Multiplicity in Continuous MSMPR Crystallizers

Part I: Concentration Multiplicity in an Isothermal Crystallizer

A theory for the identification of criteria within which a continuous isothermal mixed-suspension, mixed-product removal (MSMPR) crystallizer can exhibit concentration multiplicity (i.e., multiple steady states) is developed. Power law growth and power law magma-dependent nucleation kinetic models are used to describe the crystallization kinetics. Applications to specific cases together with figures delineating regions of multiplicity are presented. The stability of these steady states is analyzed by using small perturbations around the steady state. Growth rate-dispersion is shown to be unimportant in establishing this concentration multiplicity.

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SCOPE

Several theoretical studies of crystal size distribution stability and cycling have been concerned with the operation of an isothermal continuous MSMPR crystallizer. Simple power law kinetic expressions have been assumed and a number of process modifications such as product classification and/or fines destruction schemes have been investigated. In general, linear stability analysis has been used to identify the stability regions of such crystallizer configurations over a range of kinetic and process parameters. In chemical reaction engineering the concept of concentration stability is frequently employed in the study of complex reaction systems such as heterogeneous catalytic, autocatalytic, and biochemical reactions. The present study demonstrates the application of the theory of concentration multiplicity to the isothermal continuous MSMPR crystallizer described by the population balance equation together with power law growth and magma-dependent power law nucleation kinetics. The effect of adding a growth dispersion term in the population balance equation is also investigated and an analysis of linear stability applied to infinitesimal disturbances around the steady state is included.

CONCLUSIONS AND SIGNIFICANCE

The analysis of concentration multiplicity and stability of an isothermal continuous MSMPR crystallizer with power law growth and magma-dependent power law nucleation kinetics indicates that the kinetic orders, dimensionless saturation concentration, and slope parameter are the important quantities in defining system behavior. The necessary and sufficient conditions for the existence of concentration multiplicity together with the uniqueness criterion are developed in terms of these quantities using steady state information alone. Multiple steady states are possible over a certain range of kinetic and physical parameters provided the order of nucleation rate with respect to magma density is sufficiently high. A simple linear stability analysis of the dynamic solute balance using an infinitesimal perturbation about the steady state shows that the middle of the three possible steady states is normally unstable. The growth dispersion term, when incorporated into the population balance, has no significant influence on the existence of multiplicity. Although the phenomenon of multiplicity may be encountered only occasionally in actual practice, an awareness of such ranges of parameters over which multiplicity might occur is important in design, start-up, and control of crystallization systems.

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INTRODUCTION

Motivation to study the dynamics of continuous crystallizers was originally provided by observations that under some operating conditions industrial units exhibited inherently unstable and cyclic behavior (Saeman and Miller, 1947; Randolph and Larson, 1962). Such self-generated instabilities are caused by the interaction of system kinetics with the process configuration. Much of the analytical work on the problem of crystallizer stability under isothermal conditions has centered on study of the dynamic population balance over the configuration together with the associated mass balance, either in the form of a dynamic solute concentration or as a constraint relating the growth rate to the current value of the specific crystal surface area and corresponding specific production rate. There have been several studies of this type which have been comprehensively reviewed by Randolph (1980).

The importance and advantages that arise from building on the established theory of chemical reaction engineering to develop procedures for the analysis of crystallization systems are well known (Nyvlt, 1969). The chemical engineering literature is replete with both theoretical and experimental stability studies of chemical reactors, and one aspect of such work is the concept of concentration stability of an isothermal reactor. This was first introduced for complex reaction systems by Matsuura and Kato (1967) who showed that multiplicity (i.e., multiple steady states) was possible within a certain range of operating conditions.

Although the basic theory which enables prediction of regions of multiplicity is well established and experimental corroboration has been demonstrated (Denn, 1975; Perlmutter 1972; Lin, 1979; Uppal and Ray, 1977), application to simple crystallizing systems has not been attempted. The objective of the present communication is to develop such a theory. The crystallization configuration considered is a continuous mixed-suspension, mixed-product removal (MSMPR) crystallizer as described by population balance equations. The specific aim of this work is to present some exact uniqueness and multiplicity criteria, together with a stability analysis in terms of the solute concentration for a continuous MSMPR crystallizer. The effect of growth dispersion on the occurrence of multiplicity is also considered. The analysis should be useful in the identification of parameter ranges within which concentration multiplicity is expected, and the information should be useful in design, start-up, and control of crystallizer systems.

THEORY

Solute Balance

Using the dimensionless variables defined by $x = c/c_f$, $\xi = c_s/c_f$, the solute balance for a steady state continuous MSMPR crystallizer of the type shown in Figure 1 can be written as

$$\frac{M_T}{c_f} = 1 - x \tag{1}$$

The overall linear growth rate of a crystallizing system will be represented by an empirical power law relation

$$G = k_g(c - c_s)^g \tag{2}$$

while the nucleation rate will be described empirically by

$$B = k_b(c - c_s)^b M_T^j \tag{3}$$

Both the rate coefficients k_g and k_b may be functions of many variables, in particular temperature, slurry hydrodynamics, the presence of impurities, and perhaps some crystal properties. Use of the power law term M_T^j in the nucleation rate expression accounts for secondary nucleation effects occurring within the crystallizer.

For the steady state continuous MSMPR crystallizer operating with a clear feed and negligible crystal agglomeration and breakage, the suspension density obtained by moment transformation of the population balance equation is given by (Randolph and Larson, 1971)

$$M_T = 6k_v\rho\tau^4G^3B \tag{4}$$

Using Eqs. 2–4, the solute balance, Eq. 1, can be rewritten in terms of dimensionless variables as

$$(1 - x)^j(x - \xi)^k = \frac{1 - x}{\alpha} \tag{5}$$

where $$\alpha = 6k_v\rho\tau^4k_g^3k_bc_f^{(k+j-1)} \tag{6}$$

and $$k = 3g + b \tag{7}$$

The lefthand side of Eq. 5 will be defined as

$$f(x) = (1 - x)^j(x - \xi)^k \tag{8}$$

where $f(x)$ is the characteristic dimensionless function used in multiplicity analysis and can be seen from Eqs. 1 and 5 to be equal to $(M_T/\alpha c_f)$.

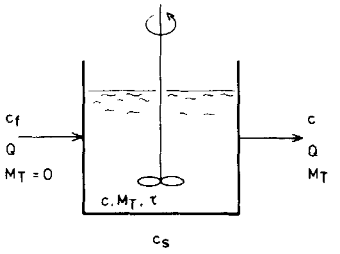
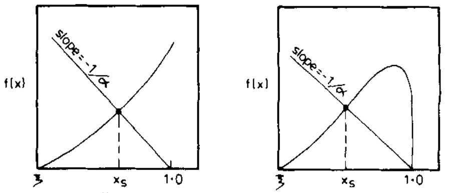
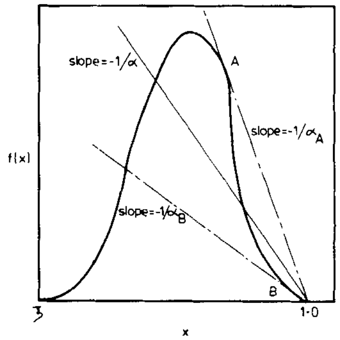


Figure 1. Schematic representation of a continuous MSMPR crystallizer.



(a) no maximum in f(x), no multiplicity

(b) A maximum in f(x) but no multiplicity



(c) A maximum in f(x) and multiplicity

Figure 2. Schematic form of the dimensionless function *f*(*x*).

Existence of Multiplicity

To illustrate the existence of multiplicity consider a graphical solution of Eq. 5. The intersection(s) of the curve representing the dimensionless function $f(x)$ against x with the straight line $y = (1 - x)\ \alpha$ yields a steady state solution(s). The straight line has slope $(-1/\alpha)$ and passes through the point (1,0).

If $f(x)$ is a monotonically increasing function of x, then only one such intersection is possible, implying a unique steady state as illustrated in Figure 2a. Only in the event of $f(x)$ passing through a maximum at some intermediate value of x will multiple steady states be possible, although this alone is not sufficient to guarantee multiplicity. For example, if the nature of $f(x)$ is as illustrated in Figure 2b, only a unique solution is again possible even though $f(x)$ shows a maximum. Figure 2c illustrates a case where the straight line cuts $f(x)$ at three points, so giving multiple steady states. Thus certain values of and conditions for the parameters are necessary for multiplicity to exist.

Conditions for Multiplicity

From an examination of Figure 2c it is evident that if the slope $(-1/\alpha)$ of the straight line is not within the range of slopes of tangents to the function $f(x)$ from the point (1,0) only one steady state exists. Hence a necessary condition is that it must be possible to draw two tangents to $f(x)$ from the point (1,0). A sufficient condition is that the slope of the straight line through (1,0)—i.e., $-1/\alpha$—should lie between the slopes of the two tangents to $f(x)$ from the point (1,0).

Suppose that the two tangents with their slopes $(-1/\alpha_A)$ and $(-1/\alpha_B)$ touch the function $f(x)$ at the points A and B respectively, Figure 2c. At these points both the slopes and the actual values of the function $f(x)$ must be equal to those of the straight lines (i.e., tangents) drawn from the point (1,0). The necessary condition is therefore that the points A and B should be real and distinct, i.e., that after using Eq. 8 in Eq. 5, both Eq. 5 and the equation obtained by differentiating Eq. 5 with respect to x,

$$\dot{f}(x) = -1/\alpha \tag{9}$$

should have two real distinct roots in the interval of $\xi < x < 1.0$, with ξ representing the dimensionless saturation concentration. Simultaneous solution of Eqs. 5 and 9 yields

$$x = \xi$$

$$x = \frac{k + \xi(j - 1)}{k + j - 1}$$

$$x = 1$$

as three characteristic points, of which the last two decide the limits of the multiplicity region. As two of the three characteristic points represent the bounds of x, the additional condition of having two real distinct roots to the second derivative of $f(x)$ over the range of $(\xi,1)$ gives the following constraints:

$$kj(k + j - 1)(1 - \xi)^2 > 0 \tag{10a}$$

$$(\xi^2 - 1)k^2 + k(1 + 2j\xi^2 - 2j\xi - \xi^2) > 0 \tag{10b}$$

$$k(1 - \xi)(k + j - 1) > 0 \tag{10c}$$

The sufficient condition for multiplicity to occur is that the slope of the straight line $(-1/\alpha)$ should lie between the limits of the extremities, i.e.

$$(-1/\alpha_A) < (-1/\alpha) < (-1/\alpha_B) \tag{11}$$

where α_A and α_B are the negative reciprocals of the slopes of the tangents to the function $f(x)$ through the point (1,0) at A and B respectively, Figure 2c.

Conditions for Uniqueness

A special case of the mean value theorem of elementary calculus—i.e., a continuous single-valued function can only be equal to zero at two different values of x if it has a zero derivative somewhere between these two values—can be used to derive the uniqueness criterion. Therefore the sufficient condition which now guarantees a unique solution to

$$F(x) = \frac{1 - x}{\alpha} - f(x) \tag{12}$$

is given by

$$\dot{F}(x) = -\frac{1}{\alpha} - \dot{f}(x) < 0 \tag{13}$$

Using Eq. 5 and 8 in Eq. 13, after simplification the uniqueness criterion may be derived as

$$x < \frac{k + \xi(j - 1)}{k + j - 1} \tag{14}$$

Thus Eq. 14 sets the limit on x for given system parameters (k, j, and ξ) below which a unique and stable solution exists.

APPLICATION

The characteristic dimensionless function, $f(x)$, is dependent on the kinetic orders and the dimensionless saturation concentration, while the slope of the operating line $(-1/\alpha)$ is characterized by the physical parameters, the rate constants, and the mean residence time of the crystallizer. The necessary conditions are independent of this slope parameter and depend only on kinetic orders and the dimensionless saturation concentration. Figure 3 maps the constraints represented by Eqs. 10a–c for a typical value of $\xi = 0.7$ (i.e., $c_f = 1.43\ c_s$) in the $k - j$ parameter plane. These equations are quadratics and the two corresponding solutions are shown for each equation. The hatched area on the righthand side of the curve shows the region where all three constraints are satisfied. Within this region the second derivative of $f(x)$ has two real distinct roots over the range $(\xi,1)$.

Using a representative value of $k = 5$ together with $\xi = 0.7$, the plots of $f(x)$ against x for $j = 0$, 0.5, and 2.0 (corresponding to the three points indicated in Figure 3) are depicted in Figure 4 and those of $\dot{f}(x)$ and $\dot{f}(x)$ in Figure 5. When $j = 0$ (no secondary nucleation effects) a monotonically increasing $f(x)$ (similar to Figure 2a) guarantees a unique steady state without any possibility of

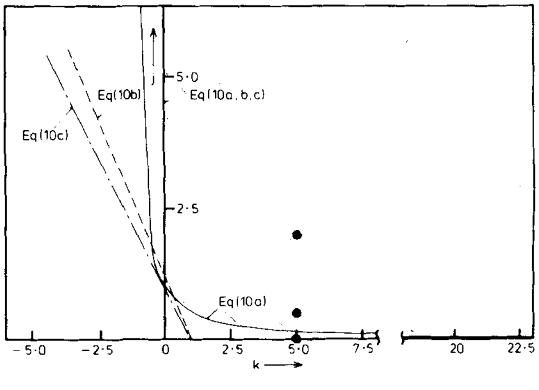


Figure 3. Constraints represented by Eqs. 10a–c for $\xi = 0.7$. Each equation gives rise to two constraints, both depicted on the diagram.

multiplicity as indicated even by the uniqueness criterion, Eq. 14, yielding $x < 1.175$. Although both the other cases are within the shaded region of Figure 3, the uniqueness criterion predicts that the entire range of x is safe from multiple unstable solutions for $j = 0.5$ ($x < 1.033$), whereas a possibility of multiplicity or unstable behavior exists beyond $x = 0.95$ for $j = 2.0$ as predicted by Eq. 14.

Figure 5 accords a better understanding of this phenomenon, as for $j = 2$ both the derivatives $\dot{f}(x)$ and $\ddot{f}(x)$ give three roots, while with $j = 0.5$ only two are possible. Thus there exists a possibility of multiple solutions if the slope condition, Eq. 11, is satisfied.

STABILITY ANALYSIS

The analysis described in the previous sections is concerned with steady state behavior and indicates the range of parameter values within which multiplicity will lie. In this section the stability of these steady states is examined for the case of a small perturbation about the steady state.

The dynamic solute balance as written for the solution in the crystallizer can be formulated in terms of dimensionless variables as

$$\frac{dx}{dt} = (1 - x) - \alpha f(x) \tag{15}$$

where t represents the dimensionless variable defined as t'/τ. The steady state value (denoted as x_s) is obtained by letting $dx/dt = 0$ in Eq. 15. Subtracting this from Eq. 15 results in

$$\frac{d\epsilon}{dt} = -(x - x_s) - \alpha[f(x) - f(x_s)] \tag{16}$$

where ϵ represents the deviation from the steady state and is defined as $\epsilon = x - x_s$.

For small perturbations from the steady state, the term in the square bracket of Eq. 16 can be linearized using a Taylor series expansion as

$$f(x) - f(x_s) = \epsilon \left.\frac{df(x)}{dx}\right|_{x_s} \tag{18}$$

Substituting Eq. 18 into Eq. 16 and integrating the resulting equation gives

$$\epsilon = \epsilon_0 \exp(-mt) \tag{19}$$

where ϵ_0 is the value of the deviation variable at $t = 0$ and m is given by

$$m = 1 + \alpha \left.\left(\frac{df(x)}{dx}\right)\right|_{x_s} \tag{20}$$

For a steady state to be stable the perturbation ϵ must decay with time. This is possible for $m > 0$. It can be shown that m is negative for the range $x_A < x_s < x_B$ (Figure 2c) and hence the steady state lying within this range is unstable. The condition of $m > 0$ is also satisfied for the range of x represented by the uniqueness criterion, Eq. 14. Normally the middle of the three steady states is one such case for which $m < 0$ and the other two steady states lie outside the unstable region.

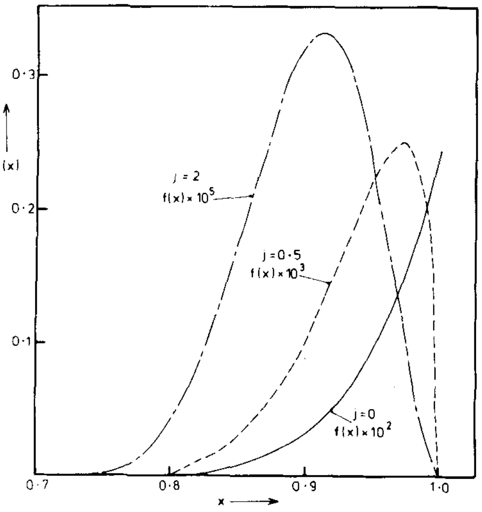


Figure 4. The characteristic dimensionless function $f(x)$ for $k = 5.0$, $\xi = 0.7$.

DISCUSSION

The analysis based on simple formulation of the steady state solute balance alone shows the existence of multiple steady states for an isothermal MSMPR crystallizer over a certain range of kinetic and physical parameters. Such behavior is accomplished by a high order ($j > 2$ for the present case) term of magma density in a nucleation model; this exerts a significant influence on the form of the characteristic dimensionless function $f(x)$. The analysis predicts unique and stable behavior of the MSMPR configuration with $j = 0$. When a Volmer type nucleation kinetics model (Randolph and Larson, 1971) is used in the analysis instead of Eq. 3, it also predicts a stable MSMPR configuration except at $x = \xi$.

The degree of stability for multiplicity cannot however be inferred from such a steady state analysis alone, as stability is a dynamic concept and requires detailed analysis of the configuration in its transients. The stability of these steady states has been examined by simple linear stability analysis using a dynamic solute balance for small perturbations about the steady state. Normally

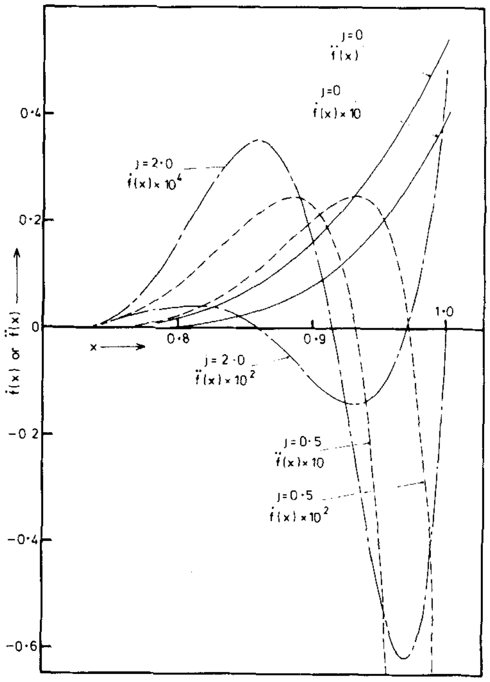


Figure 5. Higher derivatives of $f(x)$ for $k = 5.0$, $\xi = 0.7$.

the conditions of stability are satisfied for upper and lower steady states; the middle steady state violates these conditions and therefore is unstable. However, the magma density term used in the dynamic solute balance, Eq. 15, was evaluated from the steady state analysis ignoring its dynamic behavior. Rigorous analysis involving evaluation of the characteristic matrix $A = |J - \lambda I|$ for the set of differential equations describing dynamic moments of crystal size distribution (CSD) along with the dynamic solute balance for the conditions of stability is presented in Appendix 1 to this paper. Thus detailed dynamics of the configuration may be necessary to provide more information and a better understanding.

The linear stability analysis for a class II type of MSMPR representation as used in almost all of the previous work (Randolph, 1980) indicates stable behavior over the entire range of positive kinetic parameters. The classical stability criterion deduced for the class II MSMPR configuration using the Routh-Hurwitz stability test and expressed using the present kinetic relations, Eqs. 2 and 3, can be written as

$$\frac{d \ln B}{d \ln G} = \frac{b}{g} - \frac{j(x - \xi)}{g(1 - x)} < 21 \qquad (21)$$

and Eq. 21 yields a constraint on x as

$$x < \frac{\left(\frac{b}{g} - 21\right)\frac{j}{g} + \xi}{\left(\frac{b}{g} - 21\right)\frac{j}{g} + 1} \qquad (22)$$

Equation 22 indicates stable behavior over the entire range of x except for very high b/g (>21).

It is shown in Appendix 2 that growth rate dispersion is not important in forcing the system to multiple solutions under steady state, as the term associated with the dispersion effect, $g(x)/\alpha$ in the solute balance, Eq. A2.1, makes an insignificant contribution to the characteristic dimensionless function $f_D(x)$. The present analysis tends to suggest that any cause or function exerting an influence on the form of $f(x)$ may be important in deciding the existence of multiplicity or unstable behavior. It is possible that strong product classification together with a fines destruction loop in the mixed crystallizer configuration (Randolph et al., 1973) or superimposition of several nucleation mechanisms (Randolph and Larson, 1971) may have a significant influence on the form of the characteristic dimensionless function $f(x)$ as they show unstable behavior over certain ranges of operating conditions.

Finally, an important question is whether these multiple steady states are possible in practical situations. The analysis for the present configuration predicts the possibility of multiple steady states for a high-order magma density term ($j > 2$) in the nucleation kinetic expression over a narrow range of operating conditions. These may not be encountered in actual practice. Such high-order magma-dependent nucleation kinetics seem rare in published crystallization kinetics from laboratory crystallizers (Garside and Shah, 1980, partly perhaps due to the implicit technique used in deducing kinetics and the particular range of operating conditions used. In the design of a crystallizer by a steady state analysis, the conservation laws of mass, energy, and entity should be applied together with appropriate rate expressions with the object of attaining what is sometimes called a balance between input and output for a given system. The idea of such balances does not in itself guarantee a unique set of condition, and the designer should recognize that for some choices of system parameters these balances at various levels may exist for crystallizer conditions quite removed from those intended. Such conditions may be rather drastic. It is therefore necessary to be aware of the operating conditions and crystallization parameters within which multiple steady states can be experienced. These limits may in particular be extremely narrow so that the phenomenon of multiplicity would be limited to special cases or to localized situations in the crystallizer and so have little effect on its overall behavior.

APPENDIX 1. RIGOROUS LINEAR STABILITY ANALYSIS FOR A CONTINUOUS MSMPR CRYSTALLIZER USING SMALL PERTURBATIONS AROUND THE STEADY STATE.

The dynamic population balance equation for an MSMPR crystallizer is

$$\frac{\partial n}{\partial t} + G\tau \frac{\partial n}{\partial L} + n = 0 \qquad (A1.1)$$

where t is the dimensionless time defined as t'/τ, and τ the mean residence time.

System kinetics are given by

$$\text{growth } G = G(\Delta c) \qquad (A1.2)$$

$$\text{nucleation } B = B(\Delta c, \mu_3) \qquad (A1.3)$$

Moment equations obtained by the moment transformation of Eq. A1.1 with respect to size are

$$\frac{d\mu_0}{dt} = B\tau - \mu_0 = f_1 \qquad (A1.4)$$

$$\frac{d\mu_1}{dt} = \mu_0 G\tau - \mu_1 = f_2 \qquad (A1.5)$$

$$\frac{d\mu_2}{dt} = 2\mu_1 G\tau - \mu_2 = f_3 \qquad (A1.6)$$

$$\frac{d\mu_3}{dt} = 3\mu_2 G\tau - \mu_3 = f_4 \qquad (A1.7)$$

$$\frac{d\Delta c}{dt} = \Delta c_f - \Delta c - k_v \rho \mu_3 = f_5 \qquad (A1.8)$$

The set of nonlinear differential equations, Eqs. A1.4–A1.8, can be linearized over a short period of time by using a first-order approximation of a multivariable Taylor series as

$$f(x) = J_s x \qquad (A1.9)$$

where J_s is the Jacobian matrix of the first partial derivatives having its elements as $J_{ij} = \partial f_i / \partial x_j$

The characteristic equation

$$\det[J - \lambda I] = 0 \qquad (A1.10)$$

must be satisfied to yield the solution of a set of simultaneous linear algebraic equations (other than $x = 0$). The values of λ that satisfy Eq. A1.10 are the eigenvalues of the characteristic matrix.

$$\det[J - \lambda I] = \begin{vmatrix} -(1+\lambda) & 0 & 0 & \beta_j\tau & \beta_b\tau \\ G\tau & -(1+\lambda) & 0 & 0 & \beta_g\mu_0\tau \\ 0 & 2G\tau & -(1+\lambda) & 0 & 2\beta_g\mu_1\tau \\ 0 & 0 & 3G\tau & -(1+\lambda) & 3\beta_g\mu_2\tau \\ 0 & 0 & 0 & -k_v\rho & -(1+\lambda) \end{vmatrix} = 0 \qquad (A1.11)$$

where

$$\beta_g = \frac{\partial G}{\partial \Delta c} \quad \beta_b = \frac{\partial B}{\partial \Delta c} \quad \text{and} \quad \beta_j = \frac{\partial B}{\partial \mu_3}$$

Simplifying Eq. A1.11, the characteristic equation may be written as

$$\lambda^5 + 5\lambda^4 + 10\lambda^3 + 10\lambda^2 + \alpha_1\lambda + \alpha_0 = 0 \qquad \text{(A1.12)}$$

where

$$\alpha_1 = 5 + 6G^2\tau^3k_v\rho\beta_g\mu_0 - 6G^3\tau^4\beta_j$$

$$\alpha_0 = 1 + 6G^2\tau^3k_v\rho\beta_g\mu_0 + 3G^2\tau^3k_v\rho\beta_b - 6G^3\tau^4\beta_j$$

For the system to be stable:

(i) All the coefficients of the characteristic equation must be of the same sign, i.e., α_1 and α_0 should be positive.

(ii) To satisfy the Routh stability criterion, the elements of the first column in the Routh array must be positive, which yields

$$\alpha_0 - 5\alpha_1 + 80 > 0 \qquad \text{(A1.13)}$$

Condition (i) is necessary to have only roots with negative real parts for a polynomial of higher order, whereas the Routh criterion provides a necessary and sufficient condition for the same so that absolute stability is guaranteed.

Class II MSMPR Crystallizer with Power Law Kinetics

From the supersaturation balance Eqs. A1.7 and A1.8

$$G = \frac{\Delta c_f}{3k_v\rho\tau\mu_2} = \frac{k'}{\mu_2} \qquad \text{(A1.14)}$$

k' being a constant, and

$$B = k_RG^i\mu_3^j = k_R'\mu_2^{-i}\mu_3^j \qquad \text{(A1.15)}$$

where k_R and k_R' are relative rate constants.

The characteristic equation for this case is

$$\det\{\boldsymbol{J} - \lambda\boldsymbol{I}\} = \begin{vmatrix} -(1+\lambda) & 0 & -ik_R'\mu_2^{-(i+1)}\mu_3^j\tau & jk_R'\mu_2^{-i}\mu_3^{j-1}\tau \\ \dfrac{k'\tau}{\mu_2} & -(1+\lambda) & \dfrac{-k'\mu_0\tau}{\mu_2^2} & 0 \\ 0 & \dfrac{k'\tau}{\mu_2} & -\left(1+\lambda+\dfrac{2\mu_1\tau k'}{\mu_2^2}\right) & 0 \\ 0 & 0 & 0 & -(1+\lambda) \end{vmatrix} = 0 \qquad \text{(A1.16)}$$

On simplification the characteristic equation is

$$\lambda^4 + \alpha_3\lambda^3 + \alpha_2\lambda^2 + \alpha_1\lambda + \alpha_0 = 0 \qquad \text{(A1.17)}$$

where

$$\alpha_3 = 4 + \frac{2\mu_1\tau k'}{\mu_2^2}$$

$$\alpha_2 = 6 + 6\frac{\mu_1\tau k'}{\mu_2^2}$$

$$\alpha_1 = 6 + 6\frac{\mu_1\tau k'}{\mu_2^2} + ik_R'\mu_2^{-(i+1)}\mu_3^j\tau$$

$$\alpha_0 = 1 + 2\frac{\mu_1\tau k'}{\mu_2^2} + ik_R'\mu_2^{-(i+1)}\mu_3^j\tau + \frac{k'^2\tau^2}{\mu_2^2}\left(\frac{\mu_0}{\mu_2} + 1\right)$$

All the coefficients of the characteristic equation are positive for all positive kinetic and physical parameters.

Routh's stability criterion requires the following constraints to be satisfied for a stable system:

$$\alpha_3 > 0$$

$$\alpha_3\alpha_2 - \alpha_1 > 0$$

$$\frac{\alpha_3\alpha_2\alpha_1 - \alpha_1^2 - \alpha_3^2\alpha_0}{\alpha_3\alpha_2 - \alpha_1} > 0 \text{ or } \alpha_1 - \frac{\alpha_3^2\alpha_0}{\alpha_3\alpha_2 - \alpha_1} > 0$$

APPENDIX 2. EFFECT OF GROWTH RATE DISPERSION

In the treatment discussed in this paper a simple description arising from a linear first-order differential equation for the population balance around a continuous MSMPR crystallizer was used. Randolph and White (1977) in their modeling of size dispersion phenomena in different crystallizer configurations used an additional parameter, the effective growt rate diffusivity, to account for the effects of random variations in growth rates on the product crystal size distribution (CSD). They thus described continuous operations by the population balance involving a second-order differential equation with suitable boundary conditions. Using their description of the crystallizer configuration, the characteristic dimensionless function, $f_D(x)$, with dispersion effects may be derived by moment transformation of the population balance equation as

$$f_D(x) = f(x) + \frac{1}{\alpha}g(x) \qquad \text{(A2.1)}$$

where

$$g(x) = D_G\{a_1(x-\xi)^{b+g}(1-x)^j + a_2(x-\xi)^{b-g}(1-x)^j + a_3(x-\xi)^{3g} + a_4(x-\xi)^q\} \qquad \text{(A2.2)}$$

$$a_1 = 18\,k_v\rho c_f{}^{b+g+j-1}k_gk_b\tau^3$$

$$a_2 = 6\,k_v\rho c_f{}^{b-g+j-1}k_g^{-1}k_b\tau^2D_G$$

$$a_3 = -6\,k_v\rho c_f^{3g-1}k_g^{3g}\tau^4\dot{n}_0$$

$$a_4 = -12\,k_v\rho c_f^{g-1}k_g\tau^3\dot{n}_0D_G \qquad \text{(A2.3)}$$

Simultaneous solution of the equations representing equal slopes and the values of the function $f_D(x)$ and the tangents drawn from the point (1,0) to the function $f_D(x)$ at the point of the intersection yields the implicit relation.

$$\frac{g(x) + \alpha f(x)}{(1-x)} + \dot{g}(x) + \alpha\dot{f}(x) = 0 \qquad \text{(A2.4)}$$

The necessary condition for multiple solutions is that Eq. A2.4 should have two real distinct roots in the interval $\xi < x < 1.0$. The sufficient condition which will guarantee a unique solution to the solution balance may analogously be derived as

$$1.0 + \alpha\ddot{f}(x) + \dot{g}(x) > 0 \qquad \text{(A2.5)}$$

Using typical values of the parameters as given in Table A2.1 for evaluation of $f_D(x)$, $\dot{f}_D(x)$ and $\ddot{f}_D(x)$ it was found that over the entire range of x these functions have almost identical values to those of $f(x)$, $\dot{f}(x)$ and $\ddot{f}(x)$ respectively, indicating that the additional term, $(1/\alpha)g(x)$, in Eq. A2.1 representing the effect of dispersion, is insignificant. Such an observation was verified for this particular set of k and j values by varying all other parameters (e.g., D_G, $\dot{n}_0$, k_g, k_b, τ, etc.) over a wide range on either side of their specified values given in Table A2.1. The changes in values of functions $f_D(x)$, $\dot{f}_D(x)$ and $\ddot{f}_D(x)$ were trivial for large changes in these parameters. Hence, for all practical purposes these functions may be represented by the corresponding functions of $f(x)$ and all the indications are that the dispersion effects, being very small, will not exert any influence on the magma density function. The description of the configuration used suggests that it is the dispersion effect on the CSD that is significant rather than that on the solute concentration.

TABLE A2.1. TYPICAL PARAMETER VALUES USED IN SIMULATION OF DISPERSION MODEL

Parameter	
Solubility of the salt	
c_s, kg solute/kg solvent	0.15
Dimensionless saturation conc., ξ	0.7
Density of crystals, ρ, kg/m^3	2,662.0
Volume shape factor, k_v	0.525
Growth rate order, g	1.0
Nucleation rate order, b	2.0
$k = 3g + b$	5.0
Exponent of magma density, j	0, 0.5 and 2.0
Growth rate coeff.,	
k_g, m/s(kg/kg)^g	1.0×10^{-3}
Nucleation rate coeff.,	
k_b, no/s·kg solvent(kg/kg)^b(kg/kg)^j	1.0×10^{10}
Effective growth rate diffusivity,	
D_G, m^2/s	1.0×10^{-12}
Slope of the population density function	
at $L = 0$, $\dot{n}_0$, no/m^2·kg solvent	-1.0×10^{10}
Mean residence time of crystallizer, τ, s	10^4

NOTATION

A = characteristic matrix
a_i = constants, Eq. 13
b = nucleation order
B = nucleation rate, no/s·kg solvent
c = concentration of solute, kg solute/kg solvent
Δc = concentration driving force, kg solute/kg solvent
D_G = effective growth rate diffusivity, m^2/s
f_i = ith element of vector $\mathbf{f}(x)$
$\mathbf{f}(x)$ = vectorial representation of a set of derivatives
$f(x)$ = characteristic dimensionless function, Eq. 8
$f_D(x)$ = characteristic dimensionless function with dispersion, Eq. A2.1
$F(x)$ = dimensionless function, Eq. 12
g = growth rate order
$g(x)$ = dimensionless function associated with dispersion effect Eq. A2.1–A2.2
G = overall linear growth rate, m/s
j = exponent of magma density in the nucleation kinetics, Eq. 3
J_s = Jacobian matrix evaluated at steady state
k = constant, Eq. 7
k_b = nucleation rate constant, no/s·kg solvent (kg/kg)^b·(kg/kg)^j
k_g = growth rate constant, m/s(kg/kg)^g
k_v = volume shape factor
L = crystal size, m
m = constant, Eq. 20
M_T = magma density, kg crystal/kg solvent
n = population density function, no/m·kg solvent
$\dot{n}_o$ = slope of the population density function, n vs. L, at $L = 0$, no/m^2·kg solvent
Q = mass flowrate of solvent, kg/s
t' = time, s
t = dimensionless time, t'/τ
x = dimensionless concentration, c/c_f
$\mathbf{x}$ = vector of variables
x_j = jth element of $\mathbf{x}$
y = dummy variable

Greek Letters

α = slope parameter, Eq. 6
α_i = coefficients of λ^i in characteristic equation
ϵ = deviation variable of concentration from the steady state, Eq. 17
ξ = dimensionless saturation concentration, c_s/c_f
λ = eigenvalues of the characteristic matrix
μ_i = ith moment of the population density with respect to size, no·m^i/kg solvent
ρ = density of crystals, kg/m^3
τ = mean residence time, s

Subscripts

D = dispersion
f = feed
o = initial
s = saturation, steady state

Superscript

$\cdot$ = derivative with respect to x

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