The degree of degradation was a function of the crystal system, ammonium sulfate moderately affected and sodium chloride greatly affected. The total time required to approach steady state was also a function of the systems, sodium chloride requiring a longer time.

Equation 30 was solved for various numerical values of the kinetic order of the nucleation rate, using Equation 36 to
Figure 14. Transient response of size distribution to a step change in residence time

$T_0$ - 45 minute residence time

$T$ - 15 minute residence time

10/3 ratio ammonium sulfate-water solution to methanol

57 grams ammonium sulfate per 100 milliliters water
Figure 15. Transient response of size distribution to a step change in residence time

$T_0$ - 45 minute residence time

$T$ - 15 minute residence time

5/1 ratio sodium chloride-water solution to ethanol

34 grams sodium chloride per 100 milliliters water
define growth rate. The curve was adjusted to the experimental data by varying only the kinetic order $i$ of the nucleation model. The results of this analysis are shown by Figure 16. A kinetic order for the nucleation rate of 4.0 for the ammonium sulfate system is seen to correlate with the experimental transient data. The initial values and the final values of the population densities for the various crystal size fractions are seen to agree with that predicted theoretically. In addition, the model predicts the degradation of crystal size before a size fraction passes through its minimum value. However, the degree of overshoot predicted by the model, and experienced experimentally, are significantly different; but the time at which these transients occur is closely predicted.

It should be pointed out, however, that the plots obtained from the numerical solution represent "point" values of population density. That is, the plotted values are size averaged over a very narrow size range. Experimentally, the data points are obtained from a screen analysis which, in effect, gives values of population density size averaged over a very wide size range. It is evident that such experimental averaging will give results much less sensitive to time variation; and, consequently, the experimental data will not exhibit as wide a fluctuation as does the computed distribution. The numerically obtained size distributions were size
Figure 16. Dimensionless transient response of size distribution to a step change in residence time

$T_0$ - 45 minute residence time
$T$ - 15 minute residence time

10/3 ratio ammonium sulfate-water solution to methanol

57 grams ammonium sulfate per 100 milliliters water

$i = 4.0$ for numerical solution
$j = 1.0$ for numerical solution
averaged over the same size range as were the experimental distributions. However, only a small reduction in peak height was obtained.

The numerical solution's stability was found to be a function of the kinetic order of the nucleation rate. The higher kinetic order required to analyze the sodium chloride system was such that an unstable numerical solution resulted. However, the similarity of experimental data strongly suggests that these data are of the form predicted by the theoretical model of Randolph and Larson (22). Consequently, a stable numerical solution would be expected to be similar to the experimental observations. The observed degree of size degradation of the larger sized crystals is more pronounced than that observed for the other system. Thus, the data strongly indicate a higher kinetic order for the nucleation rate.

Murray and Larson (16) analyzed similar transient data for the alum system in terms of moment equations which are defined by the following relationships:

\[
N_T = \int_0^\infty ndL \tag{65}
\]

\[
L_T = \int_0^\infty nhdL \tag{66}
\]

\[
A_T = \int_0^\infty nL^2dL \tag{67}
\]
This type of analysis is readily performed by analog computation, but possesses a major disadvantage. Namely, the moments are total quantities, the total number of crystals and their total length, area and mass that are contained in a defined suspension volume. Experimentally, a significant percentage of the total number of crystals is contained in crystals that are too small to analyze with a high level of competence and, therefore, is experimentally undefined. The total mass of crystals, although accurately defined by laboratory analysis, remains constant for a step change in production rate. The length and area moments have a higher level of experimental competence than the numbers moment, but less than that of the mass moment. A numerical solution has the disadvantage of computational cost, but it has a major advantage in calculating theoretical data corresponding to crystal size fractions which may be analyzed by conventional methods.

Effect of Suspension Density on Steady State Crystal Size Distribution

Subjected to the constraints and assumptions imposed in the development of the size distribution equation, Equation 30, expressions relating growth rate in terms of system parameters
have been derived. These expressions demonstrate the effect that suspension density has upon crystal growth rate. In addition, a nucleation model, Equation 43, has been proposed which emphasizes a similar influence upon nucleation. In general, these two factors, nucleation and growth, would, therefore, be expected to affect the crystal size distribution at different levels of suspension density. Equation 41 will apply for each steady state level of suspension density and thus provides a tool for determining the steady state nuclei population density and growth rate, as a function of suspended magma concentration and its size distribution.

The steady state size distributions for the alum and ammonium sulfate crystal systems are plotted in Figures 17 and 18, respectively. It is evident that the linear relationships are approximately parallel, being displaced by an amount equal to the change in suspended magma concentration. Thus, the overall crystal size distribution was not appreciably altered by a significant step change in the feed's solute concentration. Pertinent experimental operating conditions and the steady state growth rates and nuclei population densities are tabulated in Table 1.

From Equations 46 and 59, it follows that for different levels of suspension density at a constant residence time

\[
\frac{n_o^1}{n_o^2} = \left(\frac{M_1}{M_2}\right)^{\frac{1}{r_o}} \left(\frac{r_o^1}{r_o^2}\right)^{i-1}
\]  

(69)
Figure 17. Steady state size distributions at different suspension densities

15 minute residence time

3/1 ratio alum-water solution to ethanol

6 grams alum per 100 milliliters water

10 grams alum per 100 milliliters water
SYSTEM: Alum - H₂O - EtOH
TEMPERATURE: 80°F
RESIDENCE TIME: 15 min.
SUSPENSION DENSITY: 2.0 5.4 gm/100 ml
SIEVES
COULTER COUNTER

POPULATION DENSITY (n - numbers/mm)

CRYSTAL DIAMETER (L-mm)
Figure 18. Steady state size distributions at different suspension densities

15 minute residence time

10/3 ratio ammonium sulfate-water solution to methanol

50 grams ammonium sulfate per 100 milliliters water

72 grams ammonium sulfate per 100 milliliters water
where the subscripts \(1\) and \(2\) refer to the different levels of suspension density. And

\[
\frac{r_0}{r_0} = \frac{(M_1/M_2)^{(1-j)}/(i+3)}{}
\]

(70)

\[
\frac{n_0^0}{n_0^0} = \frac{(M_1/M_2)^{(1-i-1)/(i+3)}}{}
\]

(71)

\[
\frac{L_d}{L_d} = \frac{(M_1/M_2)^{(1-j)/(i+3)}}{}
\]

(72)

From the above equations, it is evident that log-log plots of \(r_0, n_0\), and \(L_d\) as functions of suspension density will be straight lines with slopes equal to the respective exponents shown.

For the case where \(j = 0\), homogeneous nucleation, the following set of relationships applies.

\[
\frac{r_0}{r_0} = \frac{(\Delta C_1/\Delta C_2)^{1/(i+3)}}{(M_1/M_2)^{1/(i+3)}}
\]

(73)

\[
\frac{n_0^0}{n_0^0} = \frac{(M_1/M_2)^{(i-1)/(i+3)}}{}
\]

(74)

\[
\frac{L_d}{L_d} = \frac{(M_1/M_2)^{1/(i+3)}}{}
\]

(75)

Thus, in general, a step increase in solute feed concentration will cause a new steady state size distribution that may be characterized by an increase in nucleation rate accompanied by an increase in growth rate. The net effect would be an overall size distribution enhancement. The dominant particle
size at the higher suspension density is greater than that of the lower suspension density. The lower the kinetic order \( i \), the greater will be the size distribution enhancement.

For heterogeneous nucleation, \( j \) is greater than 0. If \( j = 1.0 \), the following steady state relationships may be developed:

\[
\frac{r_0_1}{r_0_2} = \frac{L_d_1}{L_d_2} = 1.0 \tag{76}
\]

\[
\frac{n^o_1}{n^o_2} = \frac{M_1}{M_2} \tag{77}
\]

Such a system will have a constant growth rate and an increased nucleation rate which is directly proportional to the increase in \( M \).

For the heterogeneous nucleation case in which \( 0 < j < 1.0 \), an increase in suspension density will result in an enhanced crystal distribution. The smaller the value of \( j \), the greater will be the crystal distribution enhancement. If \( j \) is greater than 1.0, such a system's size distribution will be degraded by increasing \( \Delta C \). Thus, the importance of knowing the value of \( j \) for a crystal system is self evident.

Experimental steady state data were analyzed for two crystal systems, alum and ammonium sulfate, at different levels of suspension density. These data are plotted according to Equations 70 and 71 in Figures 19 and 20, respectively. Figure 19 shows that for both systems linear crystal growth
Figure 19. Growth rate versus suspension density
SLOPE: $\frac{1-j}{i+2}$

SYSTEM:
- ○ Alum
- □ $\text{(NH}_4\text{)}_2 \text{SO}_4$

GROWTH RATE ($r_0$) vs. SUSPENSION DENSITY (M)
Figure 20. Nuclei population density versus suspension density
NUCLEI POPULATION DENSITY (n° - numbers/mm)

SUSPENSION DENSITY (M gm/ml)

SYSTEM: O Alum
(NH₄)₂ SO₄

SLOPE: \( \frac{1+4j-1}{1+3} \)
rate is a constant function of the suspended magma concentrations, thus $j = 1.0$. Similarly, Figure 20 indicates that nuclei population density and suspension density are directly proportional to each other, substantiating that $j = 1.0$. Thus, the dominant source of new particles is heterogeneous nucleation.

If homogeneous nucleation were observed experimentally, the slopes of Figure 19 would be approximately $1/4$ for alum and $1/7$ for ammonium sulfate; and the slopes of Figure 20 would be approximately $0$ for alum and $3/7$ for ammonium sulfate. These latter slopes are significantly different than those observed experimentally. Thus, homogeneous nucleation is not the major source of new particles for these two crystal systems.

Transients Crystal Distribution Dynamics for a Step Change in Solute Feed Concentration

A transient response was forced on an initial steady state crystal size distribution by a step increase in solute feed concentration. Knowing that crystal nucleation and growth are complex mass transfer processes, the experiments were designed to maintain a constant liquid phase composition so that concentration factors would not affect the experimental observations. Data were collected for a period of twenty residence times after the step disturbance.
Figures 21 and 22 show the resulting transients for the alum and ammonium sulfate systems as functions of population density and crystal size. Experimental operating conditions are tabulated in Table 1. The figures show that the step change produced a definite disturbance in the nuclei size fraction, caused by the sudden increase in supersaturation. This disturbance then grew through the larger size fractions. It should be noted that the form of these transients is distinctly different from those observed for a step disturbance in residence time.

Previous investigations concerning the effect of residence time have established that for the alum system, $i = 1.25$ (28) and for the ammonium sulfate system, $i = 4.0$. Therefore, Equation 30 was solved numerically for step changes in solute feed concentration, utilizing this information and the results of the steady state suspension density experiments, $j = 1.0$. Equation 3^4 was used to define linear crystal growth rate. The dimensionless results are shown in Figures 23 and 24. The numerical solution approximates the experimental observation. The initial and final steady state population densities agree quantitatively. However, the model again predicts a transient response having a higher degree of overshoot than observed experimentally.

The above discrepancies between experimental transient observations and numerical simulation may, in part, be caused
Figure 21. Transient response in size distribution to a step increase in solute feed concentration

$T = 15$ minutes

$\frac{\Delta C}{\Delta C_0} = 2.70$

3/1 ratio alum-water solution to ethanol

6.0 and 10.0 grams alum per 100 milliliters water
Figure 22. Transient response in size distribution to a step increase in solute feed concentration

\( T = 15 \) minutes

\( \Delta C / \Delta C_0 = 3.68 \)

10/3 ratio ammonium sulfate-water solution to methanol

50.0 and 72.5 grams ammonium sulfate per 100 milliliters water
Figure 23. Dimensionless response in size distribution to a step change in solute feed concentration

$T = 15$ minutes

$\Delta C/\Delta C_0 = 2.70$

3/1 ratio alum-water solution to ethanol

6.0 and 10.0 grams alum per 100 milliliters water

$i = 1.25$ for numerical solution

$j = 1.00$ for numerical solution
Figure 24. Dimensionless response in size distribution to a step change in solute feed concentration

\[ T = 15 \, \text{minutes}\]
\[ \Delta C / \Delta C_0 = 3.68\]

10/3 ratio ammonium sulfate-water solution to methanol

50.0 and 72.5 grams ammonium sulfate per 100 milliliters water

\[ i = 4.0 \text{ for numerical solution} \]
\[ j = 1.0 \text{ for numerical solution} \]
by an inadequate transient nucleation relationship. Previous investigators, working with nucleation from clear solutions, have frequently referred to induction time which may be as large as several minutes. Such phenomena could result in a delayed nucleation mechanism which, conceivably, could be related to an average supersaturation and not to the instantaneous supersaturation now imposed on the model through the power nucleation relationship. However, the concept of an induction time is not clearly pertinent for the specific class of mixed suspension crystallizations.

Growth Rate Independent of Particle Size

The assumption that McCabe's ΔL Law holds is quite necessary for ease in solution of the model, but it does impose some limitations on the applicability of the results. McCabe (12) observed that under a variety of operating conditions, crystal growth rate is independent of particle size. However, later observations have shown that large deviations from this law may occur if diffusional resistance is a dominant factor in the crystal growth mechanism. McCabe and Stevens (13) reported that the law did not apply for the crystallization of copper sulfate. In their investigation a monosized sample of crystals was placed on a retaining screen and grown for a period of time. The growth rates for various sized crystals, all subjected to a similar environment, were
calculated from a material balance.

In these experiments crystals subjected to different fluid velocities grew at different rates, but different sized crystals grew at a constant rate when subjected to a constant fluid velocity. In a suspended magma sample, large crystals will be subjected to a higher relative settling velocity than small ones. Consequently, growth rate will be expected to be a function of particle size. However, similar conditions are not always approximated in commercial crystallizers. The latter may be more accurately characterized by high magma concentrations so that free settling laws do not apply, but rather a condition of hindered settling exists. In this case, growth rate as a function of crystal size will be much less probable. Data collected in this investigation indicate that for the three crystal systems analyzed, McCabe's ΔL Law is a valid assumption for the observed size fractions. However, if the crystal sizes and growth kinetics were such that growth rates were observed to be appreciably affected by particle size, the basic number balance model could be altered to account for such behavior. Canning and Randolph (5) and Abegg (1) considered such phenomena in detail.
DISCUSSION

A macroscopic analysis of a continuous crystallization process was conducted to demonstrate that a previously developed model adequately describes experimental crystal size distributions. It was demonstrated that steady state size distributions do follow the relationships of this model. Furthermore, equations were developed which explain experimentally observed effects of residence time and of suspended magma concentration on crystal size distributions. In addition, transient data were simulated by a numerical analysis. The results of the study showed that heterogeneous nucleation does significantly contribute to the rate of formation of new particles in such a crystallization system.

The applicability of the ideas expressed in this dissertation should apply directly to the design and to the evaluation of other crystallization systems, including evaporative and cooling crystallizers. However, because the effects of operating parameters, such as temperature, degree of mixing, attrition, surface nucleation, crystal habit and entrance effects, are in general not fully understood, generalizations specifically dealing with the kinetic order of the nucleation rate for a particular solute in different types of crystallizers, including salting out, evaporative and cooling, or in scale-up design considerations, are not yet feasible. For example, Chambliss (6), reporting observations in a laboratory
cooling crystallizer, observed the same kinetic order for ammonium alum as found in this work, but found a different kinetic order for ammonium sulfate. He showed, however, that the nucleation rate for both solutes is linearly related to suspension density, as was demonstrated in this work. The important concept at this stage of the theoretical development is not that these two works found different kinetic orders for ammonium sulfate crystallized under significantly variant operating conditions, but that the model provided a tool for the evaluation of observed crystal size distributions from which nucleation kinetics could be defined.

The previously discussed experimental work has demonstrated that nucleation rate may be adequately expressed as a power function of growth rate. If growth rate is a power function of supersaturation, the nucleation kinetics are also power functions of supersaturation, the fundamental mass driving force. In the development of kinetic expressions for nucleation, relationships in terms of supersaturation are desirable on a fundamental basis. However, in the analysis of continuous processes which deal with the precipitation of materials containing relatively small amounts of solute in the level of supersaturation compared to the total solute in solution, the determination of supersaturation is extremely difficult. Bransom et al. (4), while studying a continuous crystallization process, reported for identical operating
conditions large variations in measured supersaturation, but highly reproducible growth rates.

The assumption that linear crystal growth rate is not a function of particle size is quite convenient in the development of the mathematical description of crystal size distributions. However, this concept is quite controversial. In particular, a reasonable model for growth rate, assuming that diffusion and surface reaction are the controlling resistances, clearly indicates that crystal growth rate will be determined, in part, by the film thickness of an enveloping stagnant region. As the relative velocity between the particle and mother liquor is increased, this film thickness will decrease, thereby increasing the rate of crystal growth. In a perfectly mixed, highly concentrated suspension, the relationships governing the relative liquid settling velocity and particle size are not completely understood. In fact, it is conceivable that such effects could be considerably reduced over similar effects observed for single particle settling rates.

A second possibility of particle size influence on growth rate is the effect of fluid velocity in non-ideally mixed crystallizers, as found in large industrial equipment. In such equipment, different regions of the vessel will contain significantly different fluid velocities. These velocities will have two net effects. The first effect is that of
allowing concentration gradients to be established within the equipment. The second is the classification of the suspension into regions containing primarily large particles and regions containing primarily small particles. It is conceivable that due to imperfect mixing, different sized crystals will, therefore, be exposed to regions of different solute concentrations, and thereby exhibit different growth rates. It is evident, therefore, that an important area of study in the consideration of large crystallizing processes is the study of the residence time distributions of both the mother liquor and the suspended crystals.
CONCLUSIONS

1. The analysis of steady state crystal size distributions obtained from a continuous, mixed suspension, mixed product removal, salting out crystallizer indicated that crystal nucleation kinetics can be related to crystal growth kinetics by a simple power function over a wide range of operating conditions and for systems exhibiting either high or low order kinetic relationships. This conclusion also implies, assuming power law growth kinetics, that nucleation kinetics can be represented as a power function of supersaturation. Such growth-nucleation relationships, if known for a given system, can be used in the design of crystallization equipment and in the prediction of crystal size distributions in continuous crystallization processes.

2. The analysis of size distribution data obtained at various suspension densities demonstrated pronounced heterogeneous effects on nucleation kinetics. For two of the systems studied, ammonium alum and ammonium sulfate, the nucleation rate was linearly related to the mass of crystals in suspension. The results for the third system, sodium chloride, were not conclusive. Intuitively, it seems equally reasonable to conclude that the nucleation rate is linearly related to the surface area of the crystal suspension. On the basis of the observed data, it was not possible to distinguish between these two possible explanations.
3. For systems exhibiting the kinetic behavior discussed in Conclusions 1 and 2, increases in residence time will tend to enhance the size distribution. However, changes in suspension density will have no effect on the size distribution obtained. These conclusions are in accord with both theoretical analyses and experimental observations.

4. For the three crystal systems studied, linear crystal growth rate was not a function of crystal size in the size ranges obtained experimentally. It is reasonable to expect, however, that in industrial crystallizers larger sized crystals and non-ideal crystallization conditions may result in crystal product size distributions that indicate a growth dependency on particle size.

5. The kinetic models obtained from steady state experiments can be used in a qualitative simulation of the dynamic behavior of continuous, mixed suspension, mixed product removal crystallization with some confidence. However, the simulation shows behavior closer to instability than is observed experimentally.
RECOMMENDATIONS

1. An experimental procedure should be developed so that steady state and nonsteady state data can be collected to aid in the development of a heterogeneous nucleation mechanism, preferably in terms of supersaturation. Such investigations, using sparingly soluble salts or materials which possess a high level of supersaturation compared with total solute concentration, could prove invaluable in the transient analysis of crystal distribution dynamics.

2. Further experimental data should be collected to aid in the development of relationships defining crystallization kinetic dependency on temperature, agitation, crystal habit and classification.

3. Process control experiments, designed to control product size distribution, should be investigated.

4. An extension of the numerical analysis should be continued so that a stable solution can be obtained for systems with high nucleation kinetics, such as the sodium chloride system. Present transient analyses suggest that an inadequacy between theory and experimental observations may exist in the crystallization kinetics or in the conservation of crystal population balance.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>surface area, ( \text{mm}^2 )</td>
</tr>
<tr>
<td>( A_t )</td>
<td>total suspension crystal area, ( \text{mm}^2 )</td>
</tr>
<tr>
<td>( a )</td>
<td>growth rate dependency on supersaturation</td>
</tr>
<tr>
<td>( C )</td>
<td>solute feed concentration, liquid phase, ( \text{gm/ml} )</td>
</tr>
<tr>
<td>( C )</td>
<td>number of particles counted by Coulter Counter</td>
</tr>
<tr>
<td>( \Delta C )</td>
<td>change in solute concentration across crystallizer, liquid phase, ( \text{gm/ml} )</td>
</tr>
<tr>
<td>( C_{eq} )</td>
<td>equilibrium solute concentration, ( \text{gm/ml} )</td>
</tr>
<tr>
<td>( C_f )</td>
<td>solute concentration of feed, ( \text{gm/ml} )</td>
</tr>
<tr>
<td>( C_i )</td>
<td>input feed concentration, ( \text{gm/ml} )</td>
</tr>
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<td>( C_i )</td>
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<tr>
<td>( C_o )</td>
<td>mother liquor solute concentration, ( \text{gm/ml} )</td>
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<tr>
<td>( D )</td>
<td>solute diffusivity, ( \text{cm}^2/\text{hr} )</td>
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<tr>
<td>( G )</td>
<td>mass of crystals in a given size fraction, ( \text{gm} )</td>
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<tr>
<td>( \Delta G )</td>
<td>Gibbs free energy of formation</td>
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<tr>
<td>( h )</td>
<td>supersaturation dependency on nucleation rate</td>
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<tr>
<td>( i )</td>
<td>nucleation rate dependency on growth rate</td>
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<td>volumetric shape factor</td>
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<td>( K_1 )</td>
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\( k \quad \text{Boltzmann's constant} \\
\( k_a \quad \text{nucleation frequency factor} \\
\( k_g \quad \text{growth rate constant} \\
\( k_n \quad \text{nucleation rate constant} \\
\( k_r \quad \text{reaction rate constant} \\
L \quad \text{average crystal diameter, mm} \\
\Delta L \quad \text{width of size fraction, mm} \\
L_T \quad \text{total length of suspended crystals, mm} \\
L_d \quad \text{dominant particle size, mm} \\
L_{d1} \quad \text{reference dominant particle size, mm} \\
M \quad \text{suspension density - mass of crystals suspended in a given volume of magma slurry, gm/ml} \\
M_T \quad \text{total mass of suspended crystals, gm} \\
M_e \quad \text{mass of crystals slurried in electrolyte, gm} \\
M_t \quad \text{mass of crystals per crystallizer sample, gm} \\
M_i \quad \text{reference suspension density, gm/ml} \\
N \quad \text{number of crystals, #} \\
\Delta N \quad \text{number of crystals contained in a size fraction, #} \\
N_T \quad \text{total number of suspended crystals, #} \\
N^o \quad \text{number of nuclei, #/ml} \\
n \quad \text{crystal population density, #/mm} \\
n^o \quad \text{nuclei population density, #/mm}
<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
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<td>$\bar{n}_o$</td>
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</tr>
<tr>
<td>$S$</td>
<td>concentration ratio, C/C*</td>
</tr>
<tr>
<td>$s$</td>
<td>supersaturation, gm/ml$^3$</td>
</tr>
<tr>
<td>$T$</td>
<td>residence time or drawdown time, hr</td>
</tr>
<tr>
<td>$T_o$</td>
<td>steady state residence time, hr</td>
</tr>
<tr>
<td>$T_o^0$</td>
<td>reference steady state residence time, hr</td>
</tr>
<tr>
<td>$V$</td>
<td>particle volume, ml</td>
</tr>
<tr>
<td>$V$</td>
<td>volume of crystallizer, ml</td>
</tr>
<tr>
<td>$V$</td>
<td>volume of suspension, ml</td>
</tr>
</tbody>
</table>
\[ v \quad \text{molar volume of solute, ml/mole} \]
\[ v \quad \text{volume of magma sample, ml} \]
\[ v_c \quad \text{volume of electrolyte-crystal slurry that traversed the aperture, microliters} \]
\[ v_e \quad \text{total volume of electrolyte, ml} \]
\[ W \quad \text{minimum energy for nucleation} \]
\[ W_s \quad \text{energy of surface formation} \]
\[ W_v \quad \text{energy of forming bulk} \]
\[ x \quad \text{dimensionless crystal size, } L/r_o T_0 \]
\[ y \quad \text{dimensionless population density, } n/n_0^0 \]
\[ \Theta \quad \text{dimensionless time, } t/T_0 \]
\[ \mu \quad \text{chemical potentials of solute} \]
\[ \sigma \quad \text{surface tension} \]
\[ \rho \quad \text{crystal density, gm/ml} \]
\[ \phi \quad \text{dimensionless growth rate, } r/r_o \]
REFERENCES CITED


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APPENDIX

The IBM 360 Model 50 digital computer was used in the numerical solution of the size distribution equation. The program logic was developed using a Modified Euler finite difference approach. Identification of the FORTRAN code words is given, followed by a photograph of the actual program, Figure 25. Minor modifications to several of the FORTRAN statements allow the use of either Equation 54 or Equation 55 to define crystal growth rate in terms of system parameters and constraints.

Code Word Definitions

X(N) set of independent variables, x
YN(N) set of dependent variables, y @ θ
YNP1(N) first estimate of y @ θ + Δθ
YNP2(N) second estimate of y @ θ + Δθ
XSQ(N) set of values of x²Δx
XCB(N) set of values of x³Δx
DELX increment in x-direction, Δx
DELT increment in θ-direction, Δθ
T initial value of θ
TMAX final value of θ
TRAY ratio of residence times, T₀/T
CRAY ratio of solute concentrations, ΔC/ΔC₀
ORDR kinetic order of nucleation minus one, i - 1
ORDM  kinetic nucleation dependency on suspension density, j
ORDG  kinetic order of growth on supersaturation, a
PHI  dimensionless growth rate $\phi @ \theta$
PHIS defined by Equation 54, $\phi^*$
PHIO initial estimate of growth rate $@ \theta + \Delta \theta$
PHI1 second estimate of growth rate $@ \theta + \Delta \theta$
PHI2 final estimate of growth rate $@ \theta + \Delta \theta$
SUMA dimensionless suspension area
SUMM dimensionless suspension mass
PERCT weight percent distribution
A dummy variable equal to 1.0
B dummy variable equal to -1.0
U fraction of nuclei dissolved, 1.0
OM initial steady state mass
GK growth rate constant, $k_g$
OR initial steady state growth rate, $r_o$
NRUN coding number for multiple solutions
ISP reference number to print data only every ISP increments of $\Delta x$
BIGP reference number to print data only every BIGP increments of $\Delta \theta$
Figure 25. Digital computer program used for the solution of the size distribution equation
Figure 25. (Continued)