Some Aspects of Crystallization Theory: Systems that Violate McCabe's Delta *L* Law

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A new empirical model has been proposed to describe crystallization systems where the growth rate increases with increasing crystal size in violation of McCabe's ΔL law. Experimental data for Glauber's salt have been presented to illustrate the fit of the new model to an actual system. Equations for steady state crystal size distributions with the use of the proposed model have been derived. Wider use of population density plots for analysis of crystallization systems along with the coefficient of variation to describe a distribution numerically is recommended.

In a continuous crystallizer operating at steady state, it is generally believed that crystal growth takes place in three steps (*7*). First, the solute being crystallized must diffuse from the bulk of the solution to the solid-liquid interface of the crystal. Second, at the interface a surface reaction occurs during which the solute becomes a part of the crystal lattice and heat of crystallization is liberated. Finally, the liberated heat must diffuse back to the bulk of the solution. Very little attention in the literature has been given the third step, and its effects on the overall process of crystallization are probably small in most systems, exhibiting relatively low heats of crystallization. The relative order of the first two steps has an important effect on the overall crystal growth rate.

In most crystallization systems the solute diffusion resistance is less than the resistance offered by the surface reaction. For these systems a common simplifying assumption made is that McCabe's ΔL law holds (*1*). This law states that geometrically similar crystals of the same material suspended in the same solution grow at the same linear rate. If crystallization is truly a surface area-dependent reaction, with all resistance concentrated at the surface, then McCabe's ΔL law can be deduced from the following physical assumptions: (1) growth rate is a function only of supersaturation, (2) solubility differences due to crystal size are negligible, and (3) crystals remain geometrically similar with growth.

Growth rate r is here defined as the rate of increase in length L of geometrically corresponding distances on the crystals. Thus

$$r = dL/dt \tag{1}$$

For many systems where crystallization from solution occurs (*1* to *3*), McCabe's ΔL law has been found to fit the experimental laboratory data well. For these systems, the diffusion resistance is probably less than the resistance due to the surface reaction, so that the rate of integration of the solute molecules into the crystal lattice determines the overall crystal growth rate. Since the solute molecules are believed to be added to the lattice much like building blocks, the growth rate as defined above should logically be essentially constant with increasing crystal size. In many industrial crystallizers that are well mixed, that is, approach closely the back-mixed or the MSMPR* concept (*4*), the ΔL law has been found to hold as well.

In a number of systems it has been observed that growth rate actually increases with increasing crystal size (*5* to *7*). Most of these systems that violate the ΔL law have been highly hydrated crystals such as $CuSO_4 \cdot 5H_2O$, $MgSO_4 \cdot 7H_2O$, and $Na_2SO_4 \cdot 10H_2O$. A diffusion mechanism can be postulated to account for violation of the ΔL law in such heavily hydrated systems where both the water molecules and the solute ions must diffuse to the solid-liquid interface before being integrated in the crystal lattice. For these systems, diffusion resistance plays a large part in determining overall reaction rate. In a mixed suspension, as the crystals grow larger, the slip velocity, or relative velocity between the crystal and its mother liquor, becomes greater, thus reducing the diffusion boundary layer surrounding the crystal and decreasing the diffusion resistance. Hence, growth rate would be expected to increase with size. Whatever the mechanism that causes the ΔL law violation, several investigators (*6*, *8*) have proposed empirical models to describe the phenomenon. For reasons that will be discussed subsequently, the past models have not been entirely adequate in describing conditions in a continuous crystallizer. Another empirical model is herein proposed that agrees well with experimental data and is consistent with the concept of conservation of population.

BACKGROUND

McCabe and Stevens (*6*) in experiments with $CuSO_4 \cdot 5H_2O$ demonstrated in unsteady state experiments that growth rate increases with increasing solution velocity past a stationary crystal but is constant with increasing crystal size. The following empirical relationship was derived:

$$\frac{1}{r} = \frac{1}{r_q + \beta U_r} + \frac{1}{r_i} \tag{2}$$

The growth rate r is expressed as a function of the growth rate at zero relative velocity between the crystal and the solution r_q, a constant β, the relative velocity U_r, and the interfacial growth rate r_i. This equation is of little value in describing a continuous crystallizer because of the difficulty in measuring the quantities r_q, U_r, and r_i.

Based on the work of Hixson and Knox (*7*), who determined mass transfer coefficients for $CuSO_4 \cdot 5H_2O$ and $MgSO_4 \cdot 7H_2O$, Bransom proposed the empirical exponential relationship (*8*)

$$r = a_1 L^b S^\eta \tag{3}$$

which in a continuous mixed system reduces to

$$r = aL^b \tag{4}$$

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* Mixed-suspension, mixed-product removal.

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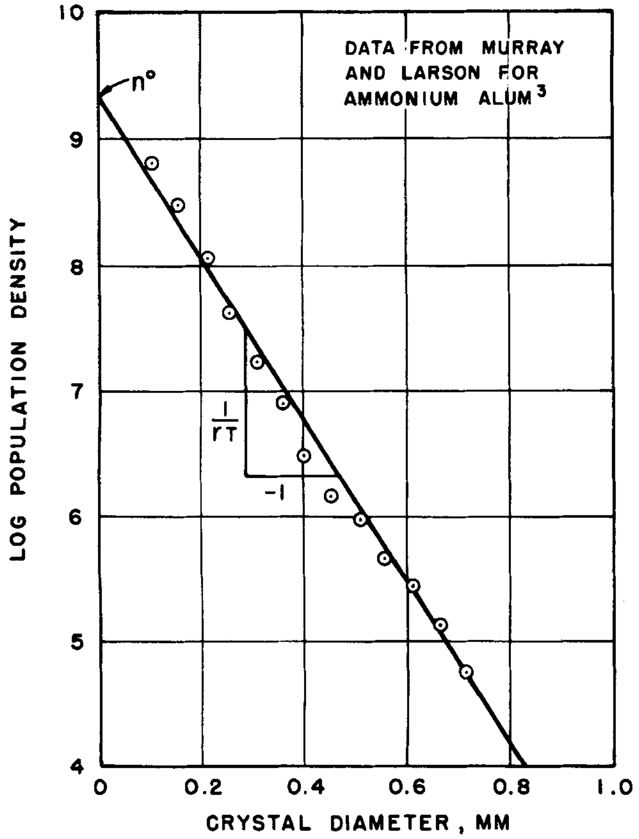

Fig. 1. Population density plot.

where the constant a now includes the supersaturation term which is constant at steady state. Data will be presented to indicate that this correlation fits experimental data obtained for Glauber's salt very well but is inconsistent with the concept of conservation of population most recently applied to crystallization by Randolph and Larson (9).

The general population balance equation may be written for a mixed crystal suspension (9)

$$V\frac{\partial n}{\partial t} + V\frac{\partial (rn)}{\partial L} + n\frac{dV}{dt} - n_iQ_i + n_oQ_o = 0 \quad (5)$$

In a MSMPR crystallizer operating at steady state with no solids in the feed, and by substituting $T = V/Q_o$, Equation (5) becomes

$$T\frac{d(rn)}{dL} = -n \quad (6)$$

When McCabe's ΔL law holds, $r \neq f(L)$, and Equation (6) may be integrated as shown by Saeman (10) and others to result in the population distribution equation

$$n = n^o \exp\left[\frac{-L}{rT}\right] \quad (7)$$

Equation (7) can be very useful in analyzing small-size crystal population and is defined at zero size. Plotting the data obtained from a screen analysis in the form of Equation (7) on semilog paper permits determination of both nucleation and growth rates. The population density for any screen fraction can be calculated by

$$n = \frac{\Delta W}{\Delta L}\cdot\frac{M_T}{\rho k_L \bar{L}^3} \quad (8)$$

where ΔW is the weight fraction of crystals found in the screen fraction ΔL, M_T is slurry density, ρ is the crystal density, k_L is a shape factor previously defined by McCabe and Stevens (6), and $\bar{L}$ is the arithmetic mean crystal size in fraction ΔL. The slope of the semilog plot of population density vs. crystal size is $(-1/rT)$, the intercept at $L = 0$ is the nuclei density n^o and the nucleation rate is given by

$$\left(\frac{dN^o}{dT}\right) = n^o r \quad (9)$$

Data obtained by Murray and Larson (3) for ammonium alum are shown in Figure 1 plotted to fit Equation (7). Study of such a population distribution can frequently be much more useful than study of a simple screen analysis in analyzing a crystallization system.

EXPONENTIAL SIZE FUNCTION

In the case where McCabe's ΔL law does not hold, then $r = f(L)$. With the use of Bransom's exponential relationship $r = aL^b$, Equation (6) becomes

$$\frac{d}{dL}(aL^b n) = \frac{-n}{T} \quad (10)$$

Integration of Equation (10) as shown by Bransom (8) and as corrected by Randolph (4) yields the population distribution equation

$$n = \frac{a'}{L^b}\exp\left[\frac{-L^{(1-b)}}{aT(1-b)}\right] \quad (11)$$

This form reduces to Equation (7) when $b = 0$, that is, when McCabe's ΔL law holds. However, as L approaches zero, Equation (11) is undefined, indicating an infinite nuclei density. Thus, Equation (11) is useless for extrapolation to obtain distribution of nuclei sized particles, however well it may fit population distributions in larger size ranges. It is precisely this extrapolation to zero size which makes the population plot useful as opposed to, say, a cumulative screen analysis on a weight basis.

Further, Equation (11) is of little direct value in analyzing a crystallization system, since the constants a and a'

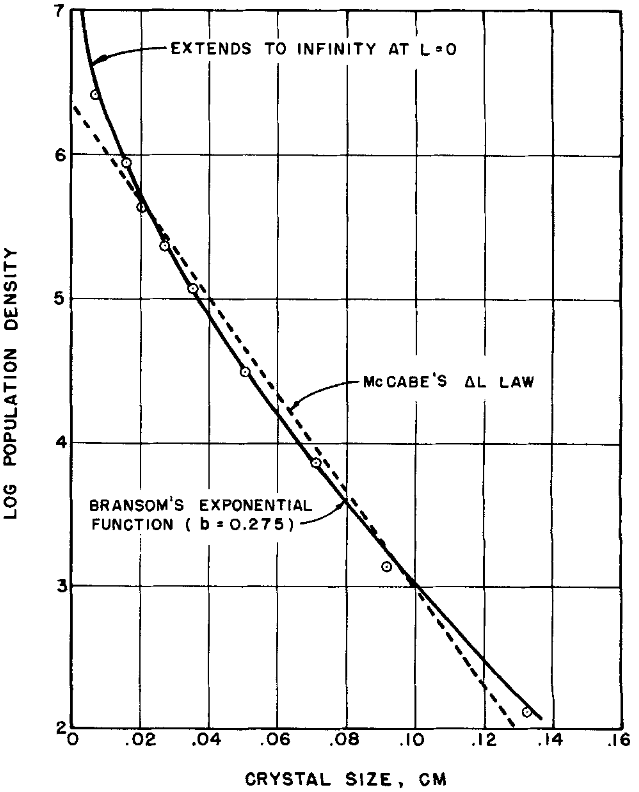

Fig. 2. Population distribution for Glauber's salt; exponential model.

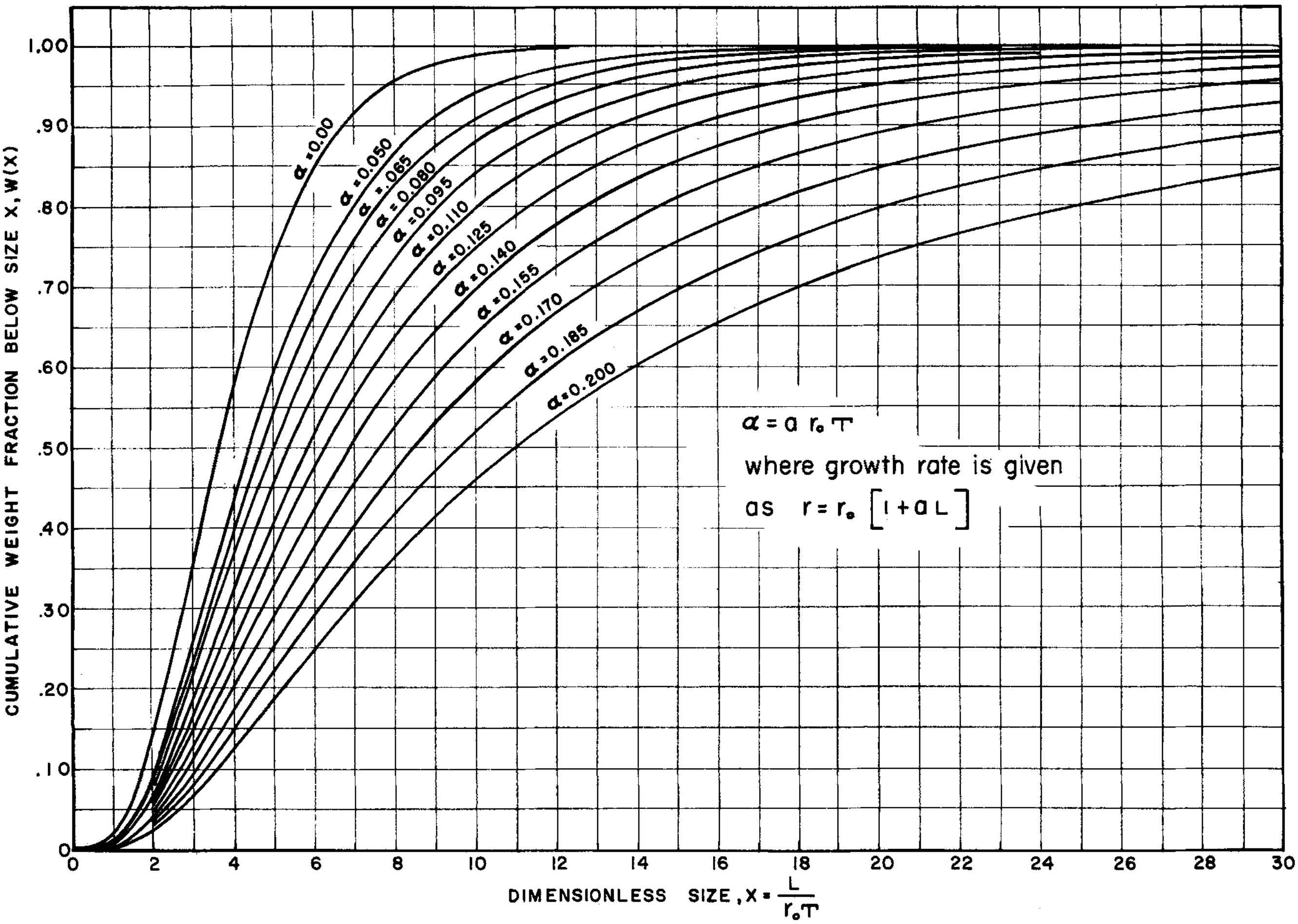

Fig. 3. Theoretical CSD curves for MSMPR crystallizer where growth rate varies linearly with size.

have no direct physical meaning as was true in the simpler case where McCabe's ΔL law held. As pointed out by Bennett (*11*) the constant b is very important and is a measure of the width of the crystal size distribution. The higher the value of b the more widespread the distribution and the more the distribution is skewed toward the larger crystal sizes.

Data were obtained in a bench-scale, continuous, draft-tube MSMPR crystallizer for Glauber's salt crystallized from a brine containing 35 wt. % total salts. The population distribution obtained by screen analysis was found to deviate from the straight line expected from Equation (7) as indicated in Figure 2. Many things can cause a deviation from a straight line such as internal classification, seed dissolving, crystals not remaining geometrically similar with growth, breakage, agglomeration, nonsteady state operation, or a change in growth rate with increasing size. Most of the variables mentioned, except the latter, could be ruled out from independent analysis of the system. For example, microscopic examination showed the crystals to be nearly cubic and geometrically similar. Thus it appeared that the system probably violated McCabe's ΔL law.

With the use of the experimental points, Equation (11) was fitted as shown in Figure 2. Bransom's model appears, at least superficially, to fit the data well in the size ranges plotted. However, crystal population (not mass) is concentrated in the small-size ranges and, as pointed out, Equation (11) extrapolates to an infinite nuclei density, a physically impossible situation. Thus it is apparent that Bransom's corrected model is inconsistent with the concept of conservation of population and is unsuitable for the purpose of describing nuclei distributions.

LINEAR SIZE FUNCTION

If McCabe's ΔL law is violated, one of the simplest empirical equations to describe this relationship between growth rate and size would be the polynomial

$$r = r_o(1 + a_1L + a_2L^2 + \dots a_nL^n) \qquad (12)$$

or

$$r = r_oP(L) \qquad (13)$$

The population balance equation, at steady state and with mixed withdrawal, then becomes

$$\frac{d[nP(L)]}{dL} = \frac{-n}{r_oT} \qquad (14)$$

Substitution of the variable $y = nP(L)$ in Equation (14) yields

$$\frac{dy}{y} = \frac{-dL}{r_oTP(L)} \qquad (15)$$

which is variables separable and has the solution

$$n = \frac{y}{P(L)} = \frac{n^o}{P(L)} \exp\left[-\frac{1}{r_oT}\int_o^L \frac{dL}{P(L)}\right] \qquad (16)$$

If the dimensionless substitutions $x = s = p = (L/r_oT)$ and $\alpha = a_1r_oT$ are made, and by using only a first-order (linear) polynomial approximation to the growth rate, Equation (16) becomes

$$n(s) = \frac{n^o}{1 + \alpha s} \exp\left[-\int_o^s \frac{dp}{(1 + \alpha p)}\right] \qquad (17)$$

where s and p are dummy variables of integration. Performing the indicated integration, we obtain

$$n(s) = \frac{n^o}{(1 + \alpha s)^{\frac{\alpha+1}{\alpha}}} \tag{18}$$

which is the form of the population density distribution when linear growth rate is given as a first-order polynomial in terms of crystal size. Note that Equation (18) is finite at $s = 0$, and in fact reduces to the nuclei density n^o. As $\alpha \to 0$, $n(s)$ approaches the exponential population distribution, Equation (7). The definition of cumulative weight fraction in terms of population density may be written as

$$w(x) = \frac{\int_o^x n(s) s^3 ds}{\int_o^\infty n(s) s^3 ds} \tag{19}$$

By substituting Equation (18) in Equation (19) and integrating by parts, cumulative weight fraction below a given dimensionless size x as defined above becomes

$$w(x) = 1 - \left[\frac{x^3(1-\alpha)(1-2\alpha)(1-3\alpha)}{6(1+\alpha x)^{1/\alpha}} + \frac{x^2(1-2\alpha)(1-3\alpha)}{2(1+\alpha x)^{1-\alpha/\alpha}} + \frac{x(1-3\alpha)}{(1+\alpha x)^{1-2\alpha/\alpha}} + \frac{1}{(1+\alpha x)^{1-3\alpha/\alpha}} \right] \tag{20}$$

For convergence of the integral in Equation (19), α must be less than 1/3. When $\alpha = 0$ (McCabe's ΔL law holds), Equation (20) reduces to the exponential form given by Saeman (*10*)

$$w(x) = 1 - e^{-x} \left[\frac{x^3}{6} + \frac{x^2}{2} + x + 1 \right] \tag{21}$$

If Equation (20) is calculated for different values of α, a series of cumulative crystal size distributions are obtained as shown in Figure 3. Determination of α for an experimentally obtained size distribution must be done by trial and error. For the Glauber's salt data, a value for $\alpha = 0.065$ was found to provide the best fit as indicated in Figure 4.

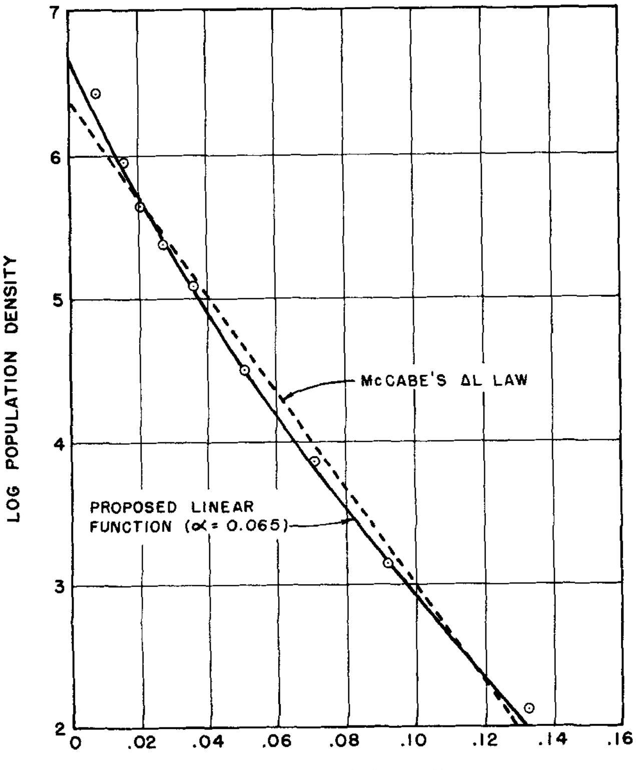

Fig. 4. Population distribution for Glauber's salt; linear model.

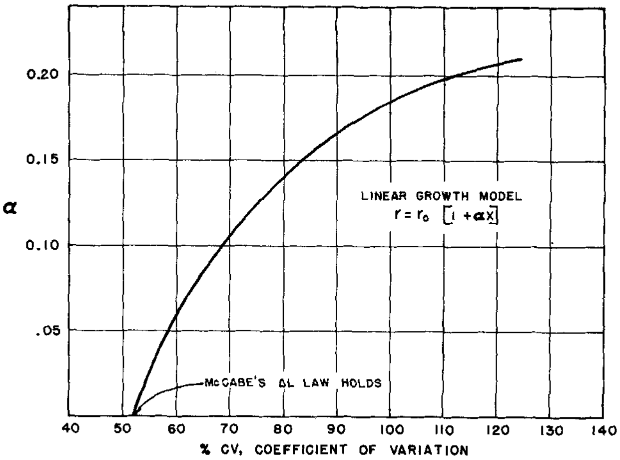

Fig. 5. The relationship between CV and α.

The proposed linear model appears to fit the experimental data for Glauber's salt as well as does Bransom's exponential model and at the same time is also consistent with the concept of conservation of population. As α decreases and approaches zero, both the CSD and the population distribution curves approach in a continuous manner the limiting case where the ΔL law holds (α and b both equal zero), expressed as Equation (7).

With the linear model, analysis of the population distribution becomes somewhat more difficult. On a semilog plot the intercept remains the nuclei density n^o but the slope no longer represents the quantity $(-1/rT)$ at any given size but now has the value

$$\frac{d(\ln n)}{dL} = -\left[\frac{1}{rT} + \frac{a}{1 + aL} \right] \tag{22}$$

The important value of growth rate is the growth rate r_o when $L = 0$, which can be determined by plotting r vs. L and getting the intercept at $L = 0$. Then the nucleation rate can again be calculated from

$$(dN^o/dt) = n^o r_o \tag{23}$$

By thus getting nucleation and growth rates at different operating conditions, the kinetic order of nucleation and growth can be determined and applied as described by Randolph and Larson (*4, 9*).

COEFFICIENT OF VARIATION

Many methods for representing and characterizing particle-size distributions have been suggested over the years. Graphical representation is the most complete method but when different distributions are compared, graphs can at best be only qualitative. Powers (*12*) devised a method for the sugar industry by using an average standard deviation of the size distribution expressed as a percentage of the mean particle size and called it the coefficient of variation CV. By plotting the distribution on arithmetic probability paper and reading the particle sizes corresponding to 15.87, 50.00, and 84.13 cumulative wt. % smaller than size L, CV can be obtained by

$$CV = 100 \left[\frac{L_{84.13\%} - L_{15.87\%}}{2L_{50\%}} \right] \tag{24}$$

Bennett (*11*) used CV's effectively to describe crystal

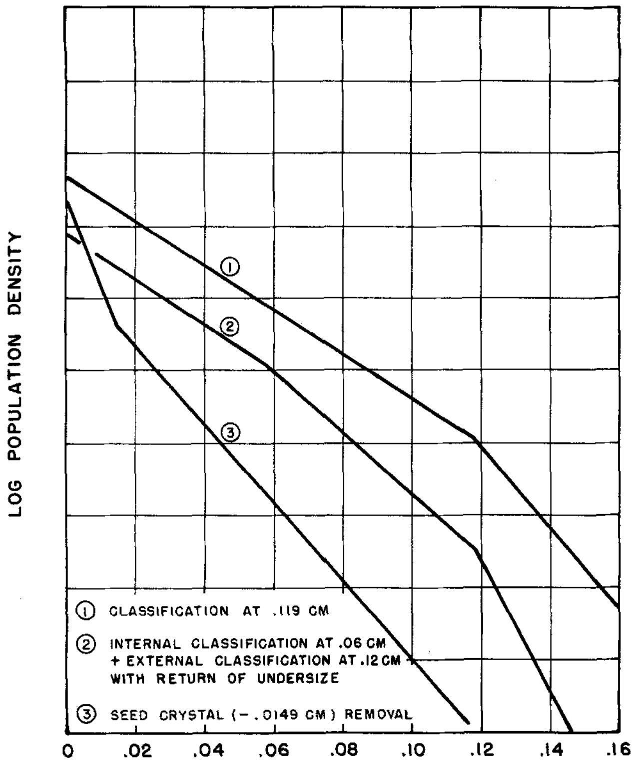

Fig. 6. Effect of various types of crystallizer operation on population distribution.

size distributions obtained from various sources. He incorrectly stated, however, that the data should be smoothed by drawing a best straight line through the data points between 10 and 90%. By doing this, he forces the data into a Gaussian distribution, and averaging the standard deviations on both sides of the distribution mean has no meaning, since a Gaussian distribution is symmetrical. Very few, if any, crystallization systems exhibit a true Gaussian weight distribution, although some approach it over portions of the size distribution. Bennett reported a *CV* of 55% for the simple case of an MSMPR crystallizer, obeying McCabe's ΔL law. The correct value should be 52.1% with the original definition used.

CV can be used in the trial and error determination of α when the linear model is used to explain ΔL law deviations. From Figure 3, *CV* was determined for different values of α and plotted in Figure 5. Thus by drawing a smooth curve through the experimental cumulative size distribution points on arithmetic probability paper and determining *CV*, an initial estimate for α can be obtained from Figure 5. If the original size distribution was reasonably good, the α thus determined should fit the data as well as is justified by the inherent inaccuracies in the CSD determination. Care should be exercised in using Figure 5, since *CV* is also influenced by other factors. As pointed out by Bennett, *CV*'s greater than 52.1 may be found in cases where fines are removed either by classification or nuclei dissolving. Also *CV*'s less than 52.1 may be observed in cases where the larger sized particles are selectively removed from the crystallizer by external classification or from the growing zone by internal classification. In both of the above cases (and assuming the ΔL law holds), a population density plot will exhibit a change in slope at the size where the classification of particles begins. Several different cases that may occur in industrial crystallizers are illustrated in Figure 6. The cases shown are not meant to be all inclusive but just illustrative of some of the more common industrial cases. All of the cases shown are for systems where the ΔL law holds as indicated by the straight lines, whereas the lines would continuously curve if the ΔL law were violated.

SUMMARY

A new empirical model has been proposed to describe crystallization systems where the growth rate increases with increasing crystal size in violation of McCabe's ΔL law. This new model is superior to previous models in that it is consistent with the concept of conservation of population. Experimental data for Glauber's salt have been presented to illustrate the degree to which the proposed model applies to an actual crystallization system. Derivation of the equations for steady state size distributions with the use of the proposed model is presented. A description of calculation methods for growth and nucleation rates has also been described.

For analysis of a crystallization system, the inadequacies of a size distribution obtained from a screen analysis by itself are pointed out. Wider use of population density plots for analysis of crystallizer conditions along with the coefficient of variation to describe a distribution numerically is recommended.

NOTATION

a = constant in size-dependent growth rate equation
a' = integration constant in size-dependent growth rate equation
b = exponent of L in size-dependent growth rate equation
CV = coefficient of variation, % [see Equation (20)]
k_L = crystal shape factor, dimensionless
L = linear crystal size, cm.
M_T = slurry density, g. solids/cc. clear mother liquor
n = crystal population density, number/(cm.)(cc. of clear mother liquor)
n^o = nuclei density or population density at $L = 0$, number/(cm.)(cc. of clear mother liquor)
dN^o/dt = nucleation rate, number/(sec.)(cc. of clear mother liquor)
p, s = dummy variables of integration
Q = suspension flow rate, cc. of mother liquor/sec.
r = linear growth rate, cm./sec.
r_i = growth rate at crystal interface, cm./sec.
r_q = growth rate at $U_r = 0$, cm./sec.
r_o = linear nuclei growth rate, cm./sec.
S = supersaturation, g./cc.
T = draw-down or retention time, sec. = V/Q_o
U_r = relative velocity of mother liquor past crystal, cm./sec.
V = volume of mother liquor in crystallizer, cc.
W = weight of crystals, g.
$w(x)$ = theoretical cumulative mass fraction of particles less than size x for MSMPR crystallizer
x = dimensionless crystal size = L/rT
α = dimensionless parameter in size-dependent size distribution = ar_oT
α_1, β, η = constants
ρ = density, g./cc.

Subscripts

i, o = inlet and outlet conditions

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Stratified Laminar Flow in Ducts of Arbitrary Shape

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A method of analysis is presented for determining closed-form solutions for two-component stratified laminar flow in horizontal ducts of arbitrary cross section. It is demonstrated that the method is remarkably easy to apply and produces results of high accuracy. As an application, solutions are obtained for stratified flow in a circular tube. The results are compared with various limiting cases and excellent agreement is found to exist. Among the limiting cases, an exact solution was derived by Green's functions for the problem in which the interface between the flow components is situated at the horizontal diametral plane.

Consideration is given to the laminar stratified flow of two immiscible fluids in horizontal ducts of arbitrary cross section. The general area of two-component laminar flows of immiscible fluids has evoked considerable interest in recent years, especially in connection with the pipeline transport of highly viscous liquids. If the component fluids are of different density and if both components experience laminar flow, then a stratified motion (heavier fluid below, lighter fluid above) appears likely. Such motions have been demonstrated experimentally (*1*, *2*). In particular, by employing visualization techniques, Charles and Lilleleht (*2*) have shown that laminar stratified flow with a smooth, ripple-free interface between the components is physically realizable.

This paper is concerned with the analytical treatment of laminar stratified flows in horizontal ducts. A general method of analysis is developed which provides *closed-form* solutions for stratified flows in ducts of arbitrary cross section while taking advantage of universally available computer routines. The method is remarkably easy to apply and, as will be subsequently demonstrated, provides results of high accuracy. Its flexibility is evidenced by the fact that once a computer program has been devised for evaluating the solution for one duct cross section, then the same program is applicable for any cross-sectional shape. These closed-form solutions provide information on local quantities such as the velocity distribution and wall shear as well as for overall quantities such as the flow rate of each component, the pressure drop, and so forth.

The solution method is illustrated by application to the technically interesting case of stratified flow in a horizontal circular tube. Results are obtained for a wide range in the ratio of the viscosities of the component fluids and for a large number of positions of the interface between the stratified layers. For the case in which the interface coincides with the horizontal diametral plane, an *exact* closed-form solution can be derived. This latter solution is employed as a standard against which are compared the results from the general solution method. Other limiting cases are also used in verifying the results of the new solution method.

As noted above, the same computer program employed in obtaining results for the circular tube is applicable, without essential modification, to ducts of any cross-sectional shape. However, no additional duct shapes were considered inasmuch as it is felt that the method is sufficiently well illustrated by the circular tube case.

Important contributions to the analysis of laminar stratified flows in circular tubes have been made by Gemmell and Epstein (*1*) and by Charles and Redberger (*3*). In the absence of a practically viable analytical solution method, these authors employed numerical finite-differ-