BATCH CRYSTALLIZATION WITH CRYSTALS ATTRITION

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The dependence of the mean crystal size of the products from batch crystallizers on the batch time occasionally exhibits a maximum, which can be explained by secondary nucleation due to attrition of crystals. A kinetic equation of nucleation, comprising a term for crystal attrition, can be used for the theoretical description of such behaviour. A mathematical model of a batch crystallizer with crystal attrition has been verified on the calcium sulfate precipitation.

The mean crystal size of products from continuous crystallizers usually increases with descreasing the feeding rate. A similar behaviour could be expected in the case of batch crystallization, where the mean crystal size should also monotonously increase with decreasing the supersaturation rate, i.e. with increasing the batch time. In many cases, however, this dependence exhibits a maximum: in the region of short batch times, the mean crystal size increases with the batch time, but with long batch times the dependence is inverse. There exists an optimal batch time, yielding maximum crystal size. This behaviour can be explained with micro- or macroabrasion of crystals leading to a decrease in the crystal size due crystal breakage and due to intensive secondary nucleation. The aim of this paper is to describe a mathematical model of the batch crystallization process with crystal attrition and to present its experimental verification.

THEORETICAL

A kinetic equation comprising two different mechanisms of nucleation has been published earlier[1]:

$$\dot{N}_N = k_N' \Delta w^n + k_A' m_c^c t_c . \qquad (1)$$

The first term on the right-hand side describes the secondary nucleation called up by the surface layer mechanisms, the second member secondary nucleation called up by micro- and macroabrasion. It has been stated that this form of equation is not convenient for consecutive treatment and another more suitable equation has been proposed:

$$\dot{N}_{\mathrm{N}} = k'_{\mathrm{NA}}\, m_{\mathrm{c}}^{\sigma c}\, t_{\mathrm{c}}^{\sigma}\, \Delta w^{(1-\sigma)n}\,, \tag{2}$$

where σ denotes the coefficient of secondary nucleation describing the proportion of the mechanism of attrition: for nucleation due to mechanisms of surface layer, $\sigma = 0$, whereas for attrition alone $\sigma = 1$. Equation (*2*) indicates that the order of secondary nucleation, n_{A}, will be lower than that of primary nucleation, n:

$$n_{\mathrm{A}} = (1-\sigma)\, n\,. \tag{3}$$

As the coefficient of secondary nucleation describes the effect of attrition, it must depend on the batch time: an empirical equation describing this dependence has been proposed[2]

$$\sigma = t/(\theta + t) = (t/\theta)/(1 + t/\theta)\,. \tag{4}$$

Balance of number of crystals

$$k'_{\mathrm{NA}}\, m_{\mathrm{c}}^{\sigma c}\, t_{\mathrm{c}}^{\sigma}\, \Delta w^{n_{\mathrm{A}}}\, t_{\mathrm{c}} = m_{\mathrm{c}} \Big/ \left(\frac{2}{9}\alpha\, \rho_{\mathrm{c}}\, \bar{L}^{3}\right) \tag{5}$$

together with the definition of the mean crystal size

$$\bar{L} = \dot{L}\, t_{\mathrm{c}} = k'_{\mathrm{G}}\, \Delta w^{g}\, t_{\mathrm{c}} \tag{6}$$

leads to the design equation

$$\bar{L}^{1+3g/n_{\mathrm{A}}} = 3\, B_{\mathrm{N}}\, m_{\mathrm{c}}^{(1-\sigma c)g/n_{\mathrm{A}}}\, (t_{\mathrm{c}}/3)^{1-(1+\sigma)g/n_{\mathrm{A}}} \tag{7}$$

with

$$B_{\mathrm{N}} = k'_{\mathrm{G}}\, [4.5/(\alpha\, \rho_{\mathrm{c}}\, k'_{\mathrm{NA}})]^{g/n_{\mathrm{A}}} \tag{8}$$

which expresses the dependence of the mean crystal size, $\bar{L}$ on the batch time, t_{c}. This dependence passes through a maximum determined by the condition

$$1 - (1+\sigma)\, g/n_{\mathrm{A}} = 0 \tag{9}$$

so that

$$\sigma_{\max} = n_{\mathrm{A}}/g - 1 \qquad [\bar{L}_{\max}] \tag{10}$$

and from Eq. (*4*) follows

$$\Theta = t_{\mathrm{c\,max}}\,(\sigma_{\max}^{-1} - 1) \qquad (11)$$

or

$$t_{\mathrm{c\,max}}/\Theta = (n_A/g - 1)/(2 - n_A/g)\,. \qquad (12)$$

With a proper choice of the relative kinetic exponent g/n_A it is thus possible to estimate the value of the constant θ and of the value of the coefficient of secondary nucleation σ at every instant *t*.

EXPERIMENTAL

The plausibility of derived equations has been checked by means of precipitation of needle-shaped crystals of calcium sulfate[3]. An amount of 50 cm^3 of 50% H_2SO_4 heated to 70 °C has been put into a breaker of capacity 1 000 cm^3 and under steady agitation the crystallizer has been fed with 470 cm^3 of 12% aqueous solution of $Ca(NO_3)_2$ with a constant rate in the range 110 to 5 000 cm^3/h. At the end of the experiment, the suspension was agitated for additional 60 min. The suspension has been then filtered, washed and dried. A part of these $CaSO_4 \,.\, 2\, H_2O$ crystals was then dried for 2 h at 150 °C; it has been checked by independent experiments that anhydrous $CaSO_4$ crystals are obtained under these conditions but the shape of crystals remains unchanged. The size distribution of $CaSO_4$ crystals has been determined by sedimentometry in ethanol (scanning fotosedimentometer Fritsch Analysette 20). An example of the size distribution as obtained from the fotosedimentometer Fritsch is shown in Fig. 1. It has been demonstrated[4] that the size distribution of needle-shaped crystals can also be determined by sedimentometry and that the dehydration of gypsum needles does not change significantly their size distribution so that the procedure described can serve our purposes.

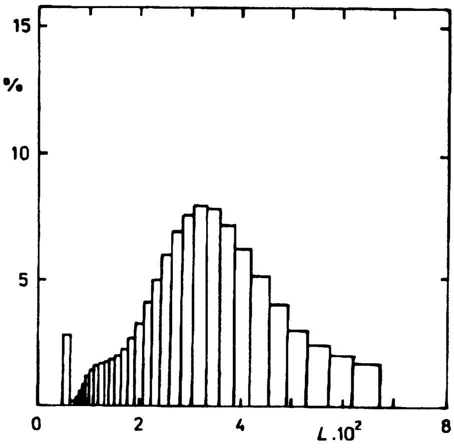

FIG. 1
Size distribution of product crystals of $CaSO_4$ from the experiment No. 6

RESULTS AND DISCUSSION

The sedimentometric data of the experiments have been linearized as z–L plots using the procedure already published[5]: the crystal population balance of a continuous mixed suspension–mixed product removal crystallizer leads to the equation

$$M(L) = 100\,(1 + z + z^2/2 + z^3/6)\exp(-z) \qquad (13)$$

which can be applied, under certain conditions, to batch crystallization as well. Applying an iterative procedure to this equation, corresponding dimensionless crystal sizes z were calculated from the experimental oversize fractions $M(L)$ and these values were then fitted by a straight line according to

$$z = 3\,L/(\dot{L}\,t_c)\,. \qquad (14)$$

An example of such a plot is shown in Fig. 2. A slight S-shaped curvature of experimental points reveals bimodal distribution which can be expected in the case of attrition. Nevertheless, the deviations from a line are small and the mean crystal size corresponding to $z = 3$ (or 64.7% oversize) can be found. So obtained mean crystal sizes are listed in Table I.

Using equations shown in the theoretical part, we adopted following procedure: we have chosen different values of n_A/g; for these values, $t_{c\,\max}/0$ was calculated using Eq. (*12*). Then we modified Eq. (*4*) for the conditions of the maximal $\bar{L}$

$$\sigma_{\max} = (t_{c\,\max}/0)/(1 + t_{c\,\max}/0) \qquad (15)$$

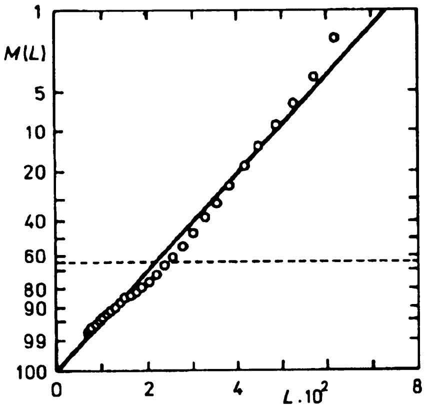

FIG. 2
Linearized size distribution of product crystals of $CaSO_4$ from the experiment No. 6

and inserted so obtained value into Eq. (*11*). Knowing 0, we then applied Eq. (*4*) to calculate σ and after that we calculated the value B_N from Eq. (*7*). Minimal deviation of B_N calculated for all experimental points determined the best value of g/n_A. We then inserted all necessary values (with $m_c = 0.125$ kg/kg H_2O, $c = 1$, $n_A/g = 1.2$, $t_{max} = 4\ 000$ s) into Eq. (*7*) to calculate the dependence of $\bar{L}$ on t_c. The result of this calculation is depicted in Fig. 3.

CONCLUSION

It can be seen from Fig. 3 that the mathematical model presented in this paper satisfactorily describes the behavior of a batch crystallizer with crystal attrition. At short batch times, the mean size of product crystals increases with increasing batch time but the dependence reaches a maximum and then the effect of longer batch times is unfavour-

TABLE I
Parameters of precipitation experiments and resulting mean crystal size

Experiment No.	$\dot{V}$, cm^3/h	t_c, s	$\bar{L}$, mm
1	5 000	338	0.01960
2	2 500	677	0.02361
3	760	2 226	0.02690
4	760	2 226	0.02380
5	380	4 453	0.02411
6	200	8 460	0.02193
7	110	15 382	0.01822

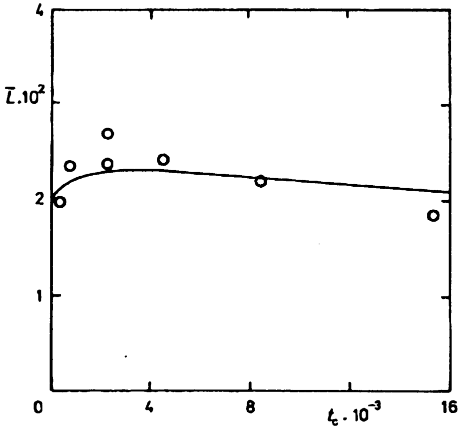

FIG. 3
Experimental (points) and calculated (curve) dependence of the mean crystal size, $\bar{L}$, on the batch time, t_c

able. This conclusion is important for batch crystallization in the industry, in particular where fragile crystals are produced.

SYMBOLS

B_N	system constant of crystallization (Eq. (8))
c	exponent of secondary nucleation for crystal – propeller collisions $c = 1$
g	growth order
k_A'	rate constant of nucleation due to attrition
k_G'	modified growth rate constant
k_N'	nucleation rate constant
k_{NA}'	rate constant of combined nucleation by surface layer mechanisms and attrition
L	crystal size
$\bar{L}$	mean crystal size
$\bar{L}_{max}$	largest mean crystal size at optimal batch time
L	linear crystal growth rate
$M(L)$	distribution function of crystal sizes (oversize)
m_c	mass of precipitated crystals
$\dot{N}_N$	nucleation rate
n	nucleation order
n_A	order of secondary nucleation
t	time
t_c	batch time
$t_{c\,max}$	batch time corresponding to the maximal crystal size
V	feed rate
Δw	supersaturation
z	dimensionless crystal size
α	volume shape factor
ρ_c	crystal density
σ	coefficient of secondary nucleation by attrition
σ_{max}	σ corresponding to $t_{c\,max}$
θ	constant

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