Crystallization, Nucleation Systems

Introduction

The successful design of crystallizers to produce a predetermined size distribution is, at best, a result of extensive past experience with the material which is to be crystallized. Little success has resulted from attempts to determine in advance the size distribution from theoretical considerations alone. It has been shown, however, that a population balance over a crystallization system can relate the constraints of the system and the crystallization kinetics of the material to be crystallized to the size distribution obtained [1]. Much qualitative and quantitative information can be obtained from the application of the population balance which will dictate design choices.

Here we briefly review the basic population balance which has been presented in previous work by the authors and give examples of several design equations which derive therefrom. Some of the equations which are derived have been developed previously by other authors by alternative approaches. Our intent here is to show how these equations developed for various design configurations all derive directly from the general population balance. It will become evident that certain data will be needed in order to apply these equations to actual design. We therefore present a discussion of the data needed and a description of methods required for obtaining this data.

The procedure is limited to those kinds of crystallization systems which are substantially well mixed in the major portion of their crystallization volume, with any classification occurring only at the discharge. In other words, the crystal size distribution will be independent of spatial location in the crystallizer. For such a system the basic population balance is

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} + \frac{n_o}{\tau} = \frac{n_i}{\tau} \tag{1}$$

where n is the number density per unit volume of nagma at size L, G is the linear growth rate and τ is the mean crystal retention time. Subscripts o and i represent output and input, respectively. The mass balances applicable to each case vary slightly according to the crystallization configuration, consequently they are given as each example is discussed. The applicable energy balances will not be discussed as they follow directly when the mass flows are known.

In addition to the above conservation equation, suitable kinetic equations are needed. Simple experimentally determined power law forms are used. For growth rate G:

$$G = k_G s^n \tag{2}$$

where s is the supersaturation. The rate constant k_G can be a function of temperature, crystal size, and degree of agitation. The nucleation rate B^0 is represented by:

$$B^0 = k_N M^j s^m \tag{3}$$

It is presumed here that the predominant nucleation phenomenon in industrial crystallization is secondary nucleation; hence the indicated dependency on the suspension density M. Usually j can be taken as unity. The rate constant k_N is likely to depend on temperature, degree of agitation, and the presence of impurities.

داریم :

$\frac{\partial x}{\partial t}$ $\frac{\partial t}{\partial y}$

طراحی یعنی حل همزمان
موازنه جرم و جمعیتی

Design of Batch Crystallizers

Evaporative

Consider first an isothermal evaporative batch crystallizer of the stirred tank type (see Fig. 1) to be operated at the highest growth rate possible without appreciable nucleation. The seeded crystallizer is intended to produce a

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مجهولات :

۱- جرم اولیه Seed

۲- نرخ تبخیر

۳- حجم کریستالیزور

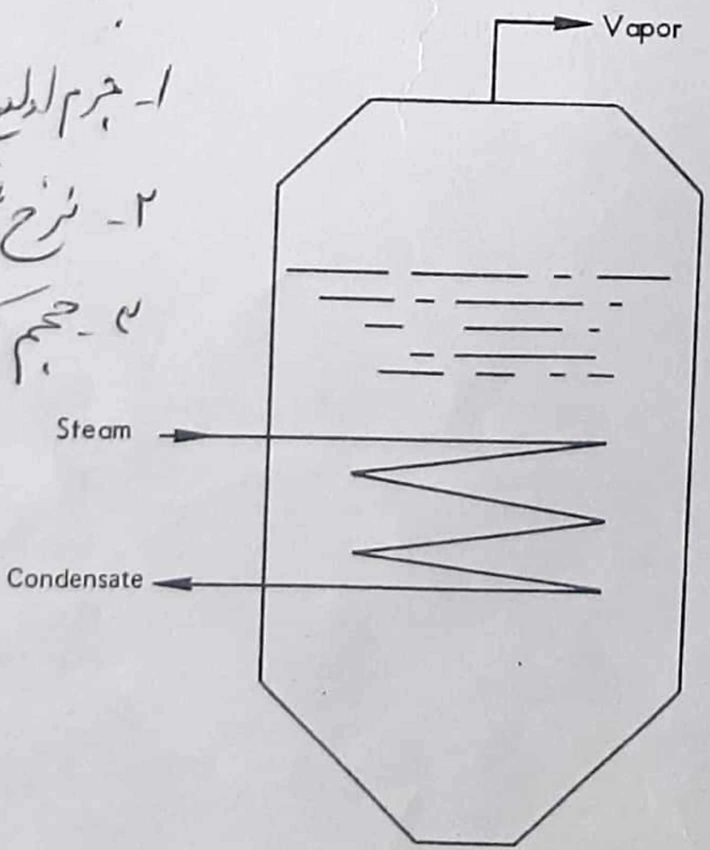

FIG. 1. Batch evaporative crystallizer.

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specified final size at a specified final suspension density. The latter is determined by the handling requirements of the slurry or by the limits of applicability of the nucleation kinetic model.

For a batch system, the population balance for nonsize-dependent growth becomes

$$\frac{\partial n}{\partial t} = -G\frac{\partial n}{\partial L'} \leftarrow \qquad \frac{\partial n}{\partial t} + G\frac{\partial n}{\partial L'} = 0 \qquad \text{جزء،} \qquad (4)$$

when n refers to the total crystallizer contents. (In batch design, n is based on the total contents of the crystallizer. For all other examples it is based on a unit volume of crystallizer contents.) The moment equations defined as

مثلا :

$$\frac{\partial x}{\partial t}\frac{\partial t}{\partial y} = -\frac{\partial x}{\partial y}$$

ن؟ :

$$G = \frac{\partial L'}{\partial t} = \frac{1}{N}\frac{\partial L}{\partial t}$$

$$L'N = L$$

$$m_j = \int_0^\infty nL^j\,dL$$

give the following set of unsteady state equations representing the number, length, area, and mass of crystals in the crystallizer [2]:

$$\frac{dN}{dt} = 0 \qquad \text{(no nucleation)}$$

$$\frac{dL}{dt} = NG$$

$$\frac{dA}{dt} = 2k_a LG$$

$$\frac{dM}{dt} = \frac{3k_v \rho AG}{k_a} \qquad (5)$$

where k_a and k_v are area and volume shape factors, respectively, and ρ is the density of the crystals.

A mass balance on the solute being crystallized gives

$$\text{غلط ثابت} \qquad C\frac{dV}{dt} + \frac{dM}{dt} = 0 \qquad \text{جزء} \qquad (6)$$

where V is the volume of solvent in the crystallizer and C is the solute concentration of the boiling liquor. Most crystallizers operate at very low supersaturation and therefore C in this equation can usually be taken as the saturation concentration at the operating temperature. M is the total mass of crystals in suspension.

By combining the moment equations and the mass balance, we obtain

$$C\frac{d^3V}{dt^3} + 6k_v \rho G^3 N = 0 \qquad (7)$$

where N is the number of seeds. The solution of this equation will give the time

↗
No Nucleation

variance of the solvent volume necessary to give the desired constant growth rate G. The initial conditions obtained from Eqs. (5) and (6) are

G = ثابت

V(t)

$$V(0) = V_0 \qquad \text{(initial solvent volume)}$$

$$\frac{dV}{dt}(0) = -3k_v G\rho(L_s^2 N)/C$$

$$\frac{d^2V}{dt^2}(0) = -6k_v G^2\rho(L_s N)/C \tag{8}$$

Here L_s is the seed size. If the seeds constitute a distribution of sizes, then L_s can be thought of as a mean size $\bar{L}_s$ and the $\bar{L}_s N$ and $\bar{L}_s^2 N$ in Eq. (8) can be computed as follows:

$$\bar{L}_s N = \int_{L_1}^{L_2} L n_s \, dL$$

$$\bar{L}_s^2 N = \frac{1}{2}\int_{L_1}^{L_2} L^2 n_s \, dL \tag{9}$$

where n_s is the distribution function of the seeds and L_1 to L_2 is the seed size range.

Integration of Eq. (7) with initial conditions (8) gives

$$C(V_0 - V) = k_v\rho G^3 N t^3 + 3k_v\rho G^2 L_s N t^2 + 3k_v\rho G L_s^2 N t \tag{10}$$

or letting

$$\phi = VC/3k_v\rho L_s^3 N = VC/3M_s \qquad \text{and} \qquad Z = Gt/L_s$$

gives

$$\phi_0 - \phi = Z^3/3 + Z^2 + Z \tag{11}$$

and

$$-\frac{d\phi}{dZ} = Z^2 + 2Z + 1 \tag{12}$$

Equation (12) thus gives the rate of solvent evaporation necessary to achieve the desired constant growth rate. It should be noted that Z_f, the *final* value of Z, is also a measure of the increase in size of the seed crystals. Thus

$$Z_f = Gt_f/L_s = (L_f - L_s)/L_s \tag{13}$$

An equation similar to Eq. (11) has been published by Nývlt and Mullin [3] for cooling crystallization and is plotted by Nývlt [4] for design purposes.

Example. Design a simple stirred batch evaporative crystallizer which must operate under the following specifications:

Product crystal size	10^{-3}m
Production per batch	1000 kg
Solubility at crystallizer temperature	400 kg/m^3 solvent
Maximum suspension density	200 kg/m^3 solvent
Density of crystal	1.5×10^3 kg/m^3
Volume shape factor	1
Maximum allowable growth rate	10^{-7}m/s
Seed size	10^{-4}m

(a) Determine crystallizer volume:

Final solvent volume	1000 kg/200 kg/m^3	= 5m^3
Solvent evaporated	1000/400	= 2.5 m^3
Total solvent per batch		= 7.5 m^3 × 1.25

= 9.4

Knowing the volume change due to dissolving the solute and the necessary vapor disengaging space, the volume of the crystallizer can be calculated.

(b) Determine number and mass of seeds:

$$\text{Number } N = 1000/(10^{-3})^3(1)(1.5 \times 10^3)$$

$$= 6.67 \times 10^8 \text{ seeds}$$

$$\text{Mass } M_s = (10^{-4})^3(1.5 \times 10^3)(6.67 \times 10^8) = 1 \text{ kg}$$

(c) Determine batch time and evaporation programme:

$$Z_f = (10^{-3} - 10^{-4})/10^{-4} = 9$$

$$t_f = (10^{-4})(9)/10^{-7} = 9000 \text{ s} = 2\frac{1}{2} \text{ h}$$

From Eq. (12):

$$-\frac{C}{3M_s} \cdot \frac{L_s}{G} \cdot \frac{dV}{dt} = \left(\frac{G}{L_s}\right)^2 t^2 + 2\frac{G}{L_s}t + 1$$

and

$$\frac{dV}{dt} = (7.5 \times 10^{-12})t^2 + (1.5 \times 10^{-8})t + (7.5 \times 10^{-6})$$

The above equation is plotted in Fig. 2 to show how the evaporation rate must increase with time. The program might be best realized using a reflux condenser. In any event, knowing the maximum rate of solvent removal and the final volume of slurry in the system, the heat exchangers can be designed. The initial rate of evaporation required, 7.5×10^6 m^3/s, is perhaps unrealizably low but must be approached to achieve the desired result.

The above treatment applies equally well when the system is operated with continuous feed in a semibatch manner. So long as the feed is introduced at the

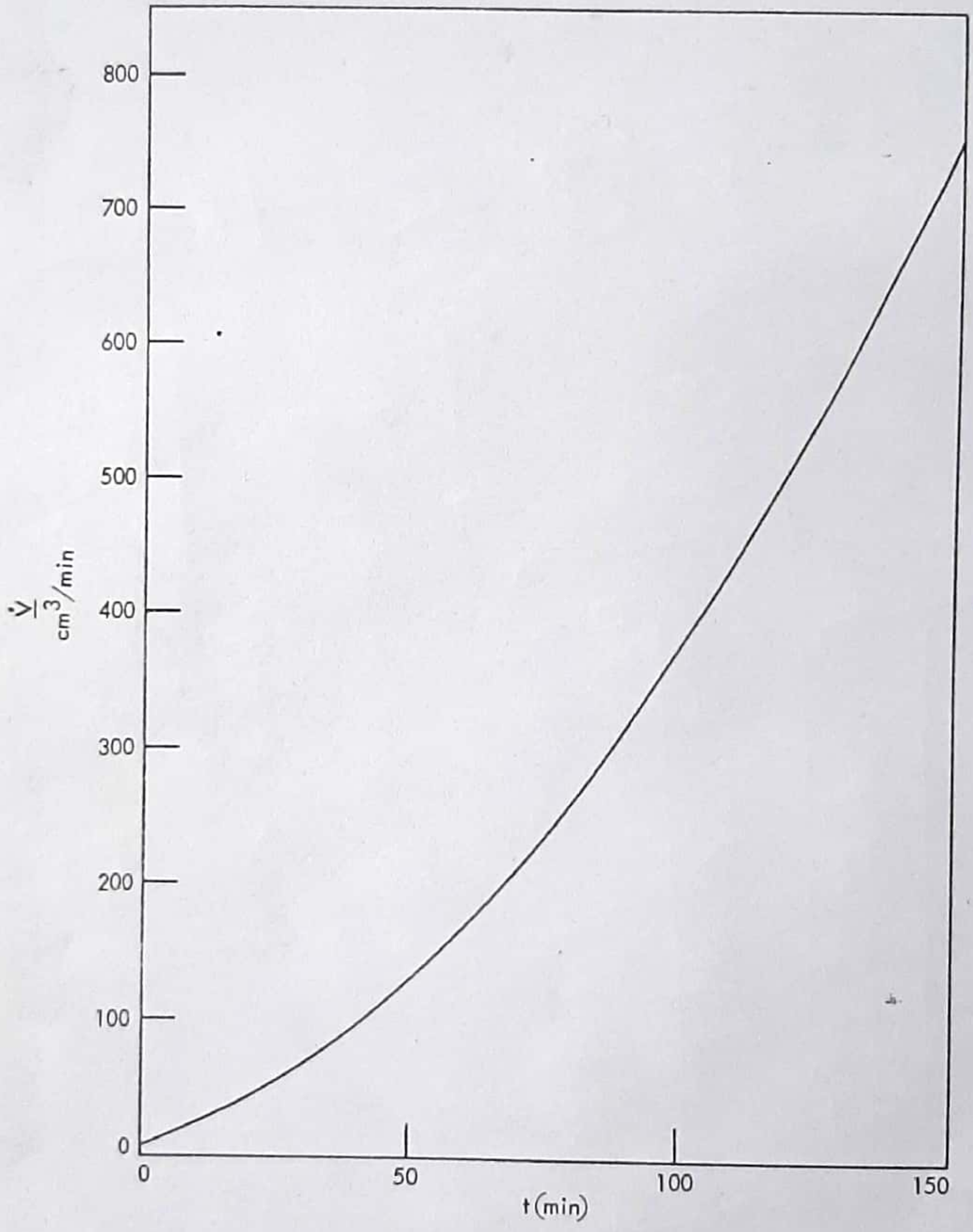

FIG. 2. Evaporation rate program.

evaporation temperature, no alteration in calculation is needed. The overall effect of the method of operation is that a smaller vessel would be needed for the same production per batch. If feed is introduced at a temperature or concentration different from that in the crystallizer, the energy input rate must be changed accordingly. The feed rate must vary with time in a manner consistent with the crystal production rate determined by Eq. (12).

Cooling

If it is desired to crystallize by cooling so that a constant optimal growth rate is maintained, the above equations still apply. As previously noted, this case has been fully treated by Nývlt and Mullin [3]. Here we show only how their result relates to the general population balance and to the evaporative case.

The mass balance is now

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$$V\frac{dC}{dt} + \frac{dM}{dt} = 0 \longrightarrow Vb\frac{dT}{dt} + \frac{dM}{dt} \qquad (14)$$

$\Delta C =$ ثابت

$C - C_s =$ ثابت

$\frac{dc}{dt} = \frac{dC_s}{dt} = b\frac{dT}{dt}$

on the same volume basis as for the evaporative case. Again if the system supports a very low supersaturation and if the saturation concentration is given as a function of temperature by

$$C_s = a + bT \qquad (15)$$

Eq. (10) becomes

$$bV(T_0 - T) = k_v \rho G^3 N t^3 + 3k_v \rho G^2 L_s N t^2 + 3k_v \rho G L_s^2 N t \qquad (16)$$

Letting

$$\phi' = \frac{bVT}{3k_v \rho L_s^3 N} = \frac{bVT}{3M_s} \quad \text{and} \quad Z = \frac{Gt}{L_s}$$

gives

Cooling Program

$$\phi_0' - \phi' = Z^3/3 + Z^2 + Z \qquad (11a)$$

and

No Nucleation

$$-\frac{d\phi'}{dZ} = Z^{2} + 2Z + 1 \qquad (12a)$$

If the temperature–solubility relationship is known, then these equations can be applied in the same manner as for the evaporative system to determine a cooling program.

If growth is a function of crystal size and the supersaturation at the growth rate fixed for the seed crystals is sufficiently low to cause no nucleation, then the function $G(L)$ can be incorporated in the formulation of the moment equations and the set solved to obtain similar results for both evaporative and cooling systems. Needless to say, the computation will be more difficult and is likely to require numerical solution.

For systems where nucleation occurs, the zeroth moment equation is no longer equal to zero. Thus the design equation will be fourth order rather than third order, and the system of equations is likely to be nonlinear.

In principle, the set can be solved but again the ease of solution and the result are highly dependent on the initial conditions which obtain in the crystallizer. Baliga [2] has analyzed several cases where nucleation occurs as well as the case of size-dependent growth.

Design of Continuously Seeded Crystallizers

We consider now a continuous mixed suspension mixed product removal (MSMPR) crystallizer which is continuously seeded with seeds of size L_s and in which no nucleation takes place (see Fig. 3). This could well be an idealized continuous sucrose crystallizer. Again there will be a maximum supersaturation permissible and hence a maximum growth rate allowable to avoid nucleation. The design now involves selecting a residence time and production rate to produce, at the required growth rate, a crystal product of some specified average, (or mean) size.

For this case the population balance becomes

$$\int_{n_s^0}^{n} \frac{dn}{n} = -\int_{L_s}^{L} \frac{dL}{G\tau} \tag{17}$$

or

$$n = n_s^0 \exp\left(-(L - L_s)/G\tau\right)$$

where L_s is the seed size.

A mass balance on the solute at steady state becomes

$$P_c = 3\frac{K_v}{K_a}G\rho\frac{V}{Q}A$$

$$\frac{A}{K_a} = \int_{L_s}^{\infty} nL^2\,dL$$

(5) معادله

$$-V\frac{dM}{dt} = 3\frac{k_v}{k_a}GA\rho V = S(C_i - C_0) \tag{18}$$

$$= \frac{m^3}{Sec}\left(\frac{kg\ solute}{m^3\ solvent\ fed}\right)$$

where A is the total surface area of crystals in suspension per unit volume of slurry, V, and ρ is the crystal density. The factor $3k_v/k_a$ arises because the growth rate G refers to the rate of growth of the characteristic crystal size, L. S is the volumetric feed rate on a solute-free basis and C_1 and C_0 are the input and output concentration based on solvent fed. (Note that the basis for continuous systems is different from that of batch systems. All solute concentrations are based on solute-free solvent volume but all slurry concentrations, for example, crystal number, crystal area, suspension density and production, P_c, are based on unit suspension volume. This is done (a) to enable the generalization of all kinds of multiple discharge systems, and (b) because nucleation kinetics must normally be determined experimentally on this basis.)

Defining the production P_c as mass of crystals per unit volume of crystallizer output magma gives

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$$P_c = \frac{S(C_i - C_o)}{Q} \tag{19}$$

$$\frac{\frac{m^3\ Solvent}{Sec} \times \frac{kg\ Solute}{m^3\ Solvent}}{\frac{m^3\ slurry}{Sec}}$$

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where Q is the total volumetric slurry and liquid withdrawal rate from the system. For this case then, the crystal mean retention time τ is V/Q.

Substituting P_c into (18) and rearranging gives

$$P_c = 3\tau G k_v \rho \int_{L_s}^{\infty} n L^2 \, dL$$

or

$$P_c = 3\tau G k_v \rho \int_{L_s}^{\infty} n_s^0 \exp\left(-\frac{L - L_s}{G\tau}\right) L^2 \, dL \tag{20}$$

Equation (20) has been previously described by Randolph and Larson [1]. The integral merely expresses crystal surface area, A, as a function of the distribution.

We note that n_s^0 is the number density of seeds per unit volume of magma at size L_s, $n_s^0 G$ is the seed number introduction rate per unit volume, and $n_s^0 G\tau$ is the number of seeds per unit volume of magma in the crystallizer. We denote the last quantity by the symbol N_s.

Performing the necessary integration in Eq. (20) and rearranging gives

$$P_c/3k_v \rho N_s = G\tau L_s^2 + 2(G\tau)^2 L_s + 2(G\tau)^3$$

or

$$\psi = \frac{P_c}{M_s} = 3\left(\frac{1}{x_s} + \frac{2}{x_s^2} + \frac{2}{x_s^3}\right) \tag{21}$$

- where M_s is the mass of seeds per unit volume of magma and x_s is the dimensionless seed size $L_s/G\tau$.

For such a crystallizer it can be shown that the maximum value of the mass distribution curve (the mode) L_D occurs at

$$L_D = 3G\tau \tag{22}$$

This is usually termed the dominant crystal size.

Characteristic sizes other than the mode can be used too, but they will all be simple multiples of $G\tau$. A characteristic size and the coefficient of variation (C.V.) completely characterize the size distribution, but the absolute values of this size and C.V. depend on seed size. In the subsequent illustration we characterize the distribution by L_D only but other criteria may also be used.

The dimensionless dominant size $x_D = L_D/L_s = 3/x_s$. Substituting into Eq. (21) gives

$$\psi = x_D + \frac{2}{3}x_D^2 + \frac{2}{9}x_D^3 \tag{23}$$

With these equations it is now possible to calculate the necessary design parameters to achieve a desired dominant crystal size.

Example. Design a simple continuous stirred cooling crystallizer of the type shown in Fig. 3 which requires continuous seeding and must operate under the following specification:

Dominant crystal size	10^{-3} m
Crystal production rate	1000 kg/h
Suspension density	100 kg/m^3 magma
Crystal density	1.5×10^3 kg/m^3
Volume shape factor	1
Maximum growth rate	10^{-7} m/s
Seed size	10^{-4} m

(a) Determine mean crystal residence time using Eq. (22):

$$\tau = \frac{L_D}{3G} = \frac{10^{-3}}{3 \times 10^{-7}} = 3333 \text{ s} = 0.93 \text{ h}$$

(b) Determine mass and number of crystals required. For this configuration:

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$$\xrightarrow{} P_c = M = 100 \text{ kg/m}^3 \text{ magma}$$

داخل کریستالیزور

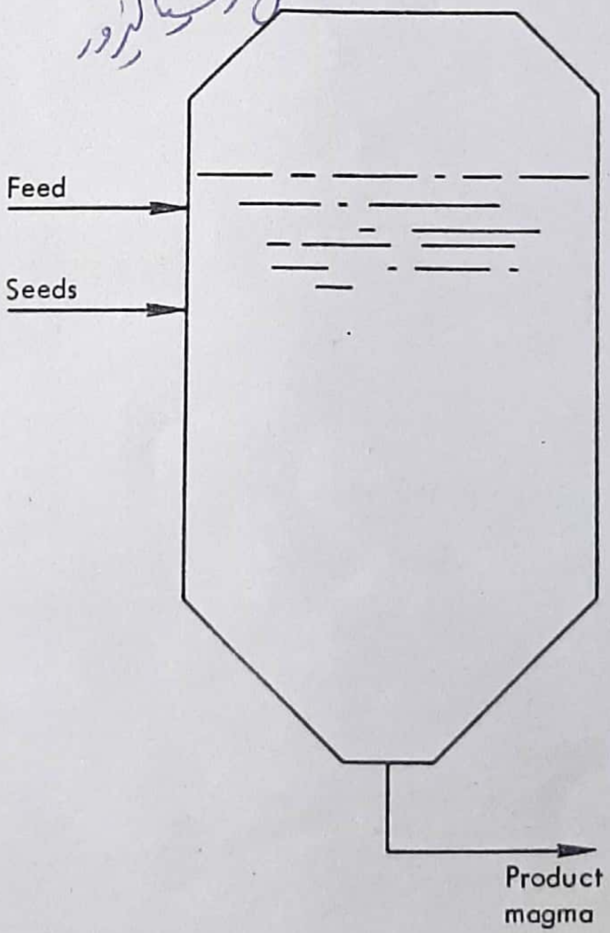


FIG. 3. Continuously seeded crystallizer.

From Eq. (23):

$x_D = \frac{L_D}{L_s} = 10$

$$\frac{P_c}{M_s} = \left[10 + \frac{2}{3}(10^2) + \frac{2}{9}(10^3)\right] = 299$$

$$M_s = 0.33 \text{ kg/m}^3 \text{ magma}$$

$$N_s = \frac{M_s}{k_v \rho L_s^3} = 2.2 \times 10^8 \text{ seeds/m}^3 \text{ magma}$$

(c) Determine volume and flow:

$$Q = \frac{1000}{100} = 10 \text{ m}^3\text{/h}$$

$$V = \tau Q = 0.93 \times 10 = 9.3 \text{ m}^3$$

(d) The input flow will be determined by Eq. (19). Clearly P_c or M for a cooling system is set to some degree by the available temperature drop and the solubility of the solute, and so itself becomes a choice variable. For evaporative systems a greater choice exists for the value of the suspension density. The calculation is the same for either case except for the application of Eq. (19) where the amount evaporated must be accounted for. Using the above basis always ensures that the proper residence time is calculated.

Design of Continuous Self-Nucleating Crystallizers

This class of crystallizers includes the MSMPR crystallizer, those with clear liquor overflow, draft-tube-baffle types with fines removal and circulating magma, as well as others with a large identifiable well-mixed section. Again for systems with size independent growth, Eq. (1) becomes

$$G \frac{dn}{dL} + \frac{n}{\tau} = 0 \tag{24}$$

where τ is the mean retention time of the *crystals*.

In the three examples previously cited, the only kinetic information really required is a clear definition of metastable region so that a maximum permissible growth rate can be prescribed. In self-nucleating systems a full knowledge of the nucleation and growth kinetics is required, and for full exploitation of the design equations the parameters and exponents in Eqs. (2) and (3) must be known.

From Eq. (24) we obtain for the MSMPR crystallizer [1]

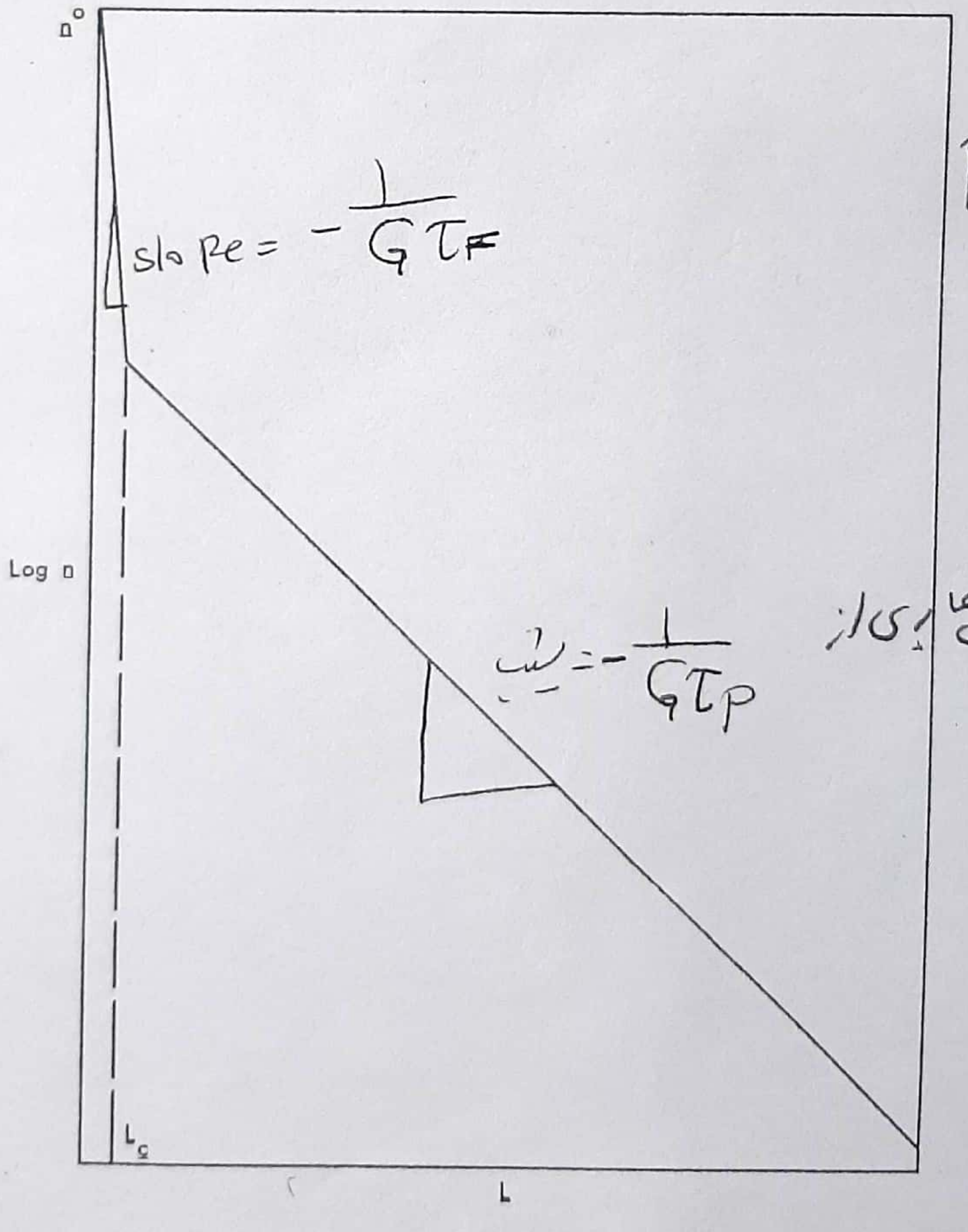
$$n = n^0 \exp(-L/G\tau) \tag{25}$$

where n^0 is the population density of nuclei.

When fines are being destroyed in the system, the above equation must be written in two parts:

$$\begin{aligned} n &= n^0 \exp(-L/G\tau_F) & L < L_c \\ &= n^0 \exp(-L_c/G\tau_F)\exp(-(L-L_c)/G\tau_p) & L > L_c \end{aligned} \qquad (26)$$

where τ_F and τ_p are the mean retention times of the fines and product crystals respectively. L_c is the largest crystal size destroyed and is called the cut size. A typical semilog plot of the size distribution for this case is shown in Fig. 4.



slope $= -\frac{1}{G\tau_F}$

شیب $= -\frac{1}{G\tau_p}$

FIG. 4. Size distribution (fines destruction).

$P_c = \bar{u}$

$M =$

$P_c =$

بازای

uation must be

(26)

oduct crystals
the cut size. A
own in Fig. 4.

$$\begin{cases} 3\frac{K_v}{K_a} G A \rho V = \text{[illegible]} = S(C_i - C_o) \\ P_c = \frac{S(C_i - C_o)}{\varnothing} \end{cases}$$

For MSMPR cases with clear liquor overflow, the mass balance, Eq. (18), becomes

$$P_c = 3\tau G k_v \rho \int_0^\infty n L^2 \, dL$$

or

$$P_c = 6 k_v \rho n^0 (G\tau)^4 \tag{27}$$

For fines destruction systems where the *mass* of fines destroyed can be neglected, the same equation applies but $n^0_{\text{eff}} = n^0 \exp(-L_c/G\tau_F)$ and $\tau = \tau_p$.

~~The important kinetic consideration~~ in design is the relationship between the growth and nucleation kinetics. As it is difficult to determine beforehand the level of supersaturation required, it is convenient for design purposes to combine Eqs. (2) and (3) to give

$B^0 = K_N M^j S^m$

$$P_c = \frac{\text{production}}{\text{unit Volume magma}} \qquad S = \left(\frac{G}{K_G}\right)^{1/n}$$

$$B^0 = \frac{k_N}{k_G^{m/n}} M^j G^{m/n}$$

or

$$M = \frac{\text{mass of crystal}}{\text{unit Volume magma}}$$

$$B^0 = k_R M^j G^i \quad , \; K_R(T, N) \tag{28}$$

Most data available indicate that *i* and *j* are not functions of temperature and agitation, only the rate constant k_R being a function of these variables. The presence of additives changes both the rate constant and the orders.

The mass balance does not contain B^0 explicitly but

$$B^0 = n^0 G = \frac{\partial N}{\partial L} \times \frac{\partial L}{\partial t} = \frac{\partial N}{\partial t} \tag{29}$$

$P_c = M$

وقتی که محصول را به صورت عاری از محلول در نظر بگیریم

for the cases to be considered.

Combining Eqs. (27), (28), and (29) gives با حذف n^0

$$P_c = 6 k_v \rho \frac{B^0}{G} (G\tau)^4 \tag{30}$$

an equation relating the kinetics, mean retention time, and the production P_c. It remains only to incorporate a representation of the crystal size distribution to obtain a suitable design equation.

For the cases to be discussed in this section it has been shown that the coefficient of variation of the size distribution is always predicted to be 50%. As a consequence the size distribution is completely described by a mean or average size. In the previous section it was noted that the mode of the mass distribution curve is $L_D = 3G\tau$. This is a suitable representation of the distribution. However, other characteristic sizes can be used in the same manner as L_D because they are all simple multiples of $G\tau$ [1]. For example, the median size, the size below which half of the mass exists, is

$$L_M = 3.67\, G\tau \tag{31}$$

L_M اندازه‌ای از ذرات است که نیمی بزرگتر، نیمی کوچکتر هستند

The subsequent use of L_D as the size characterizing the size distribution therefore does not affect the generality of the results. Substituting $L_D/3$ for $G\tau$ in Eq. (30) gives

$$P_c = 2k_v \rho B^0 L_D{}^4/27G \qquad (32)$$

با حذف τ

This is the basic design equation resulting from the population balance with L_D being the representation of the size distribution. We now illustrate its use by considering a number of cases exhibiting different kinetics and different process configurations.

Case I: MSMPR, $j = 1$, $i > 1$, $P_c = M = \dfrac{\text{جرم کریستالها}}{\text{واحد حجم خروجی از کریستالیزور}} = \dfrac{\text{جرم}}{\text{دبی خروجی}}$

This is the classic case using kinetics most often encountered, namely secondary nucleation kinetics of order greater than growth kinetics. Substituting the appropriate kinetics into (32) gives

$$\frac{B^\circ}{G} = K_R M G^{i-1}$$

$$\cancel{P_c} = 2k_v \rho G^{i-1} k_R \cancel{M} L_D{}^4/27 \qquad (33)$$

By definition of P_c, $P_c = M$ and Eq. (33) becomes

$$G = \left[\frac{27}{2L_D{}^4 k_v k_R \rho}\right]^{\frac{1}{i-1}} \qquad (34)$$

Specification of L_D permits the calculation of the appropriate growth rate, and then from Eq. (22) the retention time can be calculated. Thus

$$\tau = L_D/3G \qquad (35)$$

طراحی کریستالیزور شامل تعیین τ می‌شود که ابتدا G از رابطه بالا بدست می‌شود.

For $i > 1$ the size distribution can therefore be altered to some degree by changing the retention time τ. Clearly there are limits to the degree to which the size distribution can be changed by changing residence time alone, and the specification of *any* L_D is not possible. As $i \rightarrow 1$, the range of possible values of L_D narrows and approaches one value.

For $j = 1$ the suspension density disappears from the design equation and therefore does not affect the size distribution. It must therefore be specified from other considerations such as the solubility of the solute and the handling properties of the slurry. Once M is determined and the desired production rate is known, the flow rates, crystallizer volume, and energy inputs (or removals in the case of cooling) can be determined from the calculated residence time.

Alternatively, if a growth rate is to be specified because of crystal quality considerations or other reasons, L_D can be calculated by rearranging Eq. (34) as

$$L_D = \left[\frac{27}{2k_v k_R \rho G^{i-1}}\right]^{1/4} \qquad (36)$$

Alteration in the kinetic constant k_R or order i resulting from changes in temperature or addition of additives can also be evaluated by use of Eq. (35) and (36).

Example. Design an $\boxed{\text{MSMPR}}$ cooling crystallizer of the type shown in Fig. 5 to produce a crystal product under the following specifications:

Dominant crystal size	4×10^{-4} m
Production rate	400 kg/h
Suspension density	200 kg/m^3 magma
Volume shape factor	1
Crystal density	1.8×10^3 kg/m^3
هسته‌زایی داریم Relative kinetics	$B^0 = 3 \times 10^{15}\, M G^{1.5}$ (m^3 slurry)$^{-1}$ s^{-1}

$i = 1.5$, $j = 1$

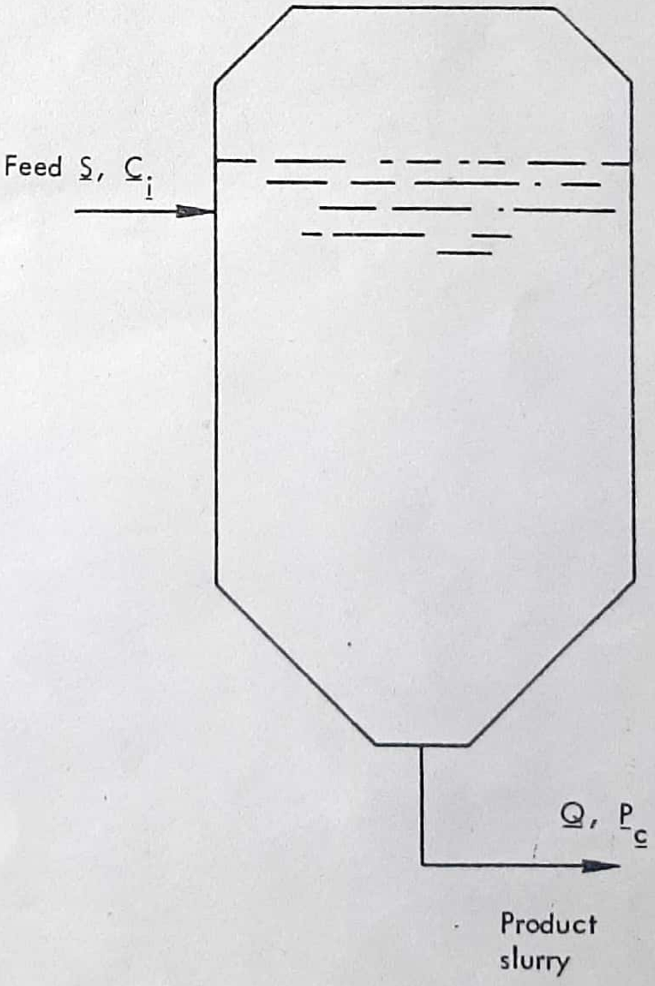


FIG. 5. MSMPR crystallizer.

(a) Determine appropriate growth rate from Eq. (34):

$$G = \left[\frac{27}{2(4)^4(10^{-16})(3 \times 10^{15})(1.8 \times 10^3)}\right]^{1/0.5}$$

$$= 9.5 \times 10^{-9} \text{ m/s}$$

(b) Determine retention time:

$$\left\{\begin{array}{l} P_c = 6K_v\rho \\ B^0 = K_R M^j \end{array}\right.$$

$$\tau = \frac{4 \times 10^{-4}}{3 \times 9.5 \times 10^{-9}} = 14030 \text{ s} = 3.89 \text{ h}$$

(c) Determine discharge flow and crystallizer volume:

$$Q = 400/200 = 2 \text{ m}^3\text{/h}$$

$$V = 2 \times 3.89 = 7.78 \text{ m}^3$$

Again the feed rate can be calculated from Eq. (19), and with a knowledge of the solubility curve and the heat capacity, the heat exchange surface can be determined and the design completed.

The same equations apply for an evaporative system so long as it is remembered that τ is the residence time of the crystals and the evaporation must be accounted for in Eq. (19). For the evaporative case it will also be necessary to alter the volume of the crystallizer body to allow for vapor disengagement space above the liquor surface. The heat exchange surface will depend on the production rate, the temperature of the feed, and the amount of vapor produced.

Case II: MSMPR, $j = 1$, $i = 1$ $P_c = M$

As previously mentioned, Eq. (34) loses its applicability as i approaches unity. It is not possible to get an arbitrary L_D by fixing residence time alone. As i gets closer and closer to unity, the choices of residence time decrease so that when nucleation and growth are of the same order and when nucleation is secondary and directly proportional to suspension density, only one size distribution can be obtained in the MSMPR configuration. Thus L_D must be calculated directly by

$$B^0 = K_R M G$$

$$L_D = \left[\frac{27}{2k_v k_R \rho}\right]^{1/4} \tag{36a}$$

Equation (36a) indicates that the only way in which the product size distribution can be altered is by a change in the rate constant k_R. This could be done by changing the temperature of operation, changing the degree of agitation, or by introducing kinetic altering additives.

Evidently in this case any residence time and any suspension density can be used so long as the suspension density lies within the validity of the kinetic model. Design parameters such as M and τ will therefore be dictated by other considerations.

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Case III: MSMPR, $j \neq 1$, $i \neq 1$, $P_c = M$

$$P_c = 6K_v\rho \frac{B^\circ}{G}(G\tau)^4$$

$$B^\circ = K_R M^j G^i$$

$$M = 6K_v \rho K_R M^j G^{i-1} \left(\frac{L_D}{3}\right)^4$$

When primary nucleation, either homogeneous or heterogeneous, is the principal mode of nucleation or when nucleation is secondary but not a linear function of suspension density, the magnitude of M enters into the calculation and the choice of suspension density becomes a design parameter. Thus rewriting Eq. (34) gives

$$G = \left[\frac{27 M^{1-j}}{2L_D^4 k_v k_R \rho}\right]^{\frac{1}{i-1}} \tag{34a}$$

For example, the design equation for a system such as that shown in Fig. 5 where the order of nucleation $i = 1.5$ and the nucleation rate depends on the square root of suspension density is

$i = 1.5$
$j = 0.5$

$$G = \left[\frac{27 M^{0.5}}{2L_D^4 k_v k_R \rho}\right]^2 \tag{37}$$

In this particular instance, for a fixed L_D the appropriate growth rate becomes a linear function of the suspension density. As a consequence there is more than one combination of M and τ which will give the desired dominant crystal size.

If the growth rate is to be set, then

$$L_D = \left[\frac{27 M^{0.5}}{2k_v k_R \rho G^{0.5}}\right]^{0.25} \tag{38}$$

mandatory ← G معلوم

Case IV: MSMPR Arbitrary Suspension

MSMPR systems are frequently operated with a clear liquor overflow, and with this configuration are sometimes called growth crystallizers. Thus a cooling crystallizer can be operated at an arbitrary suspension density, the magnitude of which is determined by the ratio of the underflow and overflow. Such a crystallizer is shown in Fig. 6. If one regards the body volume as composed of two parts, the lower containing the suspension and the upper the clear liquor free of crystals, then the volume V_u in Fig. 6 is the mixed suspension volume, Q_u is the outflow and the mean retention time of the crystals, τ is V_u/Q_u. P_c is the production per unit volume of the stream Q_u, and the production rate is $P_c Q_u$, just as in the previous examples.

In the general case for $i > 1$ and $j \neq 1$, Eq. (34a) applies as it is written. When $j = 1$ the only advantage of this configuration is to reduce the crystallizer volume for a given production rate and crystal size requirement, the limitations being only an ability to handle the suspension density obtained and the ease of separating the clear liquor in the crystallizer body. When $j \neq 1$ the suspension density will have an effect on the crystal size and therefore becomes a choice variable along with retention time.

$S = Q_o + Q_u$ موازنه حجم

وقتی برقرار است که:

$\rho_f = \rho_o = \rho_u$

$\rho_o \neq \rho_u$ که البته نمی تواند

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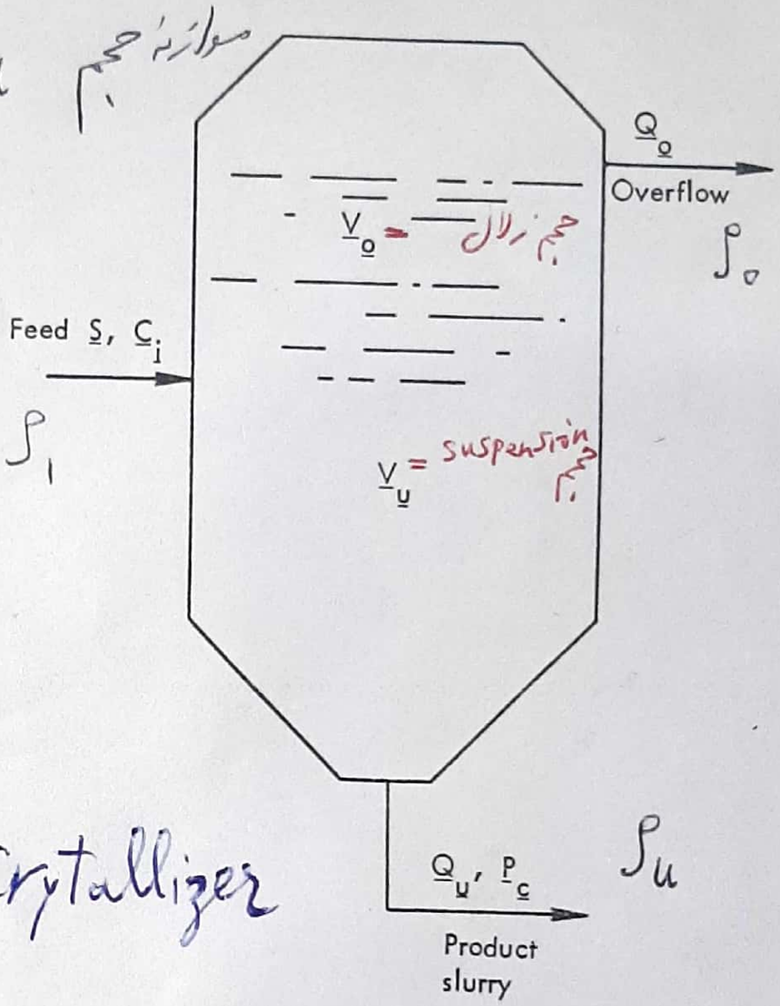

growth Crytallizer

FIG. 6. Arbitrary suspension. V_o = Clear liquor volume. V_u = Magma volume.

Once τ and P_c are fixed, the feed rate S and $C_i - C_o$ can be determined using Eq. (19). When S is known, this, along with a knowledge of the volume change due to crystallization, can be used to determine Q_u.

Example. Determine the feed rate in terms of cubic metres of solvent per hour and the overflow Q_o (m^3 suspension/h) for the following partially designed arbitrary suspension cooling crystallizer.

Production rate, P	1000 kg/h
Suspension density of product stream	400 kg/m^3 slurry
Concentration change in feed ($C_i - C_o$)	200 kg/m^3 solvent

$$P_c = S(C_i - C_o)/Q_u$$

$$Q_u = P/P_c$$

Assume no volume change on dissolution or crystallization:

$P = S(C_i - C_o)/Q_u$

دبی حجمی [illegible] خروجی ←

$$Q_u = 1000/400 = 2.5 \text{ m}^3/\text{h}$$

$$S \times 200 = 400 \times 2.5$$

حلال ورودی

$$S = 5 \text{ m}^3/\text{h}$$

$$Q_o = 2.5 \text{ m}^3/\text{h} = S - Q_u$$

Case V: Draft Tube Baffle with Fines Destruction

Frequently a crystallizer of the kind discussed as Case IV produces crystals of a larger size than predicted by the equations. This may well be because the overflow is not "clear liquor" but contains nuclei or very small crystals. The net result of nuclei removal (or destruction) is an increase in crystal size.

The draft-tube-baffle crystallizer shown in Fig. 7 exploits this effect. Here a baffle is used to form a calming section which causes the larger crystals to settle out and an overflow liquor containing only crystals from the small size range is removed. The largest crystal removed in this stream is determined by the liquid velocity and the terminal settling velocity of the crystals.

If the design is such that only very small crystals, say less than 10 μm, are removed, then the mass represented by these crystals is relatively small and can generally be neglected. From Eq. (26) the crystal distribution is approximately represented by

$$n = n^0 \exp\left(-\frac{L_c}{G\tau_F}\right) \exp\left(-\frac{L - L_c}{G\tau_p}\right) \tag{39}$$

and for $\tau_p \gg \tau_F$:

$L >> L_c$

$$n = n^0 \exp\left(-\frac{L_c}{G\tau_F}\right) \exp\left(-\frac{L}{G\tau_p}\right) \tag{40}$$

$\tau_F = \frac{V}{Q_o + Q_u}$

$\tau_p = \frac{V_1}{Q_u}$

where τ_F is the mean retention time of the fines and is equal to the total body volume divided by the sums of Q_o and Q_u. τ_p is the mean retention time of the product crystals and is equal to the volume of the mixed suspension portion of the body divided by Q_u. The plot in Fig. 4 shows a system where $\tau_p = 10\tau_F$.

We may now think of the constant term, $n^0 \exp(-L_c/G\tau_F)$ in Eq. (40) as an effective nuclei population density and thus

$$B^0_{\text{eff}} = Gn^0 \exp(-L_c/G\tau_F)$$

or

$$B^0_{\text{eff}} = k_r M^j G^i \exp(-L_c/G\tau_F) \tag{41}$$

Substituting into Eq. (32) gives

$$P_c = \frac{2}{27} k_v k_R \rho M^j G^{i-1} L_D{}^4 \exp(-L_c/G\tau_F) \tag{42}$$

↑ مد

$3(G\tau_p) = L_D$

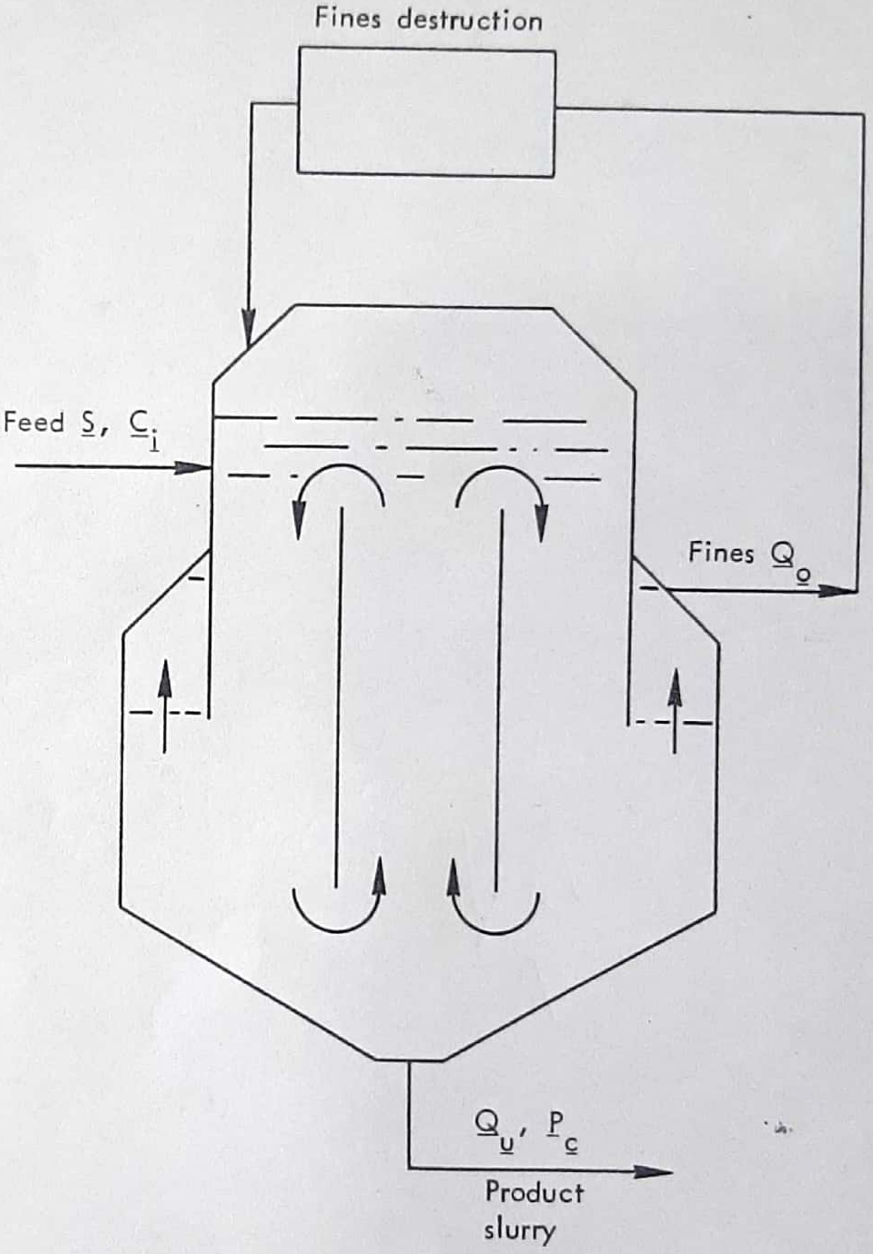

FIG. 7. Draft-tube-baffle crystallizer.

Let the ratio of the mean retention times be

$$\gamma = \tau_p / \tau_F \tag{43}$$

Using the size characterization L_D and the ratio γ, the exponential in Eq. (42) can be expressed as

با حذف G داریم

$$\exp\left(-3L_c\gamma/L_D\right)$$

where L_c and γ are choice variables, although they are not totally independent as the cut size L_c depends on the flow velocity in the baffle which in turn depends on the volumetric flow Q_o. ~~As in Case IV. P_c as defined is equal to M.~~

The basic design equation for the DTB crystallizer when the mass of fines destroyed can be neglected becomes

Eq.(34a) →
$$G = \left[\frac{27 M^{1-j}}{2 L_D^4 k_v k_R \rho \exp(-3L_c\gamma/L_D)}\right]^{\frac{1}{i-1}} \tag{44}$$

In addition to the required mean crystal size L_D, there are three other variables to fix in order to solve Eq. (44), namely L_c, γ, and M. They are not independent and therefore the freedom of choice is limited. The equation, however, is still useful for determining a feasible combination of these variables.

Example. Design a DTB cooling crystallizer to produce the product described in the illustration for Case I and to conform to the following specifications:

$$\gamma = 10 \qquad i = 1.5$$
$$L_c = 10^{-5}\ \text{m} \qquad j = 1.0$$

, Page 15

$L_D = 4 \times 10^{-4}$ m

The configuration is as shown in Fig. 7.

(a) Determine the growth rate and the retention times τ_p and τ_F.

$$G = \left[\frac{27}{2(4)^4(10^{-16})(\underset{K_R}{3 \times 10^{15}})(\underset{\rho}{1.8 \times 10^3}) \exp(-3/4)}\right]^{1/0.5}$$
$$= 4.25 \times 10^{-8}\ \text{m/s}$$

$$\tau_p = \frac{4 \times 10^{-4}}{3 \times 4.25 \times 10^{-8}} = 3140\ \text{s} = 0.87\ \text{h} \rightarrow \frac{L_D}{3G}$$

$$\tau_F = 0.087\ \text{h}$$

(b) Determine Q_u and suspension volume V_u:

$P_c = M =$ suspension density

$P =$ production rate

$$Q_u = P/P_c = 400/200 = 2\ \text{m}^3/\text{h}$$
$$V_u = \tau_p Q_u = 1.74\ \text{m}^3$$

(c) Determine Q_o and V_o:

$$\tau_F = \frac{V_0 + V_u}{Q_o + Q_u} = 0.087\ \text{h}$$

i.e.,

Baffle حجم الـ ←
$$\frac{V_0 + 1.74}{Q_o + 2.0} = 0.087\ \text{h}$$
, $Q_o =$ (عط) (سرعة)

The overhead flow and the volume in the baffle are related by the equation above and cannot be determined without consideration of the settling velocity and the crosssectional area of the baffle. The volume V_0 should be kept as small as possible because a large V_0 means a large Q_o to achieve the required τ_F.

$V_u = 1/4$ ([illegible])

The suspension volume required is approximately one quarter that of Case I to produce the same product at the same rate. If evaporation also occurred, resulting in a higher suspension density, an even smaller crystallizer body would suffice.

Case VI: Circulating Magma Crystallizers

Circulating magma evaporative crystallizers are designed primarily to provide an efficient method for heat input. Evidently fines dissolving also occurs to a considerable extent, resulting in larger crystals than the kinetics would predict for an ordinary MSMPR crystallizer.

Consider a crystallizer with forced magma circulation of the type shown in Fig. 8 (where H.E. is the heat exchanger). Clearly as the mixed magma passes through the heating tubes the temperature increases above the saturation temperature and crystals smaller than some critical size L_c are completely dissolved. This critical size L_c will depend on the residence time in the tubes, the superheating, and the dissolution rate of the solute.

G=

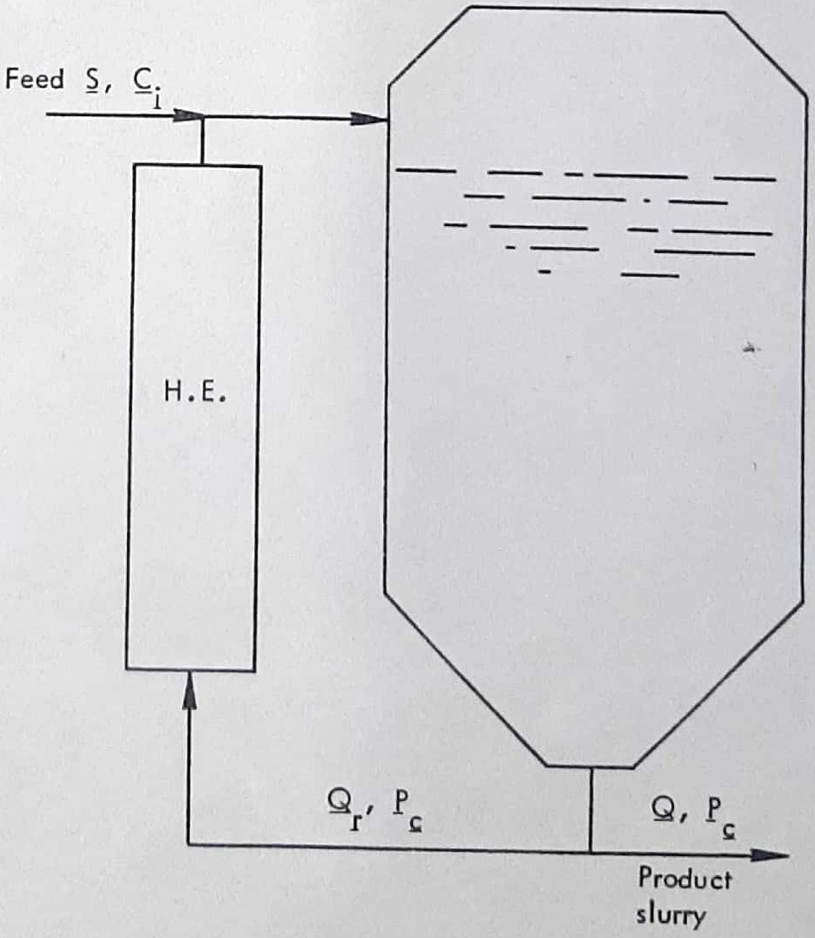

FIG. 8. Circulating magma crystallizer.

We will assume that the body of the crystallizer forms the active crystallization space. This volume is well mixed and all nucleation and growth occurs in this volume. If we regard the circulation rate as Q_o and the outflow slurry rate as Q_u, then Eq. (44) is applicable when L_c represents the largest size dissolved in one pass through the heating tubes and $\gamma = (Q_o + Q_u)/Q_u$ since the volume containing both fines and product crystals is the same. It is expected that the circulation rate would be of order 100 times that of the net throughput, and because of the short time in the tubes per pass it is expected that L_c would be very small, say of order 10^{-6} m.

$$\gamma = \frac{Q_r + Q}{Q} = 100 \quad , \quad L_c = 10^{-6}\,m$$

Example. Determine the growth rate necessary to produce the product indicated in Case I in an FC crystallizer as shown in Fig. 8 which has a circulation rate 100 times the throughput and which dissolves all particles less than 1 μm during each pass;, that is, $\gamma = 100$, $L_c = 10^{-6}$ m.

Substituting into Eq. (44):

$$G = \left[\frac{27\, M^{1-j}}{2 L_D^4 K_v K_R \rho \exp\left(-3 L_c \gamma / L_D\right)} \right]^{\frac{1}{i-1}}$$

$$G = \left[\frac{27}{2(4)^4(10^{-16})(3 \times 10^{15})(1.8 \times 10^3) \exp(-3/4)}\right]^{1/0.5} = 4.25 \times 10^{-8} \text{ m/s}$$

$K_v = 1$

$K_R = 3 \times 10^{+15}$

$\rho = 1.8 \times 10^{3}$

$L_D = 4 \times 10^{-4}\,m$

$i = 0.5$

$j = 1$

gives the same result as Case V.

Case VII: Fines Dissolving and Classified Product Removal

When systems are to be designed to destroy fines to such an extent that the mass of the fines must be considered or where the product is classified on removal, then the simple design equations given above no longer apply. For example, for classified product removal, P_c no longer equals M. In addition, the integral in the mass balance, Eq. (27), must be integrated in three parts, namely:

$$\int_0^\infty nL^2\,dL = \int_0^{L_c} nL^2\,dL + \int_{L_c}^{L_p} nL^2\,dL + \int_{L_p}^\infty nL^2\,dL \qquad (45)$$

Clearly this is rather a complex function. Furthermore, the mean particle size is no longer a simple multiple of $G\tau$ and the coefficient of variation is no longer 50%, but is dependent on L_c and L_p, the fines cut size and the classified product minimum size, respectively. The full formalism of the population and mass balances is therefore necessary for these configurations. A further complication arises because the additional constraints imposed on product size by these design features can cause process instability. Randolph and Larson [1] discuss the effects of these design features and give some of the working equations necessary for analysis of these systems. Evidently the design of these systems by the population balance must involve the complete dynamic modeling of the system and will require computer solutions.

Techniques to change the relationship between the kinetics of nucleation and the kinetics of growth are also effective in altering CSD. This can sometimes be done by changing the hydrodynamic conditions in the crystallizer. More often the addition of a trace impurity can markedly affect CSD. Large metallic ions or surface-active agents have been used with considerable success. Caution must be taken, however, so that the final products are not unduly contaminated.

Symbols

A	crystal surface area in crystallizer (batch)
A	crystal surface area/unit volume magma (continuous)
a	constant in saturation curve equation
B^0	nucleation rate (no/time, unit volume magma) (continuous)
b	constant in saturation curve equation
C_i	input concentration (mass/unit volume solvent)
C_o	output concentration (mass/unit volume input solvent)
C_s	saturation concentration (mass/unit volume solvent)
D	impeller diameter
E_c	collision energy
G	linear crystal growth rate
k	constant (Eq. 47)
k_1	constant (Eq. 48)
k_a	area shape factor
k_G	growth rate constant
k_N	nucleation rate constant
k_R	relative rate constant $(k_N/k_G{}^i)$
k_v	volumetric shape factor
L	total crystal length in crystallizer (batch)
L	crystal diameter or length
L_c	"cut" size
L_D	dominant crystal size
L_f	final crystal size
L_M	median crystal size
L_s	seed size
M	total mass of crystal in crystallizer (batch)
M	mass of crystal/unit volume magma (continuous)
M_f	final mass of crystals (batch)
M_s	mass of seeds (either basis)
m_j	jth moment of the distribution
N	number of crystals in crystallizer (batch)
N	number of crystals/unit volume magma (continuous)
N_I	impeller rotational speed
N_s	number of seeds (either basis)
n	number density (no/unit volume) (either basis)
n^0	nuclei number density (either basis)
n^0_{eff}	effective nuclei number density (either basis)
n^0_s	seed number density (either basis)

P	production rate (mass/time)
P_c	production per unit volume magma
P_o	impeller power number
Q	product magma rate (volume/time)
Q_o	overflow volumetric rate
Q_u	underflow volumetric rate
S	solvent feed rate (volume/time)
s	supersaturation $(C_o - C_s)/C_s$
T	temperature
T_0	initial batch temperature
t	time
t_f	final batch time
V	solvent volume in crystallizer (batch)
V	magma volume in crystallizer (continuous)
V_0	initial solvent volume in crystallizer (batch)
x_D	dimensionless dominant crystal size (L_D/L_s)
x_s	dimensionless seed size $(L_s/G\tau)$
Z	dimensionless time $(G\tau/L_s)$
Z_f	Gt_f/L_s
δ	$(Q_o + Q_u)/Q_u = \tau_P/\tau_F$ (dimensionless)
ε	energy dissipated by impeller per unit mass of magma
ρ	crystal density
τ	mean retention time
τ_F	mean retention time of fines
τ_P	mean retention time of product
ψ	P_c/M_s (dimensionless)
ϕ	$VC/3M_s$ (dimensionless)
ϕ'	$bVT/3M_s$ (dimensionless)
ϕ_0	initial value of ϕ
ϕ_0'	initial value of ϕ'
ω_c	collision frequency

Exponents

i	relative nucleation order
j	nucleation order related to M
m	nucleation order in supersaturation
n	growth order in supersaturation

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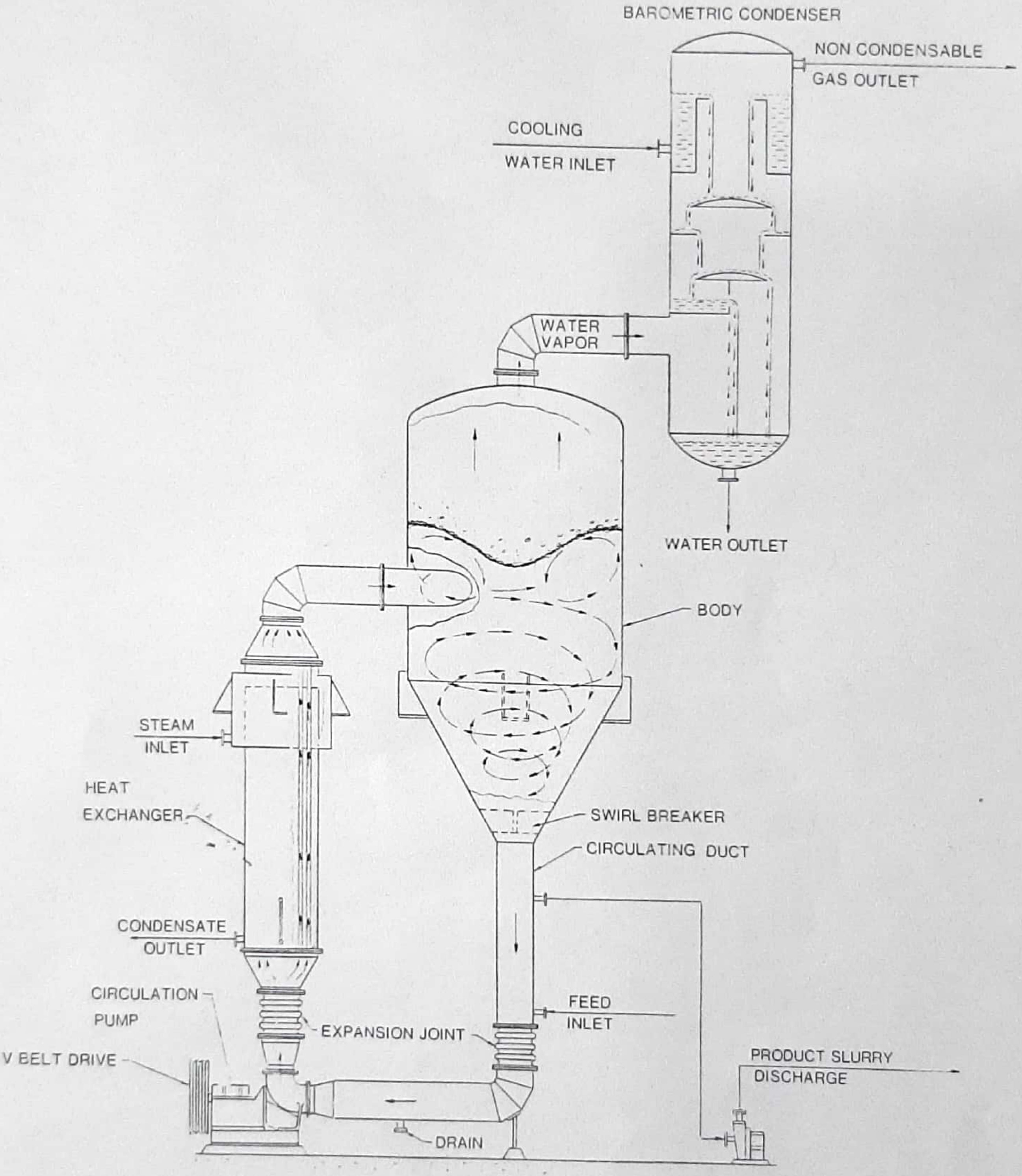

FIG. 1. Swenson forced circulation crystallizer.

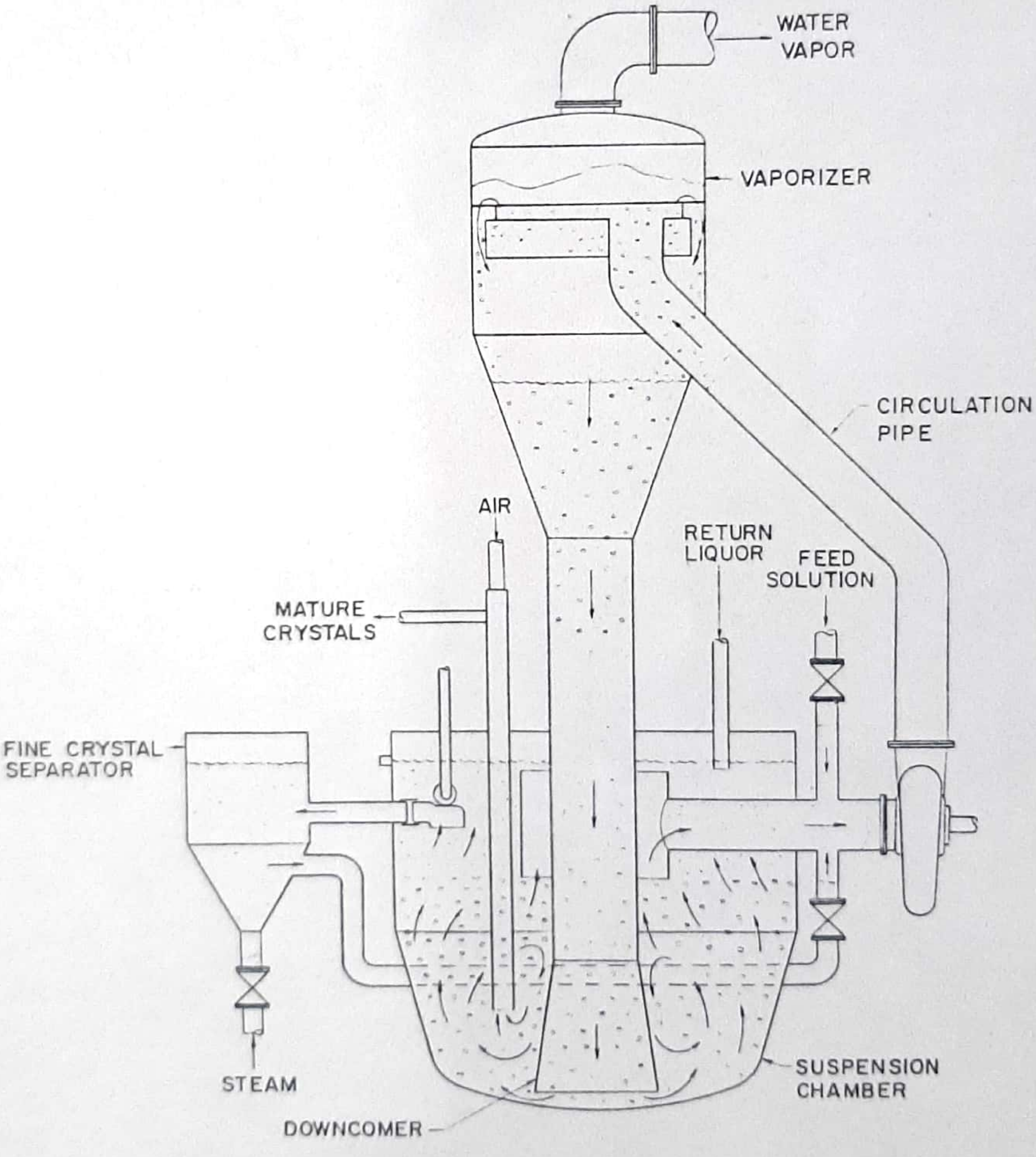

FIG. 2. "Oslo" crystallizer.

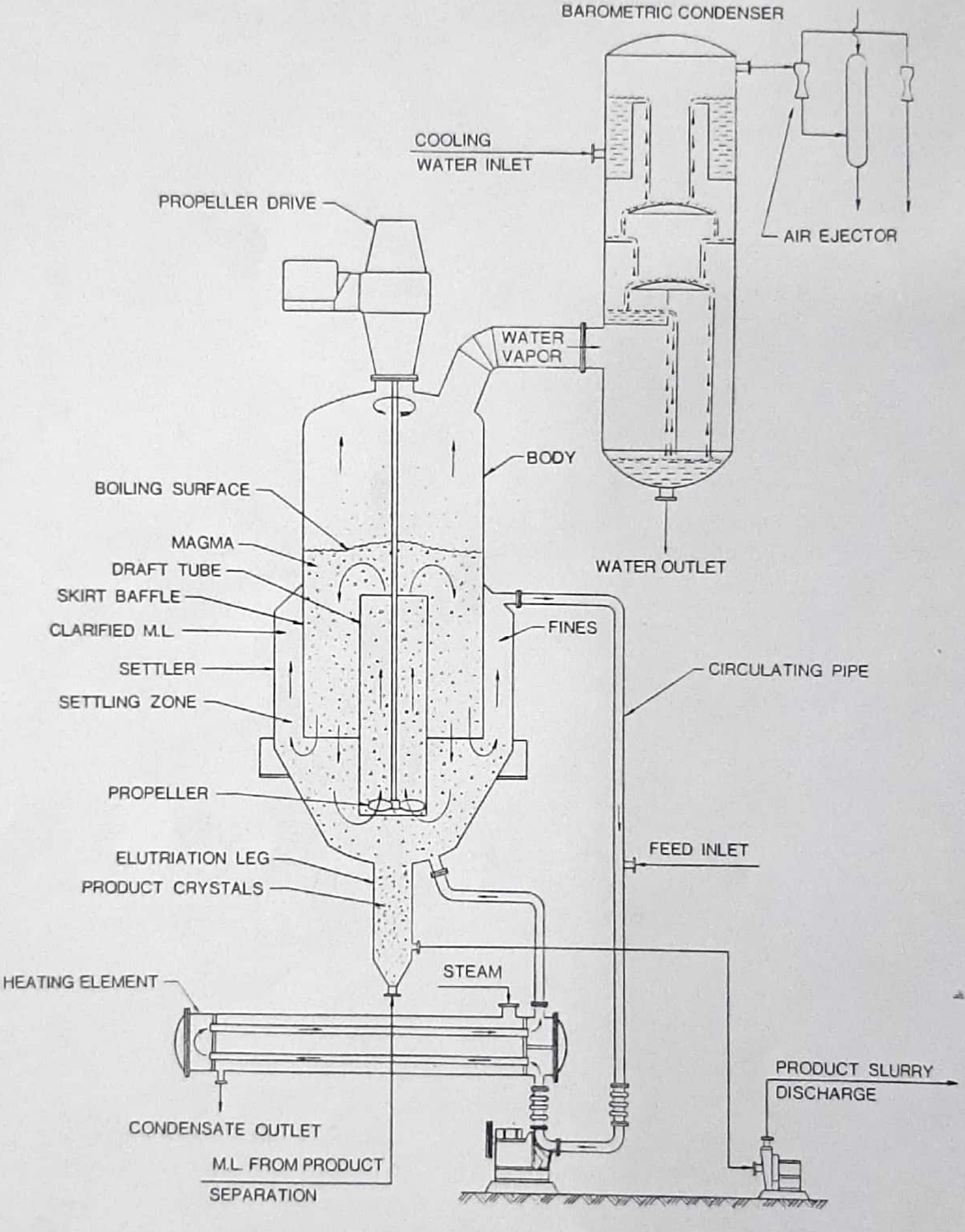

FIG. 3. Swenson draft tube baffle crystallizer.

Reactive Crystallizers

When a solid-phase crystalline material results from the reaction of two components, it is often advantageous to perform this reaction in a crystallizer rather than in a separate reactor. This is commonly done, for example, in the case of ammonium sulfate where liquid or gaseous ammonia and concentrated sulfuric acid are reacted in the crystallizer to produce ammonium sulfate crystals. The reaction is carried on in a liquid suspension of growing crystals and the heat of reaction is removed by vaporizing water which is condensed and recycled to maintain the liquid balance. Other examples are the oxidation of calcium sulfite by oxygen (air) or the neutralization of lime by waste acid.

The reactants can be mixed in the circulation piping of a forced circulation-type crystallizer or in the draft tube of a DTB-type crystallizer where a large volume of slurry is mixed continuously with the reactants so as to minimize the driving force (supersaturation) created by the reaction. Removal of heat is conveniently done by vaporizing water or other solvents as in a conventional evaporative-type crystallizer.

Surface-Cooled Crystallizers

Shown in Fig. 4 is a surface-cooled forced circulation crystallizer. The equipment consists of a tube and shell heat exchanger through the tubes of which is pumped the slurry of growing crystals, a crystallizer body to provide retention time, and a recirculation pump and piping. Internally within the crystallizer body is a baffle so that fine particles may be separated from the growing magma of crystals for size control and slurry density control.

The circulation rate through the heat exchanger tubes is normally large

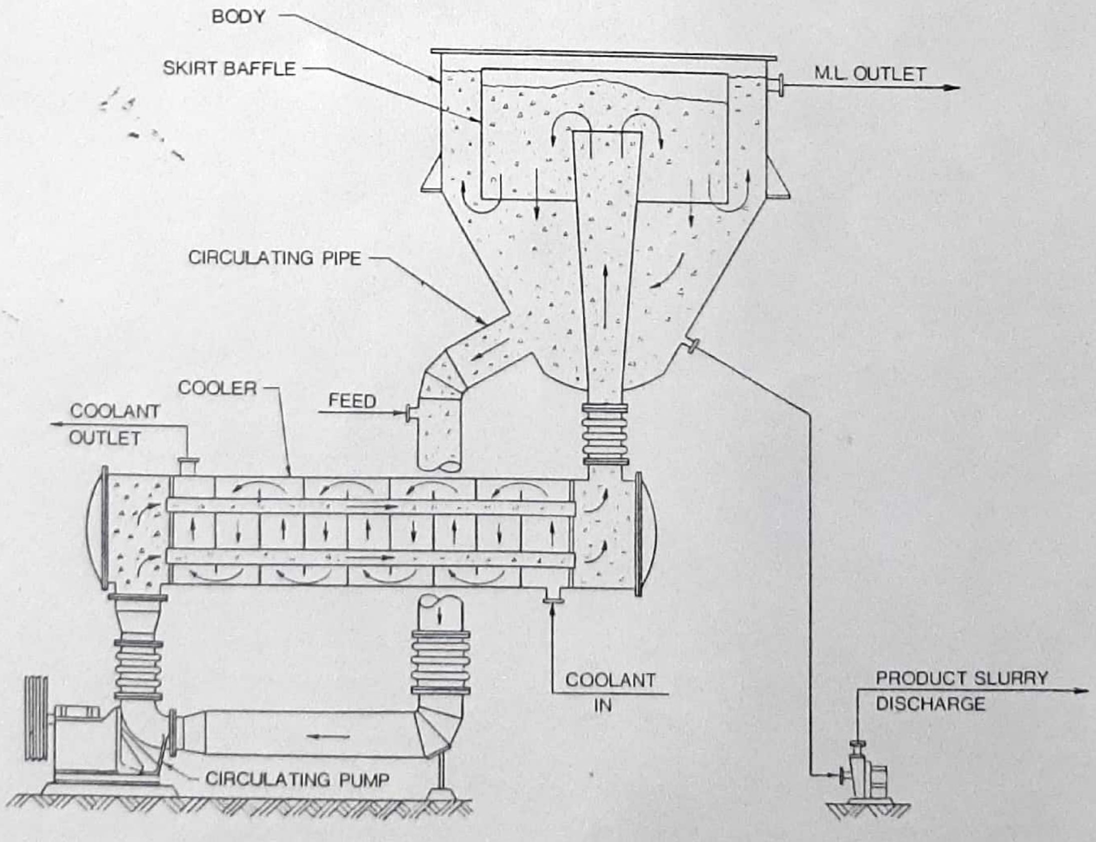

FIG. 4. Swenson surface cooled crystallizer.

enough so the temperature drop is in the range of 1 to 2°F. Surrounding the tubes is the cooling media which may be either tempered water circulated through segmental baffles or a refrigerant which is vaporized by heat removed through the tubes. Since the tube wall is the coldest part of the crystallizing system, it is important that the difference in temperature between this tube wall and the slurry pumped through the tube be as small as practical. Practical values depend on the operating cycle and, with many materials, ΔTs in the range of 5 to 15°F are required so as to achieve reasonable operating cycles.

This type of equipment is often used where the boiling point elevation of the solution is extremely high, as in the case of caustic solutions or when the temperature level is so low that there is no real possibility of using vacuum evaporation.

Typical applications are the crystallization of sodium chloride from caustic solutions, sodium carbonate from waste solutions, and sodium chlorate from solutions saturated with sodium chloride.

Direct Contact Refrigeration Crystallizers

Either the draft tube baffle as shown in Fig. 5 or the forced circulation crystallizer may be used as a direct contact refrigeration crystallizer in those cases where crystallization occurs at such a low temperature that it is impractical to use surface cooling or when the rapid crystallization of solids on the tube walls would foul a conventional surface-cooled crystallizer. In direct contact refrigeration crystallizers the refrigerant is mixed with the magma circulated within the crystallizer body where it absorbs heat and is vaporized. Refrigerant vapor leaves the surface of the crystallizer similar to water vapor in a conventional evaporative–crystallizer. The refrigerant vapor must be compressed, condensed, and then recirculated to the crystallizer to maintain the continuous operating conditions. Refrigerants chosen must be relatively insoluble in the solutions processed and have the necessary thermodynamic characteristics to minimize compressor horsepower.

Examples are the crystallization of caustic dihydrate with Freon or propane, and the crystallization of *p*-xylene with liquid propane refrigerant.

Batch Vacuum Crystallizers

For applications involving relatively small amounts of material or when the material being processed must be handled on other than a continuous basis, it is often convenient to use a batch vacuum crystallizer. Typically, the cycle on batch equipment of this type ranges from 2 to 8 h. At the conclusion of the cycle, the material is dumped into an agitated tank from which it is removed on either a batch or continuous basis for separation and drying. The time required for filling the crystallizer and dumping the crystallizer must be added to the time actually used for processing the material within the crystallizer. Other applications which are best handled in batch vacuum crystallizers are those wherein the material is cooled through a very wide range and/or to a final

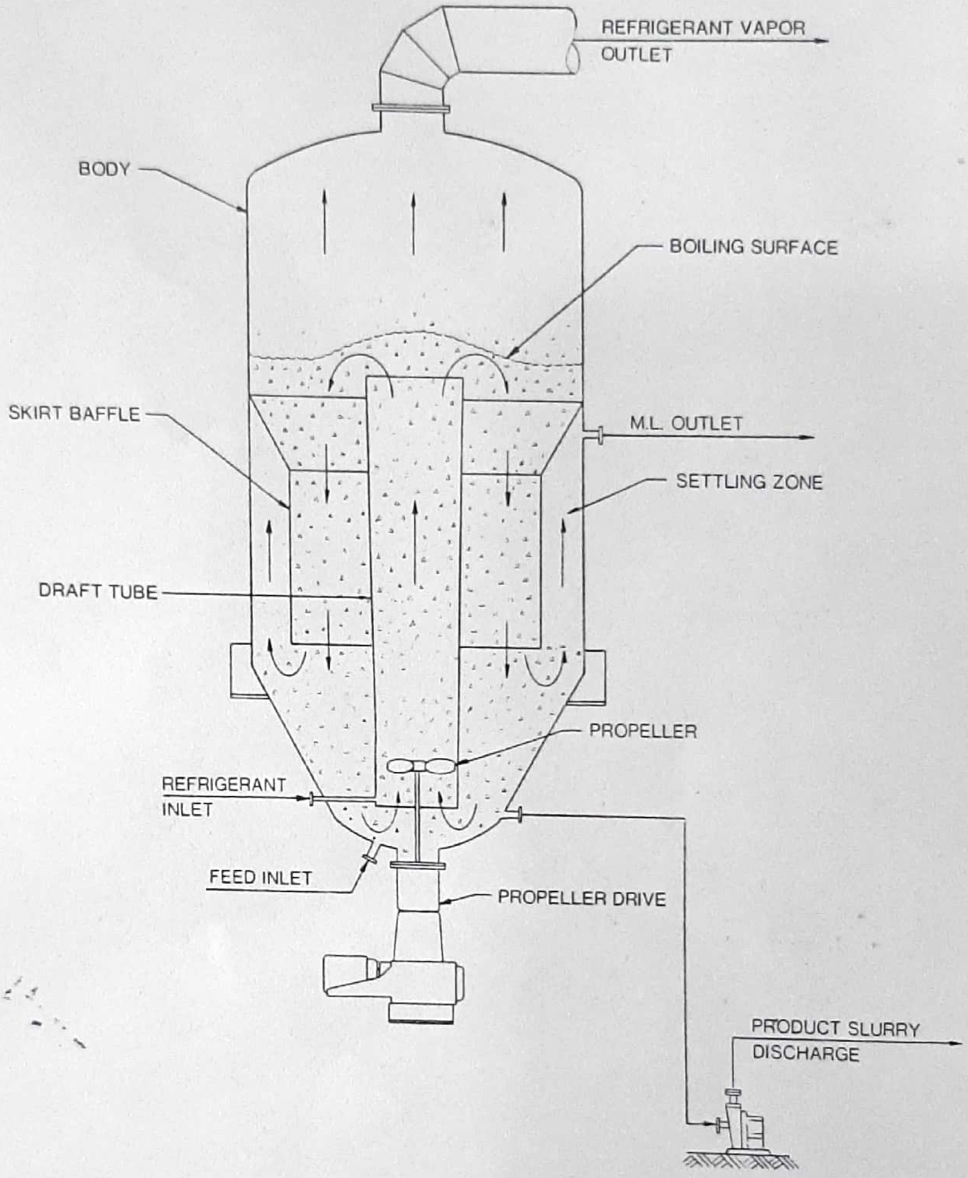

FIG. 5. Swenson direct contact refrigeration crystallizer.

temperature which requires very high vacuum. In these cases a large ejector or booster is utilized during part of the cooling to compress the vapor at the end conditions to a pressure high enough so it can be condensed with available cooling water. In such cases the batch vacuum crystallizer economies of steam usage are approached only by going to multistage continuous equipment of five or more stages.

The entire cycle for such equipment may be automated; however, in most small processing plants this expense is not justified. There is some variation in the product size made in batch equipment since the initial nucleation rate is difficult to control from one batch to the next. With those materials which are very prone to grow on the walls of the crystallization equipment and continuous nucleation rate from these data. From multiple sets of data it is possible to determine the kinetics of the system and thereby have sufficient data to predictably model the effect of other changes and modifications in the system. Although these equations are limited to fully mixed suspensions such as the forced circulation and DTB crystallizers mentioned earlier (and do not apply to agitated trough crystallizers, static tanks, etc.), they are important because this type of equipment accounts for the vast bulk of the important commercial applications. At the present time, mathematical analogs of other types of crystallizers are lacking or not as well developed.

The population density is the number of crystals per unit length (mm) and a function of the absolute size, L millimeters:

$$n = \lim_{\Delta L \to 0} \frac{\Delta N}{\Delta L} \text{ or } \frac{dN}{dL} \text{ (number/mm)} \tag{1}$$

where N = number of crystals
L = length (mm)

While the value of n at any size L may be calculated by measuring the slope of the line in a plot of N vs L, this number is most conveniently obtained from a screen analysis by computing the number of crystals in a given volume of crystallizer which are of such size that they pass through one screen and are retained on a smaller screen. This weight of crystals divided by the average diameter between the two screen openings and by the difference in length between the two screen nominal openings is the population density for that average size. The typical calculation technique for each screen size increment is

$$n_{L_a} = \frac{W_{L_a}}{\rho K_v L^3 \Delta L_a} \tag{2}$$

where K_v = volume coefficient (dimensionless)
W_{L_a} = grams of crystals of size a/volume
L_a = mean particle diameter for screen size a (mm)
ΔL_a = millimeter difference between the screen diameter and the preceding screen diameter
ρ = crystal density, g/mm^3

By plotting each population density versus the associated L, a graph may be obtained as shown in Fig. 6, where G = growth rate (mm/h), T = time = V/Q_D, V = volume of crystals (gal), and Q_D = discharge rate (gal/h).

If the crystallizer is operating at steady state, is thoroughly mixed, is discharging a representative sample of the suspended magma, and if McCabe's ΔL law is applicable, then a straight line plot of ln n vs L will result. The intercept of this straight line with the size corresponding to $L = 0$ is the nuclei population density and the slope of this straight line is equal to $(-l/GT)$. The growth rate so calculated is the diametral growth rate which is twice the facial growth rate. The retention time used in these calculations is sometimes referred to as the drawdown time and is the volume (active) of the crystallizer divided by the discharge rate. The crystal size distribution in such a machine is shown by

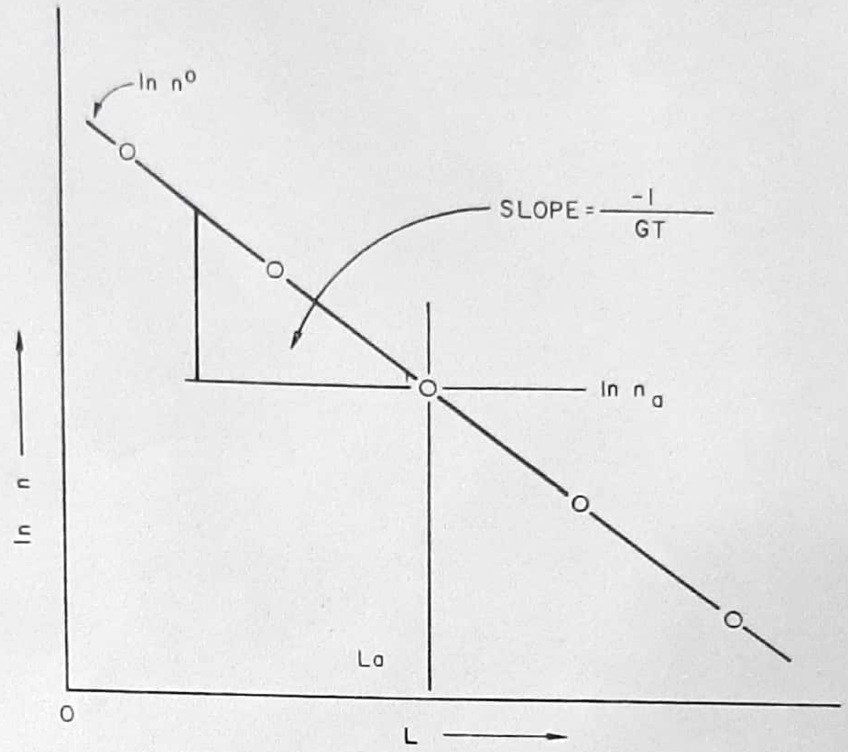

FIG. 6. Plot of nuclei population density vs length.

$$n = n^0 e^{-L/GT} \tag{3}$$

By definition, therefore, the nucleation rate, which is the birth of crystals at size 0, is shown by

$$B^0 = n^0 G \qquad \text{(no./h)} \tag{4}$$

The total number of crystals, the total area of crystals, and the mass of the crystals in the sample are shown by

$$N_T = \int_0^\infty n^0 e^{-L/GT}\, dL = n^0 GT \qquad \text{(total number of crystals)} \tag{5}$$

$$A_T = \int_0^\infty L^2 n^0 e^{-L/GT} = 2K_a n^0 (GT)^3 \qquad \text{(total area of crystals)} \tag{6}$$

$$M_T = \int_0^\infty L^3 n^0 e^{-L/GT}\, dL = 6\rho k_v n^0 (GT)^4 \qquad \text{(total mass of crystals)} \tag{7}$$

Since nucleation is also a function of supersaturation, it may be expressed in a power law model similar to that shown by

$$B^0 = k_n M^j G^i \tag{8}$$

This power law model contains an expression for slurry density and, as will be shown later, there are other considerations which could have been added that have a demonstrated influence on nucleation rate. In order to satisfy any given condition, the mass of crystals per unit volume of the crystallizer as shown in Eq. (7) must be consistent insofar as the nuclei population density and growth rate are concerned with that shown in Eq. (4). Therefore, growth rate is a restrained variable, and the correct solution to any new set of conditions involves a knowledge of both the nucleation rate and the growth rate simultaneously.

Once the growth rate at any given retention time is known, then the crystal size distribution may be computed by

$$X = L/GT \qquad \text{(dimensionless)} \tag{9}$$

and

$$W_x = \frac{M_x}{M_T} = \frac{\int_0^x X^3 e^{-x}\, dX}{\int_0^\infty X^3 e^{-x}\, dX} \qquad \text{(weight fraction to size } X\text{)} \tag{10}$$

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or

$$W_X = 1 - e^{-x}\left(1 + X + \frac{X^2}{2} + \frac{X^3}{6}\right)$$

The solution to this equation is given in table form in Appendix H of Randolph and Larson's book [7]. The generalized solution of Eq. (10) for certain specific properties such as the dominant particle is given by

$$L_D = 3GT \tag{11}$$

or the average particle by weight may be computed from

$$L_{av} = 3.67GT \tag{12}$$

The techniques for evaluating growth and nucleation rates have been widely used in the analysis of forced circulation crystallizers and other systems which are operated continuously, are thoroughly mixed, and where growth follows the ΔL law. There is good agreement between field measurements and results predicted by the theory. The nucleation sensitivity parameter (i) shown in Eq. (8) appears to be characteristic of many systems and is often the same in large-scale and in laboratory tests.

As mentioned earlier, the nucleation rate is actually not a simple power law model of growth rate and slurry density but should contain terms dependent upon contact nucleation effects caused by the pump or propeller circulator and the motion of crystals striking each other within the crystallizer suspension. This is shown algebraically by

$$B^0 = k_n M^j G^i + B_e{}^0 + B_c{}^0 \tag{13}$$

where B_e = nucleation due to impellers ?
B_c = nucleation due to crystal–crystal contacts ?

Work has been done by Bennett [5] to indicate the correlation between mechanical nucleation and crystallizer physical parameters as shown by

$$B_e = K_e\rho\left(\frac{\mathrm{TIPS}^2}{\mathrm{TO}}\right)G\int_0^{\infty} L^4 n\, dL \tag{14}$$

where (TIPS) is the tip speed of the pump or impeller and

$$(\mathrm{TO}) = \frac{\text{active volume}}{\text{circulation rate}} \qquad \text{(time/turnover)}$$

As indicated above, the nucleation term B_e used in Eq. (14) includes terms containing specific design perimeters from the crystallizer. If a straight-line plot of log n vs L is obtained, Eq. (14) can be solved by

$$B_e = K_e\rho\, n^0 G\left(\frac{\mathrm{TIPS}^2}{\mathrm{TO}}\right)L_D{}^5 \tag{15}$$

As shown above, small changes in the dominant particle size have a fifth-order influence on nucleation due to mechanical energy input, other factors being equal, thereby explaining the historical tendency of most forced circulation-type systems to operate stably with a particle size (for a given pump speed) that is changed very little by changes in slurry density or retention time.

Crystallizers of the draft tube baffle type which employ fines removal and destruction devices can also be analyzed by the techniques described above. Figure 7 is from both Perry [9] and Larson [8], where $L_F \ll L_P$ and

$$M_T = k_v\rho\int_{L_c}^{\infty}(n^0 e^{-L_F/GT_F})(e^{-L/GT_P}L^3)\, dL$$

The size removed by the baffle (crystals up to L_F) determines the nucleation rate and growth rate whereas the size of the product crystals is represented by a straight line of lower slope. As long as the particle size removed by the baffle is relatively small compared with the product size crystals, the overall distribution can be represented by Fig. 7. The size distribution from a crystallizer of the DTB type for particles up to size X is

$$W_x = \frac{6k_v\rho n^0 e^{-L_F/GT_F}(GT_F)^4\left[1 - e^{-x}\left(1 + \frac{X^2}{2} + \frac{X^3}{6}\right)\right]}{M_T} \tag{16}$$

where M_T = slurry density (g/l)
$X = L/GT$ (dimensionless)

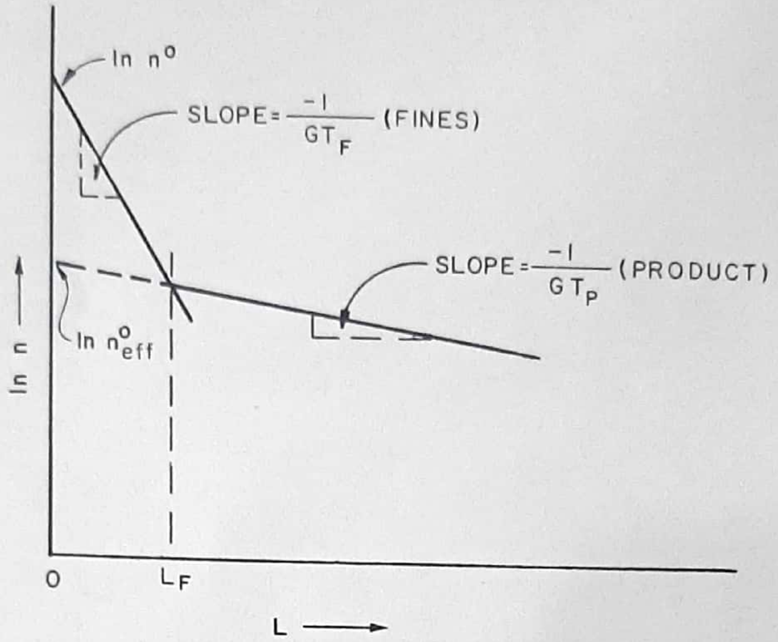

FIG. 7. Population density vs length for a draft tube baffle crystallizer.

In draft tube baffle crystallizers and others which employ fines removal and destruction, there is a limit to the flow through the fines destruction circuit and to the size of the particle (L_F) which can be removed in that circuit when working with any given product. Exceeding this limit results in unstable operation of the equipment insofar as crystal size distribution is concerned. It has been demonstrated by Randolph that this instability can occur even at very low values of the nucleation sensitivity parameter (i). Recent work on control theory by Randolph [10, 11] suggests that this instability can be controlled dynamically by modulating the overflow solution leaving the baffle and entering the fines destruction system.

For a batch crystallizer the same general scheme of calculation technique is useful as demonstrated by Larson [8] except that several samples must be taken during the batch at successive times and from these the change in length of the particles may be computed and, therefore, the growth rate calculated. Larson also outlines techniques for determining the size of the seed charge for batch equipment and the rate of change of evaporation to achieve constant growth rates.

Instrumentation and Control

Crystallization is a layer by layer process which occurs in a relatively long period of time. Therefore the mixed suspension of crystals that exists within a crystallizer is a combination of particles having a wide range of retentions. The