DETERMINATION OF CRYSTALLIZATION KINETICS FROM BATCH EXPERIMENTS II

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Relations have been derived for the size distribution of crystal product of batch crystallization with constant and variable supersaturation, applicable where the distribution cannot be approximated by the relation holding for continuous MSMPR crystallizers. In the cases considered, relative kinetic data, but not the kinetic exponents of nucleation and crystal growth, can be evaluated for model experiments involving any variation of supersaturation with time. Application of the relationships is illustrated by treating data for potassium aluminium sulphate precipitation.

In the preceding communication[1] three types of batch experiment were considered: *a*) crystallization with a constant supersaturation maintained throughout the experiment, *b*) crystallization during which supersaturation is produced at a constant rate, and *c*) crystallization where a supersaturation is formed at the beginning of the experiment, decreasing gradually as crystal growth proceeds. It has been found that in case *a*) kinetic data can be obtained in the same way as for a continuous MSMPR (mixed suspension – mixed product removal) crystallizer, whereas experiments performed under conditions *b*) and *c*) can only provide relative kinetic data with respect to a reference run. The analysis was based on the assumption that the crystal size distribution can be described satisfactorily by the following relation derived for continuous MSMPR crystallizer:

$$M(L) = 100(1 + z + z^2/2 + z^3/6)\exp(-z)\,, \qquad (1)$$

where

$$z = (L - L_N)/\dot{L}\bar{t}_1\,. \qquad (2)$$

This equation has been proved[2] to apply to some cases of batch crystallization, but may not be of general validity for this type of crystallization. The aim of the present work was to derive a more general relationship for the size distribution of crystal product from a batch crystallizer, and to illustrate its application to the evaluation of model crystallization experiments.

THEORETICAL

Mathematical simulation of the course of batch crystallization[3] has shown that the variation of supersaturation can be represented, as an approximation, by the equation

$$\Delta w = \Delta w_{\max}(t/t_{\max})^x \, t^x \exp(-Kt) . \tag{3}$$

A general explicit calculation of the crystal size distribution based on Eq. (*3*) is not feasible. We shall therefore consider separately the models discussed in the first part of this paper[1], involving *a*) constant supersaturation ($x = 0$, $K = 0$), *b*) supersaturation decreasing at a constant rate, and *c*) monotonously decreasing supersaturation ($x = 0$).

Batch Crystallization with Constant Supersaturation

For the mass of crystals in unit volume of suspension we can write

$$m_c = \int_0^{L_{\max}} \alpha \varrho_c \, n(L) \, L^3 \, \mathrm{d}L , \tag{4}$$

where, at a constant supersaturation,

$$n(L) = \dot{N}_N/\dot{L} = \text{const.} , \tag{5}$$

so that

$$m_c = \tfrac{1}{4}\alpha \varrho_c \, n(L) \, L_{\max}^4 . \tag{6}$$

Similarly, the mass of crystals larger than a certain mesh size L is given as

$$m(L) = \int_L^{L_{\max}} \alpha \varrho_c \, n(L) \, L^3 \, \mathrm{d}L = \tfrac{1}{4}\alpha \varrho_c \, n(L) \, (L_{\max}^4 - L^4) . \tag{7}$$

The oversize is defined as

$$M(L) = 100 m(L)/m_c . \tag{8}$$

Substituting Eqs (*7*) and (*8*) into (*6*), we obtain the same equation as derived previously[4]

$$M(L) = 100[1 - (L/L_{\max})^4] \tag{9}$$

which can be rearranged to

$$100 - M(L) = 100(L/L_{\max})^4 . \tag{10}$$

Taking logarithms,

$$\ln\left[100 - M(L)\right] = (4{\cdot}605 - 4\ln L_{\mathrm{max}}) + 4\ln L\,, \tag{11}$$

we have a linear equation from which L_{max} characterizing a given product can readily be calculated. The linear crystal growth rate is given by

$$\dot{L} = L_{\mathrm{max}}/t_{\mathrm{c}}\,, \tag{12}$$

and for the nucleation rate one can derive from Eqs (5) and (6)

$$\dot{N}_{\mathrm{N}} = 4m_{\mathrm{c}}/(\alpha\varrho_{\mathrm{c}}L^3_{\mathrm{max}}t_{\mathrm{c}})\,. \tag{13}$$

For a series of experiments with different supersaturations, we can use the relationship

$$\dot{N}_{\mathrm{N}} = \mathrm{const.}\ \dot{L}^{\mathrm{n}/\mathrm{g}} \tag{14}$$

allowing the relative kinetic exponent n/g to be estimated. The nuclei population density is given as

$$n^0 = 4m_{\mathrm{c}}/(\alpha\varrho_{\mathrm{c}}L^4_{\mathrm{max}})\,. \tag{15}$$

Batch Crystallization with Constantly Decreasing Rate of Supersaturation

For the supersaturation we can write

$$\Delta w = \Delta w_{\mathrm{max}}\left[1 - t/t_{\mathrm{c}}\right]. \tag{16}$$

Applying the power-law approximation, we can express the nucleation rate as

$$\dot{N}_{\mathrm{N}} = k_{\mathrm{N}}\,\Delta w^{\mathrm{n}} = k_{\mathrm{N}}\,\Delta w^{\mathrm{n}}_{\mathrm{max}}(1 - t/t_{\mathrm{c}})^{\mathrm{n}} = \dot{N}_{\mathrm{N,max}}(1 - t/t_{\mathrm{c}})^{\mathrm{n}}\,. \tag{17}$$

In like manner, we obtain for the linear crystal growth rate

$$\begin{aligned}\dot{L} &= k_{\mathrm{G}}\beta/(3\alpha\varrho_{\mathrm{c}})\,\Delta w^{\mathrm{g}} = k'_{\mathrm{G}}\,\Delta w^{\mathrm{g}} = \\ &= k'_{\mathrm{G}}\,\Delta w^{\mathrm{g}}_{\mathrm{max}}(1 - t/t_{\mathrm{c}})^{\mathrm{g}} = \dot{L}_{\mathrm{max}}(1 - t/t_{\mathrm{c}})^{\mathrm{g}}\,.\end{aligned} \tag{18}$$

By the end of the batch operation the crystals born at time t will have grown to the size

$$L = \int_t^{t_{\mathrm{c}}} \dot{L}\,\mathrm{d}t = L_{\mathrm{max}}(1 - t/t_{\mathrm{c}})^{\mathrm{g}+1}\,, \tag{19}$$

where

$$L_{\max} = \dot{L}_{\max} t_c/(g + 1) . \tag{20}$$

The total crystal mass is given by

$$m_c = \int_0^{t_c} \alpha \varrho_c \, L^3(t) \, \dot{N}_N(t) \, dt = \alpha \varrho_c L^3_{\max} \dot{N}_{N,\max} t_c/(n + 3g + 4) , \tag{21}$$

and for crystals born at time t,

$$m(t) = \int_t^{t_c} \alpha \varrho_c \, L^3(t) \, \dot{N}_N(t) \, dt =$$

$$= \left[\alpha \varrho_c L^3_{\max} \dot{N}_{N,\max} t_c/(n + 3g + 4)\right] \left[1 - (1 - t/t_c)^{n+3g+4}\right] . \tag{22}$$

Hence, the oversize is

$$M(t) = 100 m(t)/m_c = \left[1 - (1 - t/t_c)^{n+3g+4}\right] , \tag{23}$$

and after substitution from Eq. (*18*), we obtain the equation

$$M(L) = 100\left[1 - (L/L_{\max})^{(n+3g+4)/(g+1)}\right] \tag{24}$$

which can be rearranged to the form

$$100 - M(L) = 100(L/L_{\max})^{(n+3g+4)/(g+1)} \tag{25}$$

analogous to Eq. (*10*). The linear crystal growth rate is given by

$$\dot{L}_{\max} = (g + 1) \, L_{\max}/t_c , \tag{26}$$

and from Eq. (*21*) it follows that

$$\dot{N}_{N,\max} = (n + 3g + 4) \, m_c/(\alpha \varrho_c L^3_{\max} t_c) . \tag{27}$$

Hence, we get for the initial nuclei population density

$$n_0^0 = m_c[3 + (n + 1)/(g + 1]/(\alpha \varrho_c L^4_{\max}) . \tag{28}$$

It is clear that the absolute values of nucleation and growth rates cannot be evaluated unless we know the values of the nucleation and growth exponents. For the relative quantities with respect to a reference run (+) one can derive from the above relationships

$$\dot{L}_{\mathrm{rel}} = L_{\max} t_{\mathrm{c}}^{+} / L_{\max}^{+} t_{\mathrm{c}} \,, \tag{29}$$

$$\dot{N}_{\mathrm{N,rel}} = m_{\mathrm{c}} (L_{\max}^{+})^{3} \, t_{\mathrm{c}}^{+} / (m_{\mathrm{c}}^{+} L_{\max}^{3} t_{\mathrm{c}}) \,, \tag{30}$$

and

$$n_{0,\mathrm{rel}}^{0} = m_{\mathrm{c}} (L_{\max}^{+})^{4} / (m_{\mathrm{c}}^{+} L_{\max}^{4}) \,. \tag{31}$$

Batch Crystallization with One-Shot Creation of Supersaturation

For $x = 0$, Eq. (*3*) yields

$$\Delta w = \Delta w_{\max} \exp\left(-Kt\right) , \tag{32}$$

where $\Delta w_{\max}$ is the maximum (*i.e.* initial) supersaturation, and K is an adjustable parameter. Crystals are born by nucleation throughout the desupersaturation of solution. Using the power-law approximation, we can write

$$\dot{N}_{\mathrm{N}} = k_{\mathrm{N}} \, \Delta w^{\mathrm{n}} = k_{\mathrm{N}} \, \Delta w_{\max}^{\mathrm{n}} \exp\left(-nKt\right) = \dot{N}_{\mathrm{N,max}} \exp\left(-nKt\right) . \tag{33}$$

Similarly,

$$\dot{L} = k_{\mathrm{G}}' \, \Delta w^{\mathrm{g}} = k_{\mathrm{G}}' \, \Delta w_{\max}^{\mathrm{g}} \exp\left(-gKt\right) = \dot{L}_{\max} \exp\left(-gKt\right) . \tag{34}$$

By the end of the experiment (*i.e.* by complete depletion of supersaturation, characterized theoretically by $t \to \infty$) the crystals born at time t will have grown to the size

$$L = \int_{t}^{\infty} \dot{L} \, \mathrm{d}t = (\dot{L}_{\max}/gK) \exp\left(-gKt\right) . \tag{35}$$

The growth will obviously be largest for those crystals which were born first, *i.e.* at time $t = 0$:

$$L_{\max} = \dot{L}_{\max}/gK \,, \tag{36}$$

so that we can write

$$L = L_{\max} \exp\left(-gKt\right) . \tag{37}$$

The total crystal mass in unit volume of suspension will be

$$m_{\mathrm{c}} = \int_{0}^{\infty} \alpha \varrho_{\mathrm{c}} \, L^{3}(t) \, \dot{N}_{\mathrm{N}}(t) \, \mathrm{d}t = \dot{N}_{\mathrm{N,max}} \alpha \varrho_{\mathrm{c}} L_{\max}^{3} / (n + 3g) \, K \,. \tag{38}$$

By analogy, we can calculate the mass of crystals older than a certain time t, *i.e.* the crystals formed within the time interval $(0, t)$:

$$m(t) = \int_0^t \alpha\varrho_c L^3(t)\, \dot{N}_N(t)\, dt =$$

$$= [\dot{N}_{N,max}\alpha\varrho_c L^3_{max}/(n + 3g) K] \{1 - \exp[-(n + 3g) Kt)\} . \qquad (39)$$

Thus, for the oversize fraction of crystals older than a time t we can write

$$M(t) = 100\{1 - \exp[-(n + 3g) Kt]\} , \qquad (40)$$

or in terms of the crystal size L, using Eq. (*37*),

$$M(L) = 100[1 - (L/L_{max})^{n/g+3}] . \qquad (41)$$

Taking logarithms, we obtain

$$\ln[100 - M(L)] = [4{\cdot}605 - (n/g + 3) \ln L_{max}] + (n/g + 3) \ln L . \qquad (42)$$

From Eq. (*36*) the initial linear crystal growth rate can be expressed as

$$\dot{L}_{max} = gKL_{max} , \qquad (43)$$

and Eq. (*38*) provides an expression for the initial nucleation rate

$$\dot{N}_{N,max} = K(n + 3g)\, m_c/(\alpha\varrho_c L^3_{max}) . \qquad (44)$$

Hence, the initial nuclei population density is

$$n_0^0 = \dot{N}_{N,max}/\dot{L}_{max} = (n/g + 3)\, m_c/(\alpha\varrho_c L^4_{max}) . \qquad (45)$$

As in the previous case, we must refer the data to a reference run (+), so that

$$\dot{L}_{rel} = KL_{max}/(KL_{max})^+ , \qquad (46)$$

or, assuming $K \sim 1/t_c$,

$$\dot{L}_{rel} = L_{max}t_c^+/(L^+_{max}t_c) . \qquad (47)$$

Similarly, for the relative nucleation rate we get

$$\dot{N}_{N,rel} = Km_c(L^+_{max})^3/(K^+ m_c^+ L^3_{max}) \qquad (48)$$

or

$$\dot{N}_{\mathrm{N,rel}} = m_c(L^+_{\max})^3 \, t^+_c/(m^+_c L^3_{\max} t_c) \,. \tag{49}$$

The relative initial nuclei population density is then

$$n^0_{0,\mathrm{rel}} = m_c(L^+_{\max})^4/m^+_c L^4_{\max} \,. \tag{50}$$

EXPERIMENTAL

Batch precipitation of potassium aluminium sulphate from its components ((K_2SO_4 and $Al_2(SO_4)_3$)) was investigated. Both chemicals were Lachema analytical grade. The precipitation was carried out by adding in one portion 50 cm^3 of K_2SO_4 solution and 50 cm^3 of $Al_2(SO_4)_3$ solution, both of a concentration of 0·6 mol/l, to an amount of water at 25°C placed in a glass crystallizer of 180 cm^3 capacity, equipped with a temperature-controlling jacket, a stirrer, a baffle, and a thermometer. After the appearance of first crystals the suspension was stirred for an hour, then the crystals were filtered off by suction, washed with alcohol, and dried at ambient temperature. The crystal size distribution was determined by sieve analysis; the results are given in Table I.

TABLE I

Parameters of two batch experiments and the resulting crystal size distributions

Quantity	Experiment 1	Experiment 2
Initial charge of H_2O, cm^3	0	60
$S_0 = w_0/w_{eq}$	2·49	1·56
m, theoretical	17·04	11·03
m, experimental	16·17	5·01
$L \,.\, 10^3$, m	$M(L)$, %	$M(L)$, %
0·60	6·88	13·21
0·50	18·78	34·83
0·40	32·84	53·02
0·30	53·91	74·74
0·20	87·03	95·30
0·08	98·74	99·90

DISCUSSION AND CONCLUSIONS

Upon comparing Eqs (*10*), (*25*) and (*41*) one can see that the crystal size distribution for each of the models considered in this paper may be expressed by a relationship of the type

$$\ln (100 - M(L)] = (4{\cdot}605 - s \ln L_{\max}) + s \ln L\,, \qquad (51)$$

where s is the only value depending on the choice of the model. This relationship allows the largest crystal size, $L_{\max}$, to be evaluated irrespective of the particular model employed. An alternative data treatment[1] starts from Eqs (*1*) and (*2*), yielding the mean crystal size, $\bar{L}$, as a characteristic parameter of the product. One cannot guess beforehand which of the two correlations will better fit experimental data for a given product, and therefore a graphical comparison must be made.

The crystal size distributions obtained in the two experiments have been represented first by a $z - L$ diagram (Fig. 1), and secondly in the coordinate system corresponding to Eq. (*51*) (Fig. 2). It is seen that the crystal size distribution is better fitted by Eq. (*51*) in both cases.

The true (absolute) values of the nucleation and crystal growth rates can be determined with confidence only for model experiments with constant supersaturation. For

$$L_{\max} = 4^{1/3}\bar{L} \qquad (52)$$

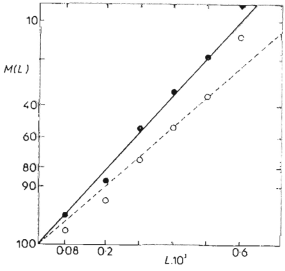

FIG. 1

Crystal size distribution represented in terms of Eqs (*1*) and (*2*) (z-L diagram)

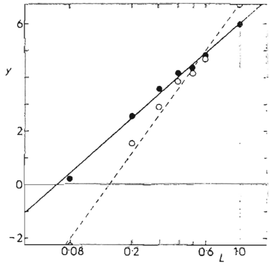

FIG. 2

Crystal size distribution represented in terms of Eq. (*51*) ($y = \ln [100\text{-}M(L)]$)

the relations (*12*) to (*15*) become identical with expressions derived[1] for a distribution of the type of Eq. (*1*), *i.e.* they are independent of the crystal size distribution function.

For batch experiments with variable supersaturation, the maximum (initial) nucleation and crystal growth rates can be determined providing the values of the nucleation and growth exponents are known. Values of the relative growth rates, Eqs (*29*) and (*47*), and of the relative nucleation rates, Eqs (*30*) and (*49*), are apparently independent of the choice of the model.

Kinetic parameters of crystallization have been calculated from experimental data illustrating the theoretical relations derived in this paper. Absolute values of the growth and nucleation rates cannot be calculated without knowing the kinetic exponents and, in contrast to MSMPR data, our experimental data do not allow these exponents to be evaluated. Using Eqs (*47*) and (*49*), we can express $\dot{N}_{\mathrm{N,rel}}$ as a function of $\dot{L}_{\mathrm{rel}}$

$$\dot{N}_{\mathrm{N,rel}} = \left[m_{\mathrm{c}}(t_{\mathrm{c}}^{+})^{4}/m_{\mathrm{c}}^{+}t_{\mathrm{c}}^{4}\right](\dot{L}_{\mathrm{rel}})^{-3}\,, \tag{53}$$

so that by plotting log $\dot{N}_{\mathrm{N,rel}}$ against log $\dot{L}_{\mathrm{rel}}$, we obtain a straight line of slope -3, independent of the values of the kinetic exponents of nucleation and growth. If, however, we do know the values of the kinetic exponents and of other parameters from separate measurements[5] ($g = 1{\cdot}60$, $n = 1{\cdot}90$, $\alpha = 0{\cdot}4714$, $\varrho_{\mathrm{c}} = 1\,760\ \mathrm{kg\,m^{-3}}$),

TABLE II

Kinetic parameters calculated from batch measurements

Quantity	Dimension	Experiment 1	Experiment 2	Eq.
$L_{\max} \cdot 10^{3}$	m	0·523	0·533	(*51*)
$\Delta w_{\max}$	kg/kg$_0$	0·200	0·076	
$\Delta w(t_{\mathrm{c}})$	kg/kg$_0$	0·010	0·041	(*54*)
$K \,.\, 10^{4}$	$\mathrm{s^{-1}}$	8·32	1·71	(*32*)
$\dot{L}_{\max} \cdot 10^{7}$	$\mathrm{m\,s^{-1}}$	7·00	1·47	(*43*)
$\dot{N}_{\mathrm{N,max}}$	$\mathrm{kg_0^{-1}\,s^{-1}}$	8 923	319	(*44*)
$n_0^0 \cdot 10^{-10}$	$\mathrm{kg_0^{-1}\,m^{-1}}$	1·27	0·22	(*45*)
$\dot{L}_{\mathrm{rel}}$	—	1·000	0·209	(*46*)
$\dot{N}_{\mathrm{N,rel}}$	—	1·000	0·036	(*48*)
$n_{0,\mathrm{rel}}^0$	—	1·000	0·171	(*50*)

we can evaluate from batch measurements even the true values of the crystal growth and nucleation rates; the constant K is obtained from Eq. (*32*) by substituting the residual supersaturation calculated from the mass balance

$$\Delta w(t_c) = \Delta w_{max} - m/m_{H_2O} . \qquad (54)$$

The calculated absolute and relative kinetic data are summarized in Table II.

LIST OF SYMBOLS

g	kinetic exponent of crystal growth
K	constant
k_G	growth rate constant
k_N	nucleation rate constant
L	crystal size
$\bar{L}$	mean crystal size
L_{max}	maximum crystal size
$\dot{L}$	linear crystal growth rate
$M(L)$	cumulative crystal size distribution
m	total mass of separated crystals
m_c	crystal mass, suspension concentration
$m(L)$	mass of crystals larger than size L
$\dot{N}_N$	nucleation rate
n	kinetic exponent of nucleation
$n(L)$	crystal population density
n^0	nuclei population density
s	slope of line represented by Eq. (*51*)
t	time
t_c	batch time
$\bar{t}_l$	mean residence time of solution in continuous crystallizer
Δw	supersaturation
x	adjustable exponent
z	dimensionless residence time of crystals
α	volume shape factor
β	surface shape factor
ϱ_c	crystal density

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