Size distribution dynamics in continuous crystallization

Donald Carlton Murray
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SIZE DISTRIBUTION DYNAMICS IN CONTINUOUS CRYSTALLIZATION

by

Donald Carlton Murray

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1964
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Volumetric Shape Factor 96
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ABSTRACT

A laboratory sized continuous mixed suspension salting out crystallizer was designed and constructed to test the crystallization theory recently developed by Randolph and Larson (4). This theory relates the crystal size distribution to nucleation growth kinetics and operating conditions. The salting out method of crystallization was selected because of its ease of operation and control. The system used was ammonium alum-ethanol-water.

The results of this work were in agreement with the steady state theory. Under the conditions of these experiments, the nucleation rate, $\frac{dN_0}{dt}$, was related to the growth rate, $r$, as follows: $\frac{dN_0}{dt} = Kr^2$. The crystallizer was operated under unsteady state conditions where both the production rate and the inlet solute concentration were varied. The theoretical model using experimentally determined parameters was simulated on an analog computer and solved for both types of upsets. The results indicated that the model fits quite well for the production rate dynamics but that in the concentration range used the inlet concentration model is not adequate to describe the system.
INTRODUCTION

Much theoretical work has been done in the area of continuous mixed suspension, mixed product removal crystallization (1, 3, 4, 6). Most of these studies used the population density of the crystal distribution as the characterizing variable. Theoretical agreement between authors is found for a steady state model of the size distribution. This steady state model is written as follows:

\[ n_Q = n_0^o \exp\left(-\frac{L}{r_0 T_0}\right) \]  

(1)

where \( n_Q \) is the steady state population density, \( n_0^o \) is the steady state nuclei population density, \( L \) is particle diameter, \( r_0 \) is the steady state growth rate and \( T_0 \) is the steady state residence time. It has been found that this equation accurately fits data taken from small experimental as well as large commercial crystallizers (1, 5).

An extensive theoretical study of unsteady state crystallization was carried out by Randolph and Larson (4). They derived from an unsteady state crystal numbers balance the following equation:

\[ \frac{\partial n}{\partial t} = -r \frac{\partial n}{\partial L} - \frac{n}{T} \]  

(2)

The constraints and boundary conditions required for this equation are continuous operation, no seeding, perfectly
mixed suspension, constant suspension density, and mixed product removal. Equation 1 is the steady state solution to this equation. This relation presents an important milestone in the field of crystallization in that its solution provides information which may be used to operate and control continuous crystallizers.

There has been no published experimental unsteady state data which may be used to verify this equation. It was the purpose of this project to develop a laboratory procedure to obtain experimental unsteady state data to check the validity of Equation 2 for upsets in the production rate of the system. The numbers balance equation was also adapted for upsets in input solute concentration. Equation 2 was solved on an analog computer to obtain the theoretical responses to upsets in production rate and input solute concentration.

A continuous, mixed suspension, mixed product removal salting out crystallizer was constructed which satisfied the constraints and assumptions incorporated in Equation 2. Several crystallization systems were tested before one was found which yielded firm, regular crystals with a fast growth rate. The system of ammonium alum-water-ethanol was found to fit all the requirements. It formed firm regular octahedral crystals with a growth rate such that 20 mesh crystals are formed in a period of thirty minutes.
The salting out method of crystallization was selected because of its many advantages in operation and control. No heating, cooling or vacuum system was needed as with evaporative or cooling type crystallizers. The use of non-saturated feed streams eliminated problems of feed line plugging during operation. No insulation of the crystallizer was necessary so a transparent vessel could be used enabling visual observation of the crystal suspension during operation. The maintaining of a constant crystal suspension during an upset in production rate did not require the simultaneous changing of heat input or vacuum level.

The particular system used, alum-water-ethanol, provided a fast growth rate, a constant shape factor for all sized crystals and an adequate density relationship between crystals and suspension. The specific gravity of the crystals and a typical suspension were 1.64 and 1.02 respectively. This enabled a close approximation to a perfectly mixed suspension. The crystals showed little sign of attrition or agglomeration.
LITERATURE REVIEW

A thorough historical review of the theory of crystallization was presented by Randolph (3). He presented the developments in the theory of growth and nucleation from as early as 1929 to the present. He justified the use of population density in the theoretical description of crystallization and used some of the well known relationships developed by others to develop a general unsteady equation which may be used for any type of crystallization.

Saeman (6) and Branson et al. (1) derived a steady state relationship between population density and particle size for continuous mixed suspension crystallization. This relationship is shown by Equation 1. A plot of ln n vs L, for a suspension from a crystallizer operating at steady state, should be a straight line with a slope of $-1/r_o T_o$ and an intercept of $n_o^0$. Population density is defined as:

$$n = \lim_{\Delta L \to 0} \frac{\Delta N}{\Delta L} \quad (3)$$

Robinson and Roberts (5) suggested a kinetic relationship between nucleation rate and supersaturation of the form

$$\text{Rate} = \frac{dN^0}{dt} = k_l s^\alpha \quad (4)$$

Making the common assumption, as pointed out by Schoen (7), that linear crystal growth rate proceeds as a first order
function of supersaturation, Equation 4 was written as

\[ \frac{dN_0}{dt} = k_2 r^\alpha \]  

(5)

The steady state nucleation rate may also be expressed as the product of the steady state growth rate and nuclei population density (3)

\[ \frac{dN_0}{dt} = r_o n_0 \]  

(6)

By combining Equations 5 and 6, a relationship between nucleation and growth rate was obtained

\[ n_0 = k_2 r^{\alpha-1} = k_2 r_0^\beta \]  

(7)

Bransom et al. (1) used Equation 1 and experimental data to determine steady state nuclei population densities and growth rates for a cyclonite-nitric acid-water continuous mixed suspension crystallization system. They plotted \( \ln n_0 \) vs L for three different residence times (growth rates) with constant and equal suspension densities.

Their data were plotted by Randolph (3) as \( \ln (dN_0/dt) \) vs \( \ln r_0 \). The plot yielded a straight line with a slope of 3. This indicated that the \( \alpha \) in Equations 5 and 7 is 3 for that particular system. The work of Bransom et al. and Randolph presents a method of obtaining the relationship between nucleation and growth (Equation 7).
Randolph (3) and Randolph and Larson (4) presented a mathematical study of the size distribution in a continuous, mixed suspension, mixed product removal crystallizer. Their studies were also based on crystal population densities. Their derivations were based on an arbitrary suspension about which the following assumptions were made:

1. The suspension occupies a variable volume \( V \) enclosed by fixed boundaries except for a free gravity surface.
2. The volume has completely mixed inputs and outputs.
3. The particles in the suspension are small enough and numerous enough to be considered a continuous distribution over a given size range of particles and over a given volume element of the suspension.
4. No particle breakage except possibly the chipping of a particle into unequal pieces so that one piece is essentially unchanged and the other small enough to be considered a nuclei.

A balance was made of the number of particles in a given size range \( L_1 \) to \( L_2 \). Using the usual conservation relationship

\[
\text{Accumulation} = \text{input} - \text{output}
\]

they obtained the following numbers balance:
By using the rule of Leibniz on the left hand side of Equation 8 and rearranging they obtained

\[ \int_V \left[ \frac{\partial \bar{n}}{\partial t} + \frac{\partial}{\partial L} \left( \bar{n} \frac{\partial L}{\partial t} \right) \right] dV + \frac{dV}{dt} \bar{n}_s - Q_1 \bar{n}_1 + Q_0 \bar{n}_0 = 0 \]  

(9)

The first term (inside integral) represents the transients in population density of a given size. The second term represents the bulk transport of crystals into and out of the size range due to their growth. The third term represents changes in population due to changes in suspension volume. The fourth and fifth terms represent the inputs and outputs of crystals resulting from bulk flow.

For continuous, mixed suspension, mixed product removal crystallization, the following assumptions were made:

1. Constant feed rate
2. Constant suspension density
3. Constant suspension volume.

After applying assumptions 1 and 3 to Equation 9, it reduced to Equation 2, where \( \bar{n} = nV, \bar{n}_1 = 0 \) for liquid feeds, \( \bar{n}_0 = \bar{n} \) for mixed product removal, \( dV/dt = 0 \) for constant volume,
\[ \frac{\partial L}{\partial t} = r \neq f(L) \text{ if McCabe's } \Delta L \text{ law holds} \] (2) and
\[ 1/T = Q_0/V, \text{ the reciprocal of the residence time.} \]

For steady state this equation has the solution which is identical to Equation 1 proposed by Saeman (6) and Bransom et al. (1). This steady state solution served as an initial condition for the solution of Equation 2. Equation 7 was a boundary condition. Using the constant suspension density assumption, a constraint on growth rate was derived

\[ r = \frac{K}{T} \int_0^T n L^2 \, dL \quad (10) \]

The following dimensionless substitutions were then applied:

Let \[ x = \frac{L}{r_0 T_0} \]
\[ y = \frac{n}{n_0} \]
\[ \theta = \frac{t}{T_0} \]
\[ \phi = \frac{r}{r_0} \quad (11) \]

These substitutions changed Equations 2, 1, 6 and 10 respectively to

\[ \frac{\partial y}{\partial \theta} = -\phi \frac{\partial y}{\partial x} - y \frac{T_0}{T} \quad (12) \]

\[ y(0, x) = e^{-x} \quad (13) \]
Equation 12 solved with initial condition 13, boundary condition 14 and growth rate constraint 15 comprise the system of equations as set forth by Randolph and Larson (4) which give the transient response of crystal population density to an upset from one steady state production rate to another.

They solved these equations on a digital computer and obtained the response of five values of crystal diameter (x) to step changes in production rate corresponding to $\frac{T_0}{T} = 0.833$ and $\frac{T_0}{T} = 1.250$ for a nucleation function $y^o = \phi^3$. They found that a period of from 6 to 8 residence times was necessary to obtain steady state for all of the values of x tested. They show that the population density of the smaller particles (small x) reach steady state sooner than the larger ones.

Randolph (3) presented a method by which Equations 12 through 15 may be solved on an analog computer. The solution was accomplished by first transforming the independent variable x in Equations 12 through 14. This resulted in the following equations written in terms of the Laplace operator s.
\[
\frac{\partial \overline{y}}{\partial \varrho} + \left[ a(\varrho) + s \varphi(\varrho) \right] \overline{y} = \varphi(\varrho)c(\varrho)g(\varrho) \tag{16}
\]

and
\[
\overline{y}(0,s) = \frac{1}{s+1} = 1 - s + s^2 - s^3 + \cdots \tag{17}
\]

where \(a(\varrho) = T_o/T\) the ratio of a fixed reference residence time to the actual residence time, \(c(\varrho)\) is a function corresponding to nuclei dissolving and \(g(\varrho)\) is a dimensionless nucleation function.

The restraint on growth rate, Equation 15, was transformed into a useful form by use of moments of the size distribution

\[
I_1(\varrho) = \int_0^\infty yx^i dx \tag{18}
\]

By using Cauchy's residue theorem of complex variables and the definition of the Laplace transform, Equation 18 was transformed to

\[
I_1(\varrho) = (-1)^i \left[ \frac{\partial^i \overline{y}}{\partial s^i} \right]_{s=0} \tag{19}
\]

The Laplace transform of the dimensionless population density, \(\overline{y}\), was assumed to be representable by an infinite power series in terms of \(s\) as follows:
\[ \bar{y} = f_0(\theta) + f_1(\theta)s + f_2(\theta)s^2 + \cdots \quad (20) \]

where the \( f_i \)'s are arbitrary functions of \( \theta \). This enabled the moments, which are measurable quantities, to be represented by

\[ I_i = (-1)^i i!f_i \quad (21) \]

If Equation 20 was to satisfy Equation 16 then the \( f_i \)'s satisfy the relationships

\[ \frac{df_0}{d\theta} + a(\theta)f_0 = \frac{a(\theta)}{f_2} c(\theta) g\left(\frac{a(\theta)}{f_2}\right) \]

\[ \frac{df_1}{d\theta} + a(\theta)f_1 = -\frac{a(\theta)f_0}{f_2} \]

\[ \frac{df_2}{d\theta} + a(\theta)f_2 = -\frac{a(\theta)f_1}{f_2} \quad (22) \]

with the initial conditions

\[ f_0(0) = 1 \]
\[ f_1(0) = -1 \]
\[ f_2(0) = 1 \]
\[ \vdots \]
\[ \vdots \]
\[ \vdots \]
\[ \vdots \] (23)
The moments, and hence the \( f_i' \)'s, have physical significance in that \( I_0, I_1, I_2 \) and \( I_3 \) are respectively the dimensionless total crystal suspension population, length, area, and mass. A method was presented whereby the \( f_i' \)'s may be obtained from cumulative weight versus size plot from a screen analysis of an experimental sample of crystals.

Thus, they reduced a difficult to solve partial differential equation to three nonlinear ordinary differential equations in terms of moments of the size distribution. These three equations were solvable on an analog computer.

Randolph (3) presented analog computer solutions to Equations 22 to upsets in nuclei dissolving rate and to upsets in residence time. He made a frequency analysis of Equations 22 and presented Bode plots of the response to sine wave and square wave disturbances in the nuclei dissolving rate, \( c \). He indicated that the equations were very sensitive to certain periodic disturbance in the nuclei dissolving rate. These frequencies were found to be from 0.15 to 0.25 cycles/residence time depending on the nucleation function \( g(\varnothing) \).
MATHEMATICAL DEVELOPMENT

Production Rate Upsets

For upsets in production rate or residence time, the nuclei dissolving function, \( c(0) \), in Equation 22 is unity. The dimensionless residence time function, \( a \), is the only forcing function in the equation. The dimensionless nucleation function, \( g(\varnothing) \), is the same function as described in Equation 7. Therefore

\[
g(\varnothing) = g\left(\frac{a}{f_2}\right) = \left(\frac{a}{f_2}\right)^\beta
\]  

(24)

Therefore, for the crystallization system studied in this work, Equations 22 are

\[
\frac{df_0}{d\varnothing} + af_0 = \left(\frac{a}{f_2}\right)^\alpha
\]

\[
\frac{df_1}{d\varnothing} + af_1 = -f_0 \frac{a}{f_2}
\]

\[
\frac{df_2}{d\varnothing} + af_2 = -f_1 \frac{a}{f_2}
\]  

(25)

The initial conditions remain as shown in Equations 23.

To scale Equations 25 and 23 for solution on the analog computer, the following substitutions were made:
\[ X_1 = 10 \text{ volts} \]
\[ A = 10 \text{ volts} \]
\[ \tau = 0 \text{ seconds} \]

These substitutions yielded the following set of equations for voltages in the analog computer simulation:

\[
\frac{dX_0}{d\tau} + \frac{AX_0}{10} = 10 \left( \frac{A}{X_2} \right)^\alpha
\]

\[
\frac{dX_1}{d\tau} + \frac{AX_1}{10} = -X_0 \frac{A}{X_2}
\]

\[
\frac{dX_2}{d\tau} + \frac{AX_2}{10} = -X_1 \frac{A}{X_2}
\]

The following are the initial conditions:

\[ X_0(0) = 10 \text{ volts} \]
\[ X_1(0) = -10 \text{ volts} \]
\[ X_2(0) = 10 \text{ volts} \]

The initial steady state value of \( \alpha \) was unity so the initial steady state value of \( A \) was 10 volts. Using these scaling factors, it was possible to upset the simulated dimensionless production rate, \( A \), by a factor of five for kinetic models with \( \alpha \) as high as 3. The circuit for the analog simulation
of the second order production rate dynamics model \((\alpha = 2)\) is shown in Appendix A.

The analog computer used for this work was a Donner Model 3500. The multipliers were Donner Model 3731 function multipliers. Offner type RS Dynograph two channel recorders were used to plot the results.

Inlet Concentration Upsets

A mathematical model was derived using Equation 2 for conditions of changing inlet concentrations to a continuous mixed suspension crystallizer. The assumptions involved in the development of this model were similar to those for the development of the changing production rate model. The assumption of constant suspension density was not used but the additional assumption was made that the change in concentration of dissolved solute during an inlet composition upset was small compared to the total amount of crystals in the suspension.

The model involves the derivation of a new constraint on the growth rate. The corresponding relationship for the production rate disturbance model is Equation 10. The derivation is based on a mass balance of solute in a crystallizer.

Consider a continuous crystallization system as shown in Figure 1. Making a solute mass balance, the following
Figure 1. Continuous mixed suspension crystallization system
An equation was obtained

$$\frac{d}{dt} \left[ CV + M \right] = C_1 Q_1 - \left[ C_0 Q_0 + \frac{M}{V} Q_0 \right]$$  \hspace{1cm} (29)$$

The first term inside the brackets on the left side of Equation 29 accounts for accumulation of dissolved solute. The second term accounts for accumulation of solid crystals. The first term on the right side is the input of dissolved solute. The second and third terms on the right account for the exit of dissolved solute and solid crystals respectively.

The following assumptions were made about the system:

1. Constant flow rates, i.e., $Q_1 = Q_0 = Q$.
2. Constant volume.
3. Perfect mixing, i.e., $C_0 = C$ and $M/V$ is not a function of position.
4. The change in dissolved solute concentration is negligible compared to the total amount of solute present, i.e., $dC/dt = 0$.

By applying these assumptions, Equation 29 reduces to

$$\frac{dM}{dt} = Q \Delta C - \frac{M}{T}$$ \hspace{1cm} (30)$$

where $\Delta C = C_1 - C$ and $1/T = Q/V$.

The left hand side of Equation 30 may be written in a different form involving the moments of the size distribution.
The total mass of solid crystals, \( M \), may be expressed as follows

\[
M = K_v \rho \int_0^\infty nL^3 dL \quad (31)
\]

By taking the derivative of Equation 31 and applying the rule of Leibniz, the following is obtained

\[
\frac{dM}{dt} = K_v \rho \frac{d}{dt} \int_0^\infty nL^3 dL = K_v \rho \int_0^\infty \frac{\partial}{\partial t} nL^3 dL
\]

\[
= K_v \rho \int_0^\infty L^3 \frac{\partial n}{\partial t} dL \quad (32)
\]

Substitution of Equation 2 into Equation 32 and integrating by parts yields

\[
\frac{dM}{dt} = 3 K_v \rho r \int_0^\infty L^2 r n dL - \frac{K_v \rho}{T} \int_0^\infty L^3 r n dL
\]

\[
= 3 K_v \rho r \int_0^\infty L^2 r n dL - \frac{M}{T} \quad (33)
\]

Equations 30 and 33 are then combined to give

\[
r = \frac{Q \Delta C}{3Kn} = \frac{k \Delta C}{\int_0^\infty nL^2 dL} \quad (34)
\]
By making the dimensionless substitutions of Equations 11 along with the additional substitution
\[ \Delta C = \sigma \Delta C_0 \quad (35) \]

Equation 34 becomes
\[ \varphi = \frac{r}{r_0} = \frac{2 \sigma}{\int_0^\infty yx^2 \, dx} \quad (36) \]

The complete set of equations for the inlet concentration dynamics is
\[ \frac{\delta y}{\delta \theta} = -\varphi \frac{\delta y}{\delta x} - ay \]
\[ y(0,x) = e^{-x} \]
\[ y(\theta,0) = \frac{n^0}{n_0} = \left( \frac{r}{r_0} \right)^\beta = g(\varphi) \]

\[ \varphi = \frac{2 \sigma}{\int_0^\infty yx^2 \, dx} \quad (37) \]

The same transformation technique can be applied to these equations as was done with the production rate dynamics equations.
\[
\frac{df_0}{dt} + f_0 = \left(\frac{\sigma}{f_2}\right)^a
\]

\[
\frac{df_1}{dt} + f_1 = -f_0 \frac{\sigma}{f_2}
\]

\[
\frac{df_2}{dt} + f_2 = -f_1 \frac{\sigma}{f_2}
\]

\[
\frac{df_3}{dt} + f_3 = -\sigma
\]  \hspace{1cm} (38)

The initial conditions for this set are

\[ f_0(0) = 1 \]

\[ f_1(0) = -1 \]

\[ f_2(0) = 1 \]

\[ f_3(0) = -1 \]  \hspace{1cm} (39)

For this work, Equations 38 and 39 were scaled for analog computer solution by making the following substitutions

\[ X_1 = 10 f_1 \text{ volts} \]

\[ S = 10 \sigma \text{ volts} \]

\[ T = 0 \text{ seconds} \]  \hspace{1cm} (40)
These substitutions yielded the following set of scaled equations for analog computer simulation

\[
\frac{dX_0}{d\tau} + X_0 = 10 \left( \frac{S}{X_2} \right) \\
\frac{dX_1}{d\tau} + X_1 = -X_0 \frac{S}{X_2} \\
\frac{dX_2}{d\tau} + X_2 = -X_1 \frac{S}{X_2} \\
\frac{dX_3}{d\tau} + X_3 = -S
\]  

(41)

with the initial conditions

\[
X_0(0) = 10 \text{ volts} \\
X_1(0) = -10 \text{ volts} \\
X_2(0) = 10 \text{ volts} \\
X_3(0) = -10 \text{ volts}
\]  

(42)

The initial steady state value of \( \sigma \) was unity so the initial value of \( S \) was 10 volts. By using these scaling factors, it was possible to upset the simulated dimensionless input solute concentration, \( S \), by a factor of five for kinetic models with \( \alpha \) as high as 6. The computer circuit diagram for this simulation is shown in Appendix A.
A laboratory sized continuous, mixed suspension crystallizer was designed and constructed to test the theoretical crystallization equations found in the literature (1, 2, 3, 4, 5, 6). The crystallizer was a 5 liter Plexiglas cylindrical vessel equipped with a propeller type agitator and a draft tube. Figure 2 shows the critical dimensions of the crystallizer assembly. The draft tube was supported on three legs which also acted as baffles. The tube was suspended at a height so that the area through which the suspension circulated was equal at all points, that is, the area inside the tube was equal to the annular area outside the tube and equal to the cylindrical areas below and above the tube. The vessel was equipped with a drain hole in the bottom. The agitator pushed the suspension down the center of the draft tube and up the outside. The two feed streams were added to the suspension at its surface from the external feed system. Figure 5 shows the crystallizer in operation.

The external flow system for the two feed streams is shown in Figure 3. It consisted of storage tanks, constant head tanks and rotameters. The alum storage tanks were 55 gallon stainless steel drums and the ethanol storage tank was a 5 gallon polyethylene bottle. All of the feed lines
Figure 2. Crystallization vessel
Figure 3. Flow diagram of crystallization system
Figure 4. Crystallization system in operation

Figure 5. Crystallizer in operation
were 3/8 inch stainless steel tubing and contained filters to remove nonsoluble contaminants. Calibrated rotameters were used to control the flows of each stream.

Two completely isolated feed systems for alum solution were used. A two way valve was used to select the stream going into the crystallizer. The alum solutions were pumped to the constant head tanks using Eastern E-1 centrifugal pumps. Figure 4 shows the entire apparatus in operation.

Initially it was planned to remove the mixed product as an overflow out the side of the vessel. This did not prove satisfactory because the overflow had a tendency to classify the product. Revisions were made and a continuous removal of the mixed product was attempted by using a suction removal system. This involved placing a suction tube at a level inside the crystallizer necessary to maintain the desired suspension volume. The product was trapped in a bottle after removal from the crystallizer.

Even though this method of removal provided a very high suspension velocity in the removal tube, it did not prove satisfactory. Because the removal tube was placed at the liquid surface, there was a classifying effect. Crystals larger than a critical size did not circulate close enough to the suspension surface to be sucked out the removal tube. If a crystal was not removed prior to growing through this critical size it was never removed. As a result, there was
a build up of large crystals during operation.

To correct for the classified product removal, an automatic level controller was used. This controller operated a semi-positive displacement pump (Jabsco) which pumped suspension from below the liquid surface. The controller consisted of a float to which was fastened a flexible conducting wire. When the level rose high enough, a contact was made with a stationary plate. This contact closed an electrical circuit which turned on the pump. The electrical circuit consisted of a set of delay relays enabling the selection of the pump operating time after contact of the float switch. The circuit for the float control switch was 6 volt D.C. The entire circuit for the controller is shown in Figure 6. The circuit was so constructed that there would be no "chatter" from the switch.

Samples of the suspension in the crystallizer were removed through a second suction tube placed midway in the annular channel. The samples were trapped in a calibrated 1000 ml Erlenmeyer flask. The samples were screened by suction through a 300 mesh screen.

Screen analyses were made using calibrated U. S. Standard 3 inch screens. The screens used were the following U. S. Standard mesh sizes: 16, 18, 20, 25, 35, 40, 50, 70, 100, 140 and 200. Because of the symmetry of the crystals, reproducible screen analyses were easily achieved. Several methods of
**Figure 6. Circuit diagram for level controller**

<table>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>S₁</td>
<td>SPST Toggle switch</td>
</tr>
<tr>
<td>S₂</td>
<td>SPST Toggle switch</td>
</tr>
<tr>
<td>S₃</td>
<td>SPST Toggle switch</td>
</tr>
<tr>
<td>S₄</td>
<td>SPST Toggle switch</td>
</tr>
<tr>
<td>S₅</td>
<td>Three position rotary switch</td>
</tr>
<tr>
<td>F₁</td>
<td>10 amp fuse</td>
</tr>
<tr>
<td>F₂</td>
<td>10 amp fuse</td>
</tr>
<tr>
<td>R₁</td>
<td>Normally closed 115 volt AC 2 second thermal delay relay</td>
</tr>
<tr>
<td>R₂</td>
<td>Normally closed 115 volt AC 5 second thermal delay relay</td>
</tr>
<tr>
<td>R₃</td>
<td>Normally closed 115 volt AC 10 second thermal delay relay</td>
</tr>
<tr>
<td>R₄</td>
<td>Normally opened 115 volt AC 3PDT relay</td>
</tr>
<tr>
<td>R₅</td>
<td>Normally opened 6 volt DC SPST relay</td>
</tr>
<tr>
<td>L₁</td>
<td>115 volt AC post light</td>
</tr>
<tr>
<td>L₂</td>
<td>115 volt AC post light</td>
</tr>
</tbody>
</table>
shaking were tried and the results were reproducible. Therefore, a simple mechanical device was used. If the crystals had been irregular, a more standard procedure would have been necessary.

Materials

The alum used for this work was aluminum ammonium sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 24\text{H}_2\text{O}$. It was obtained from the General Chemical Division, Allied Chemical Corporation. It was sold under the name of "Ammonium Alum, Code 125, Rice Statuary" in 100 pound paper bags. This material had the typical alum octahedral crystal habit for all sized crystals as can be seen in Figure 7. The other components were technical grade ethyl alcohol and distilled water.

Procedure

After preparation of the desired solutions, the alum feed pump was started to establish the constant head for the alum feed stream. The crystallizer was charged with the proper ratio of alum solution to alcohol and the agitator and liquid level controller were turned on. The two feed streams were started and set at their proper flow rates. This completed the start up routine. The flows were then maintained or changed depending on the type of run which was to be made. For the production rate step change runs, the
Figure 7. Photomicrograph of ammonium alum crystals

Alum crystals, +70 - 50 mesh*

Alum crystals, +40 - 35 mesh*

Alum crystals, +25 - 20 mesh*

*U. S. Standard mesh
two incoming flows were simply changed at the proper time. For the concentration step change runs, the two way valve was changed at the proper time.

Samples of the crystal suspension were taken through the submerged sampling tube. They were removed by vacuum into a calibrated 1000 ml Erlenmeyer flask. The sample size varied from 500 to 700 ml depending on the density of the suspension at the time of sampling. The volume of sample was recorded.

The suspension was separated by suction filtering through a 300 mesh screen in a Buchner funnel. Twenty ml samples of the mother liquor were then placed in a tared one ounce sample bottle and evaporated to dryness. The crystals were washed several times with acetone taking care that as much liquor as possible was removed before the introduction of acetone. The crystals were then dried by continuing the suction. This step produced extreme problems on days when the relative humidity was high. The evaporating acetone cooled the crystals so that moisture from the air condensed on them. When the acetone was completely evaporated the crystals would return to room temperature and the crystals would be left in a very badly agglomerated condition. Because of non-cooperating weather conditions, a number of good runs were ruined by this annoying feature in the sampling technique.

When the crystals were dry, they were placed in a nest of calibrated U. S. Standard 3 inch screens and subjected to
ten minutes of shaking. Each size fraction was separated and weighed in one ounce sample bottles.

Samples were taken every two residence times during normal operation. Immediately after a step change in operation however, they were taken more frequently to obtain a close measure of the transient results.
RESULTS

Treatment of Data

The experimental data for this work was obtained in the form of screen analyses. The crystal distributions obtained had a size range from 0.081 to 1.1 millimeters. The screen analyses divided the distributions into twelve size fractions. The increments along the size axis were not equal due to the manner in which the screens are made.

In order to represent the size distribution in terms of the population density variable, the distribution was converted from the weight fraction form obtained from the screen analyses in the following manner.

1. The arithmetic average diameter of each size fraction was determined.

2. The total weight of crystals of a given size fraction was then divided by the crystal density, the cube of the average diameter and a volumetric shape factor. This gave the number of crystals in the size fraction.

3. The number of crystals was then divided by the width of the size range of the crystals in the fraction. This gave the population density of crystals in the size fraction.

The theoretical calculation and experimental verification of the shape factor may be found in Appendix B.
The entire procedure for calculating the population density may be summarized in the following equation:

\[ n = \frac{G}{v} V \frac{1}{\rho} \frac{1}{(K_v L^3) \Delta L} \]  

(43)

where \( G \) was the mass of the size fraction, \( v \) the suspension sample volume, \( V \) the total volume of the crystallizer, \( \rho \) the density of the crystal material, \( K_v \) volumetric shape factor, \( L \) the average diameter of the size fraction and \( \Delta L \) the width of the size range in the fraction.

The calculation of the total numbers, length, area and mass of the suspension involved the use of the cumulative weight per cent plot. The experimental data was plotted as cumulative weight per cent versus crystal size. This curve for a steady state condition had the typical sigmoid shape. The abscissa of this curve was broken into twenty equal segments of 0.05 mm width. This covered the entire size range of the data. The incremental value of the cumulative weight per cent was read for each segment of the abscissa. The population density for each segment was then calculated by

\[ n = D \frac{v}{\rho} \frac{\Delta wt \%}{K_v L^3 \Delta L} \]  

(44)

where \( D \) was suspension density, \( \Delta wt \% \) the incremental weight per cent corresponding to \( \Delta L \), and \( L \) the average crystal size in \( \Delta L \). This method of calculation of population density was
used rather than Equation 43 because it tended to "smooth" any errors introduced by the unequal size widths from the screen analysis. The total number of crystals was obtained by numerically integrating the above data to give

\[ N = J_0 = \int n \, dL \quad (45) \]

The above population density values were also multiplied in turn by \( L \), \( L^2 \) and \( L^3 \). The total length, area and mass were obtained by numerically integrating these products to give

\[ l = J_1 = \int nL \, dL \quad (46) \]
\[ A = J_2 = K_a \int nL^2 \, dL \quad (47) \]
\[ M = J_3 = \rho K_v \int nL^3 \, dL \quad (48) \]

respectively.

The calculation of the transformed functions \( f_1 \) was made using the \( J_1 \) integrals in Equations 45 through 48. The initial or steady state \( (J_1)_0 \) were calculated. These are the values prior to the step change disturbance introduced into the system. The normalized moments of the size distribution as defined in Equation 18 were obtained as follows
The transient values of the $f_i$'s were obtained by rearranging Equation 21 as follows

$$I_i = \frac{J_i}{(J_i)_0}$$ (49)

$$f_i = \frac{I_i}{(-l)^i i!}$$ (50)

Steady State Results

As is indicated by Equation 1, the steady state plot of log of population density versus crystal size should give a straight line with a slope proportional to $-\frac{1}{r_o T_o}$ and an intercept of log of nuclei population density. Figures 8 and 9 show this steady state plot for two different runs with residence times of 45 and 15 min. respectively. The alum solution concentration was 10 gm/100 ml water and the ratio of alum solution to ethanol was 5/1 for both runs. The figures show that there was good agreement with theory. By using the respective $T_o$ for each line and the Naperian log to $\log_{10}$ conversion factor, the growth rates were calculated to be 0.107 mm/hr for the 45 minute residence time and 0.272 mm/hr for the 15 minute residence time. The intercepts yielded nuclei population densities of $8.7 \times 10^8$ and $1.95 \times 10^9$ numbers/mm for the 45 and 15 minute residence times respectively.
Figure 8. Plot of log steady state population density versus crystal diameter

45 minute residence time
5/1 ratio of alum solution to ethanol
10 gm/100 ml water alum solution concentration
LOG POPULATION DENSITY

CRYSTAL DIAMETER, MM

0.0 0.2 0.4 0.6 0.8 1.0

5 6 7 8 9 10
Figure 9. Plot of log steady state population density versus crystal diameter

15 minute residence time
5/1 ratio of alum solution to ethanol
10 gm/100 ml water alum solution concentration
Equation 7 provided a method whereby the kinetic relationship between nucleation and growth could be obtained. This equation shows that a steady state plot of log nuclei population density versus log growth rate should yield a straight line whose slope gives the kinetic order of the system under study. This plot for the alum-ethanol-water salting out system is given in Figure 10. Data for this plot were obtained from several steady state runs with different residence times. All of the points were from runs with an alum solution inlet concentration of 10 gm/100 ml water, and with an alum solution to ethanol ratio of 5/1. The data covered three different residence times. They were 15, 30 and 45 minutes. As can be seen, there was some scatter in the data. The correlation of the data has a slope of unity. Therefore, $\beta$, in Equation 7 is equal to 1. Using the intercept and slope from Figure 10, Equation 7 becomes

$$n_0^0 = 6.6 \times 10^9 r_0$$  \hspace{1cm} (51-a)$$

For residence times of 15, 30 and 45 minutes, sample growth rates were 0.272, 0.156 and 0.124 mm/hr respectively. The respective nucleation rates obtained by Equation 6 were $4.56 \times 10^8$, $1.87 \times 10^8$ and $8.23 \times 10^7$ nuclei/hr.

The slope of Figure 10 indicates that the exponent, $\alpha$, in Equation 5 is 2 and the constant is the same as in Equation 51-a.
Figure 10. Plot of log steady state nuclei population density versus log steady state growth rate
\[
\frac{dN^0}{dt} = 6.6 \times 10^9 r^2 \quad (51-b)
\]

Using this equation, nucleation rates may be calculated when growth rates are known. For example, for a growth rate of 0.20 mm/hr, the nucleation rate is calculated to be \(2.64 \times 10^8\) nuclei/hr or \(4.8 \times 10^4\) nuclei/hr ml.

Production Rate Upsets

The experimental procedure for determination of responses to changes in production rate was first to run at one production rate for twenty residence times to obtain steady state. Then a step change in feed rate was made to provide a different residence time. Start up was accomplished by first filling the crystallizer with the proper proportion of alum solution and ethanol and then continuing to feed at the required flow rates.

Figure 11 shows a plot of log of population density versus dimensionless time. The parameters for this plot are the mean crystal diameters for various size fractions. The data for this plot were taken from a run with an alum solution concentration of 10 gm/100 ml water and a 5/1 ratio of alum solution to ethanol. A 45 minute residence time was used to attain steady state. Then the production rate was increased such that the residence time became 15 minutes. The start up
Figure 11. Plot of log population density versus dimensionless time for start up and production rate change

- 5/1 ratio of alum solution to ethanol
- 10 gm/100 ml water alum solution concentration
- 45 minute initial residence time
- 15 minute final residence time
- $T_0 = 45$ minutes
transient provides a vivid picture of the initial shower of crystals induced by the sudden supersaturation caused by the mixing of the alum solution and ethanol. This shower "grew" its way through the size fraction and was observed as maximum points in subsequent sizes.

The minimum in the curve may be explained by considering what the initial shower of nuclei did to the system. This shower was caused by a sudden increase in supersaturation. The shower propagated as a wave like disturbance. As this wave disturbance traveled along the size axis, the total area changed. This change in area altered the degree of supersaturation causing reductions in the growth and nucleation rates. The disturbances dampened out very early for the small size fractions. A period of twenty residence times was required before these start up disturbances dampened out and a steady state distribution was reached.

After a steady state condition was reached, the residence time change was made. Figure 11 shows that this step change introduced a definite disturbance to the size distribution. Here again the disturbance first occurred in the small crystals and "grew" its way through the size fraction. A new final steady state condition was reached approximately 4.5 hours after the change. This corresponds to 18, 15 minute residence times or six dimensionless residence times. Therefore a period of 18 to 20 residence
times was required to attain steady state after an upset. The new steady state condition had a different growth rate. As can be seen, however, the distribution of the portion of the size fraction plotted was not much different after the step change.

Randolph (3) solved Equations 12 through 15 on an IBM 704 computer for a fourth order kinetic model. His plot was qualitatively comparable to Figure 11.

Figure 11 has a log scale on the ordinate. Because of the compression effect of the log scale it is difficult to grasp the extreme amplitude of the disturbances. Figure 12 is a rectilinear plot of the portion of Figure 11 after the step change. Even though it was necessary to use a varying ordinate scale to present this plot, it provides a better realization of the large amplitudes observed. This rectilinear plot also brings out the fact that the measurements of the small crystals were not very reproducible. This is born out by the apparent erratic steady state condition which was achieved in the two smaller size fractions. The comparative sizes of the wave amplitudes is also apparent from Figure 12. This shows that the small size fractions made a much larger contribution to the particle dynamics than did the large crystals.

Another way of comparing the experimental and theoretical dynamics is with the moments of the size
Figure 12. Plot of population density versus dimensionless time for production rate change

5/1 ratio of alum solution to ethanol
10 gm/100 ml water alum solution concentration
45 minute initial residence time
15 minute final residence time
distribution. The moment related dependent variables, \( f_i \), in the transformed equations (Equation 25) could, in theory, be calculated from the experimental data by using Equations 44 through 50. In practice, however, this did not prove to be a satisfactory method. The reason that this method alone did not prove satisfactory was the problem of measuring the distribution of the small crystals. The experimental data for the small end of the distribution was in itself rather inconsistent. These errors were magnified when Equation 44 was used to calculate the population density because of the division by the cube of the crystal diameter. Because of the large contribution made to the total numbers, length and area by the small crystals, the calculation of the dynamic values of the \( f_i \)'s was inconclusive.

A method was worked out whereby the data could be put in a usable form. This method was based on an extrapolation to \( L = 0 \) of the plot of log population density versus crystal diameter. This extrapolation was assumed to be valid because of the reproducible straight line obtained in the region where the distribution could be measured accurately. The values of \( r_0 \) and \( n_0^0 \) obtained were used to calculate the theoretical total steady state crystal numbers, length, area and mass. The equations used to do this were obtained by combining Equation 1 with Equations 45 through 48.
The values of the \( J_1 \)'s thus calculated were assumed to be correct for their respective steady state conditions.

The cumulative weight per cent plots were not extrapolated to estimate the small end of the size distribution because the screen analyses did not provide consistent data for a small enough crystal size. The cumulative plots were of a sigmoidal shape and hence could not be extrapolated as confidently as the straight \( \ln n \) versus \( L \) plots.

The calculation of the \( J_1 \)'s during the transient period just after an upset required an additional assumption. The \( \ln n \) versus \( L \) plots did not yield a straight line during transient conditions. Therefore, they could not be used to calculate the moments in Equations 52 through 55 during unsteady state operation. To overcome this, it was assumed that the transient values of the \( J_1 \)'s were oscillations about their final steady state values. In other words, this

\[
N_o = (J_0)_o = n_o^0 (r_o T_o) \tag{52}
\]
\[
l_o = (J_1)_o = n_o^0 (r_o T_o)^2 \tag{53}
\]
\[
A_o = (J_2)_o = 2! K_a n_o^0 (r_o T_o)^3 \tag{54}
\]
\[
M_o = (J_3)_o = 3! \rho K_v n_o^0 (r_o T_o)^4 \tag{55}
\]
assumes that the "rise time" of the moments was very short. It was felt that this assumption was valid because of the rapid attainment of steady state of the small crystals. This can be seen in Figure 11. This assumption made the final steady state values correct but the transient values were not completely correct.

The calculation the \( J_i \)'s after a step change incorporating the above assumptions is shown below

\[
J_i = (J_i)_{\text{exp}} \left[ \frac{(J_i)_{\text{theo}}}{(J_i)_{\text{exp}}} \right] T_F
\]

(56)

where the subscript exp denotes experimental value obtained from Equations 45 through 48, theo denotes theoretical values obtained from Equations 52 through 55 and the \( T_F \) denotes evaluation at the final steady state conditions. The values of \( f_i \)'s were then obtained by using Equations 56, 49, and 50.

As a result of these assumptions, it was expected that the calculated transient would rise more rapidly than it should and the initial period would be in error. As time goes on after the step change, the assumption of reaching the final symmetric value immediately becomes in less error. Therefore, this method did provide a suitable procedure for determining the length of the transient period.

The analog computer solution to Equations 25 (second order model) along with the \( f_i \)'s calculated by the above
method are plotted on Figures 13 and 14. Figure 13 shows $f_0$ and $f_2$ and Figure 14 shows $f_1$ and $f_3$. The plots are for the transient period after the residence time was decreased by a factor of 3 ($a = 3$). The data are from a run where the initial and final residence times were 45 minutes and 15 minutes respectively. The input alum concentration was 10 gm/100 ml water and the alum solution to ethanol ratio was 5/1.

As was expected the initial experimental rise time was much shorter than the computer initial rise time. These plots show, however, that there were indeed transients in the experimental data and that they were similar to those found in the theoretical computer solution.

The final values of the predicted $f_1$'s were different from the experimental values because, although the theoretical change in $f_3$ was zero, there was a slight difference in mass as calculated from the slopes and intercepts of Figures 8 and 9. It was found experimentally that the mass ($f_3$) was constant during the experimental step change. It is felt that the difference was quite small considering the extremely large numbers involved in measuring the experimental distribution. It should be noted that the length of the transient period of the experimental $f_1$'s is very close to that of the computer solution. This shows that the errors introduced by the assumption made when calculating the $f_1$'s do become less as time goes on.
Figure 13. Plot of experimental and second order theoretical change in dimensionless numbers \( f_0 \) and area \( f_2 \) versus dimensionless time as a result of a threefold step increase in production rate

\[
T_0 = 45 \text{ min} \\
T_{\text{final}} = 15 \text{ min}
\]
Figure 14. Plot of experimental and second order theoretical change in dimensionless length (-f₁) and mass (-f₃) versus dimensionless time as a result of a threefold step increase in production rate.

\[ T_o = 45 \text{ min} \]
\[ T_{\text{final}} = 15 \text{ min} \]
Figure 15. Plot of experimental and third order theoretical change in dimensionless numbers ($f_0$) and length ($-f_1$) versus dimensionless time as a result of a threefold step increase in production rate.
Figure 15 shows a similar plot of $f_0$ and $f_1$ along with the computer solution to a cubic model. It can be seen that there was little similarity between this cubic model and the data.

The conclusion that can be drawn from these dynamic plots is that the second order model was the best one. But further than that, this provides another method of estimating the kinetic order of the crystallization system under study. The steady state technique outlined by Figure 10 provides one method but this method by itself does not have the strength that the combined dynamic and steady state methods have.

Inlet Concentration Upsets

Steady state data were taken for several different inlet alum concentrations, alum to ethanol ratios, residence times and combinations thereof. The nuclei population density and growth rates were determined for each of these following the method used on Figures 8 and 9. Figure 16 shows a log log plot of $n_0$ versus $r_0$ for these data. This plot also includes the points shown in Figure 10. It can be seen that for a constant residence time the points do not follow the slope of unity. In fact if a line were drawn through the points of constant residence time it would be nearly vertical. One explanation of this may be that the concentrations used in this work were outside the concentration range where the proposed theory applies.
Figure 16. Plot of log steady state nuclei population density log steady state growth rate

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Residence time, min</th>
<th>Alum concentration gm/100 ml water</th>
<th>Alum solution/ethanol ratio</th>
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<tbody>
<tr>
<td>•</td>
<td>15</td>
<td>10</td>
<td>4/1</td>
</tr>
<tr>
<td>□</td>
<td>15</td>
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</tr>
<tr>
<td>□</td>
<td>45</td>
<td>10</td>
<td>4/1</td>
</tr>
</tbody>
</table>
An experimental run was made in which the inlet alum concentration was step changed. A residence time of 45 minutes and an alum solution to ethanol volume ratio of 5/1 was used. The run consisted of starting up and running for twenty residence times with an inlet alum concentration of 6 gm/100 ml H₂O. The inlet concentration was then changed to 10 gm/100 ml H₂O. The residence time and feed ratio were held constant during the entire run. The total length of the run was forty residence times. Figure 17 shows a plot of log population density versus dimensionless time for the period starting just prior to the step change and continuing to the end of the run. When the step change was made, the sudden increase in supersaturation caused a shower of nuclei. This shower caused the expected wave disturbance in the population density. This wave "grew" its way through the size fraction. The fact that the final alum concentration was higher than the initial caused the final steady state values to be higher.

An interesting transient was observed during this build up in suspension density. The 0.098 mm size fraction shows an obvious dip during the build up period. This wave can be easily explained. The initial shower increased the area so much that it reduced the supersaturation considerably. This reduction in turn decreased the nucleation. As time went on, a portion of these nuclei were removed from the crystallizer through the exit and the remainder grew to a larger size.
Figure 17. Plot of log population density versus dimensionless time for inlet alum concentration change

45 minute residence time
4/1 ratio of alum solution to ethanol
6 gm/100 ml water initial alum concentration
10 gm/100 ml water final alum concentration
The larger size had a smaller specific area (mm²/gm). Thus the initial increase in area was depleted and the supersaturation increased again. This in turn caused more nucleation. This cycling was dampened out by the time the new suspension density was attained.

The final distribution after the step change was nearly the same as the initial distribution but there was a higher suspension density. This means that the final nuclei population density was higher than the initial but that growth rate remained essentially unchanged. This accounts for the fact that the points on Figure 16 for constant residence time were almost in a vertical configuration.

The data from the run described in Figure 17 were used to calculate the experimental values of the transformed dependent variables of Equations 38 and 39. Equations 38 and 39 (second order model) were solved on the analog computer for a disturbance in inlet alum concentration comparable to the experimental run (i.e. $\sigma = 3.3$). Figures 18 and 19 show plots of both the experimental and computer results for the period after the step change. All of the experimental values seem to approach nearly the same final values whereas the computer solutions do not.

Up to sixth order models were solved on the analog computer. It was found that the higher the order, the closer the final values were to each other. It was also found that
Figure 18. Dimensionless plot of experimental and second order theoretical change in total numbers ($f_0$) and area ($f_2$) versus time as a result of a factor of 3.3 step increase in inlet alum concentration.
Figure 19. Dimensionless plot of experimental and second order theoretical change in total length $(-f_1)$ and mass $(-f_3)$ versus time as a result of a factor of 3.3 step increase in inlet alum concentration.
the higher the order the more dynamic was the transient period following the upset.

These dynamic results verify what was predicted from the steady state results on Figure 16. That is, that the order of the model for a concentration upset was very high and a method was not available for accurately determining it for the concentration range used in this work.

Influence of Small Crystals

The screen analysis was used to determine the size distribution needed for this work. The dependent variables involved in the theoretical work are total quantities. That is, the total number, length, area and mass of the distribution. It turned out that the contribution made to the total number by the very small crystals was several orders of magnitude greater than the contribution of the larger crystals. A typical distribution had \(1.63 \times 10^8\) crystals with an average diameter of 0.05 mm and \(6.25 \times 10^5\) crystals with an average diameter of 0.50 mm. The total number of crystals for this sample was \(2.24 \times 10^8\). As can be seen, the small size dominates the larger size by almost three orders of magnitude. Yet for this same sample, the mass of crystals with the 0.05 mm average diameter was only three times that of the 0.50 mm crystals. The technique of the screen analysis is least accurate for measuring crystals of
the smaller diameter. Consequently a better method of size distribution measurement was badly needed. Such a method was not available for this work.

The numbers given above for a typical distribution points out a very important problem in the study of crystallization. Almost one thousand crystals with a diameter of 0.05 mm were formed to produce just one crystal with a diameter of 0.50 mm.

Crystallization is a mass transport process, so the area for deposition is the critical variable in a distribution. The specific area (mm²/gm) of the small crystals is very high compared to that of the large crystals. Consequently, a relatively small disturbance in the rate of nucleation in a crystallizer will cause a large disturbance in the area for deposition. Figure 12 shows the relative magnitude of these disturbances as a result of a step change in production rate.

Because of this, the method of screen analysis for measuring crystal size distributions was not very adequate. Recent advances have been made in the technology of measuring small particle distributions. Commercial equipment is now available to do this. Every effort should be made to utilize these devices. The significance of this and future crystallization research rests in the ability to accurately measure the distribution of small crystals.
ACCOMPLISHMENTS AND CONCLUSIONS

1. A small pilot plant scale salting out crystallizer was designed and constructed for a simple laboratory test of the current crystallization theory.

2. The salting out of alum with ethanol from an aqueous alum solution was found to be a suitable system for testing the theory relating nucleation and growth.

3. Start up data as well as unsteady state data resulting from process upsets in a continuous mixed suspension mixed product removal crystallizer were obtained for the first time under clearly defined and controlled conditions.

4. Steady state data were obtained for operation with various residence times and feed conditions. These data were in agreement with the theoretical steady state exponential relationships found by previous investigators and were used to determine relationships between nucleation rates and growth rates. This relationship for the alum-ethanol-water system was found to be:

\[
\frac{dN^0}{dt} = Kr^2
\]

5. The data obtained for inlet concentration disturbances were not conclusive and the theoretical model probably was not applicable for the wide range of concentrations used in these tests.
6. Using the kinetic relationship obtained from the steady state data and the dynamic equations developed by previous investigators the dynamic behavior of the size distribution resulting from a step change disturbance in production rate was predicted. These predictions were in qualitative agreement with measured dynamic response.

7. It is advisable to use both dynamic and steady state data to determine the kinetic relationship between nucleation rate and growth rate because of the low sensitivity of the steady state analysis technique to differences in kinetic order.

8. Extremely large amplitudes of the population density were observed during the transient period following a disturbance to the system. These amplitudes covered nearly half an order of magnitude even for the relatively low order kinetics for this system. This behavior is in agreement with previous conclusions drawn from qualitative observations concerning the causes of the instability of crystallizers.

9. It was shown quantitatively that for a second order system the crystal distribution had nearly three orders of magnitude more crystals of size 0.05 mm diameter than of size 0.50 mm diameter. Thus, more than a thousand nuclei are formed to obtain just one crystal of 35 mesh size. This further demonstrates the importance of the kinetic relationship between nucleation and growth in crystallization technology.
10. It was found that screen analysis was not a very satisfactory method to determine the size distribution for the smaller end of the size range. It was the least accurate in the small range where the vast majority of the crystals were found.
RECOMMENDATIONS

1. Another salting out system should be found to use the present equipment to check the theoretical solutions to the numbers balance equation.

2. Experimental work should be done using this or other systems to investigate more fully the results from inlet concentration disturbance.

3. A pilot plant crystallizer should be built which is more analogous to a commercial cooling or evaporative crystallizer.

4. Theoretical research should be carried out investigating some of the assumptions made in this work such as the validity of McCabe's $\Delta L$ law.

5. Future experimental work should be carried out under controlled conditions where the humidity would not affect the results.

6. A better method of analyzing the size distribution should be found. Equipment to do this is commercially available. Further work in this area should involve the use of equipment to count crystals in the near micron range.
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$A$</td>
<td>computer scaled dimensionless ratio of residence times, volts</td>
</tr>
<tr>
<td>$A$</td>
<td>area of an individual octahedron, $\text{mm}^2$</td>
</tr>
<tr>
<td>$A$</td>
<td>total crystal area, $\text{mm}^3$</td>
</tr>
<tr>
<td>$A_0$</td>
<td>steady state total crystal area, $\text{mm}^3$</td>
</tr>
<tr>
<td>$a$</td>
<td>area of a pyramid</td>
</tr>
<tr>
<td>$a$</td>
<td>dimensionless ratio of residence time, $T/T_0$</td>
</tr>
<tr>
<td>$C$</td>
<td>concentration of dissolved solute, $\text{gm/mm}^3$</td>
</tr>
<tr>
<td>$C_i$</td>
<td>inlet concentration of dissolved solute, $\text{gm/mm}^3$</td>
</tr>
<tr>
<td>$C_o$</td>
<td>outlet concentration of dissolved solute, $\text{gm/mm}^3$</td>
</tr>
<tr>
<td>$\Delta C$</td>
<td>inlet minus outlet concentration of dissolved solute ($C_i - C_o$), $\text{gm/mm}^3$</td>
</tr>
<tr>
<td>$\Delta C_0$</td>
<td>steady state reference $\Delta C$, $\text{gm/mm}^3$</td>
</tr>
<tr>
<td>$c(\theta)$</td>
<td>dimensionless perturbation imposed as coefficient of nucleation function</td>
</tr>
<tr>
<td>$D$</td>
<td>suspension density, $\text{gm crystal/mm}^3$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>input average suspension density, $\text{gm crystal/mm}^3$</td>
</tr>
<tr>
<td>$D_o$</td>
<td>output average suspension density, $\text{gm crystal/mm}^3$</td>
</tr>
<tr>
<td>$f_i(\theta), f_i$</td>
<td>arbitrary time function in series expansion which is proportional to $i$'th moment of size distribution</td>
</tr>
<tr>
<td>$G$</td>
<td>mass of crystals in a given size fraction, $\text{gm}$</td>
</tr>
<tr>
<td>$g(\tilde{\theta})$</td>
<td>functional relationship between nucleation rate and crystal growth rate</td>
</tr>
<tr>
<td>$H$</td>
<td>altitude of pyramid, $\text{mm}$</td>
</tr>
<tr>
<td>$h$</td>
<td>slant height of pyramid, $\text{mm}$</td>
</tr>
<tr>
<td>$I_i(\theta), I_i$</td>
<td>$i$'th moment of dimensionless size distribution</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$J_i$</td>
<td>$i$'th moment of size distribution</td>
</tr>
<tr>
<td>$K_a$</td>
<td>area shape factor</td>
</tr>
<tr>
<td>$K_V$</td>
<td>volumetric shape factor</td>
</tr>
<tr>
<td>$L$</td>
<td>crystal length, mm, measured along a characteristic axis</td>
</tr>
<tr>
<td>$\Delta L$</td>
<td>width of a size range, mm</td>
</tr>
<tr>
<td>$l$</td>
<td>total crystal length, mm</td>
</tr>
<tr>
<td>$l_o$</td>
<td>steady state total crystal length, mm</td>
</tr>
<tr>
<td>$M$</td>
<td>total mass of crystals, gm</td>
</tr>
<tr>
<td>$M_o$</td>
<td>steady state total crystal mass, gm</td>
</tr>
<tr>
<td>$N$</td>
<td>total number of crystals, numbers</td>
</tr>
<tr>
<td>$N_o$</td>
<td>steady state total number of crystals, numbers</td>
</tr>
<tr>
<td>$N^o$</td>
<td>total number of nuclei, numbers</td>
</tr>
<tr>
<td>$N_o^o$</td>
<td>steady state total number of nuclei</td>
</tr>
<tr>
<td>$n$</td>
<td>total crystal population density, numbers/mm</td>
</tr>
<tr>
<td>$n_o$</td>
<td>steady state total crystal population density, numbers/mm</td>
</tr>
<tr>
<td>$n^o$</td>
<td>total nuclei population density, numbers/mm</td>
</tr>
<tr>
<td>$n_o^o$</td>
<td>steady state total nuclei population density, numbers/mm</td>
</tr>
<tr>
<td>$\bar{n}$</td>
<td>point crystal population density, number/mm/mm³</td>
</tr>
<tr>
<td>$\bar{n}_i$</td>
<td>suspension input point population density, number/mm/mm³</td>
</tr>
<tr>
<td>$\bar{n}_o$</td>
<td>suspension output point population density, number/mm/mm³</td>
</tr>
<tr>
<td>$\bar{n}_s$</td>
<td>point crystal population density at suspension surface, number/mm/mm³</td>
</tr>
</tbody>
</table>
$Q$  total suspension flow rate, mm$^3$/hr
$Q_i$  suspension input rate, mm$^3$/hr
$Q_o$  suspension output rate, mm$^3$/hr
$R_i$  suspension input rate, gm/hr
$R_o$  suspension output rate, gm/hr
$r$  crystal growth rate along characteristic crystal axis, mm/hr
$r_o$  steady state growth rate, mm/hr
$S$  computer scaled dimensionless ratio of concentration difference, volts
$s$  supersaturation in solution, gm/mm$^3$
$s$  Laplace transform variable
$T$  residence time, hr
$T_o$  steady state reference residence time, hr
$t$  time, hr
$V$  volume of octahedron, mm$^3$
$V$  total suspension volume, mm$^3$
$v$  volume of pyramid, mm$^3$
$v$  suspension sample volume, mm$^3$
$X_i$  computer scaled $f_i$, volts
$x$  dimensionless crystal size, $L/r_o T_o$
$y$  dimensionless population density, n/n$_o$
$\bar{y}$  Laplace transformed dimensionless population density
$\Theta$  dimensionless time, t/T$_o$
$\rho$  crystal density, gm/mm$^3$
σ  dimensionless ratio of concentration difference, \( \Delta C/\Delta C_0 \)

\( \tau \)  computer scaled dimensionless time, seconds

\( \phi \)  dimensionless crystal growth rate, \( r/r_0 \)
LITERATURE CITED


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Figure 20. Schematic diagram showing analog circuitry used in solution of second order production rate upset size distribution equation.
Figure 21. Schematic diagram showing analog circuitry used in solution of second order concentration upset size distribution equation.
Volumetric Shape Factor

The determination of the volumetric shape factor for ammonium alum crystals was based on the fact that the crystals were regular octahedrons. That is, two regular four sided pyramids placed base to base. The volume of such a geometric solid was twice the volume of the pyramids. The regularity of the solid meant that all of the plane angles were 60°.

The formula for the volume of a pyramid is

\[ v = \frac{1}{3} \text{(area of base)} \text{(altitude)} \]  \hspace{1cm} (57)

It was assumed that the length of a side of the base was the characteristic dimension of the pyramid.

The determination of the altitude involved finding the slant height,

\[ h = L \sin 60° = \frac{\sqrt{3}}{2} L \] \hspace{1cm} (58)

By using the Pythagorean theorem and Equation 58, the altitude became

\[ H = \frac{L}{\sqrt{2}} \] \hspace{1cm} (59)

By combining Equations 57 through 59, the volume of the pyramid became

\[ v = \frac{L^3}{3 \sqrt{2}} \] \hspace{1cm} (60)
The volume of the octahedron thus became

\[ V = \frac{\sqrt{2}}{3} L^3 \]  (61)

Therefore, the theoretical volumetric shape factor was \( \sqrt{2}/3 \) or 0.472.

A check of this shape factor was made by making a count of several weighed samples of crystals. A comparison of the measured versus calculated mass of a crystal showed an average ratio of calculated mass to measured mass of 0.986. The closeness of this ratio to unity indicated that the theoretical volumetric shape factor was very good.

Area Shape Factor

The area shape factor was also based on the two pyramid configuration. The lateral area of a pyramid is

\[ a = \frac{1}{2} \text{(perimeter of base)(slant height)} \]

\[ = \frac{1}{2} (4L)(h) \]

(62)

Therefore the area of the octahedron was

\[ A = 2 \frac{1}{2} \left[ (4L)(\frac{\sqrt{3}}{2} L) \right] \]

\[ = 2 \sqrt{\frac{3}{2}} L^2 = 3.464 \text{ L}^2 \]

(63)

Thus the area shape factor was 3.464.