SEEDING AND ITS EFFECT ON SIZE OF PRODUCT CRYSTALS IN A BATCH CRYSTALLIZER

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The effect of seeding on product crystals size distribution was studied on a model of a batch crystallizer simulated on a digital computer under controlled cooling and at linear temperature decrease and for theoretical reasons with the temperature decrease with the third and fourth power of time. It was determined that the amount of crystals seeded was considerably affecting both the time dependence of supersaturation of solution as well as the final product crystals size distribution.

This study is related to the last publication[1] in which the effect of the mode of cooling on behaviour of a batch crystallizer was studied for the case when to the initial solution no seed crystals were added. It is demonstrated in numerous papers that the quality of the product considerably improves when the original solution at the beginning of crystallisation is seeded by a suitable amount of seed crystals[2−4]. Theoretical studies concerning the seeding of solutions are in general based on very simplified assumptions and, with exception of a single semiempirical study[5], they do not consider the crystal size distribution (CSD) from a seeded batch crystallizer in which nucleation takes place simultaneously.

In this study, we have made an attempt to characterize the behaviour of a seeded batch crystallizer for various amounts of seed crystals and different modes of cooling by use of a simple mathematical model. Together with the CSD, the time dependence of supersaturation is also studied which is one of determining quantities for properties of the product.

Mathematical model of an agitated batch crystallizer was given in detail in the last study[1]. It is based on basic kinetic equations for nucleation and crystal growth

$$\dot{m}_N = k_N \, \Delta w_{hyd}^n \, , \tag{1}$$

$$\dot{m}_G = k_G A \, \Delta w_{hyd}^g \tag{2}$$

and on the material balance of supersaturation.

The dependence of rate constants and solubility on temperature is expressed by equations of the type

$$k_N = k_{NO} \exp\left(-E_N/R(T + 273)\right), \tag{3}$$

$$k_G = k_{GO} \exp\left(-E_G/R(T + 273)\right), \tag{4}$$

$$w_{eq} = w_0 \exp\left(-E_w/R(T + 273)\right). \tag{5}$$

EXPERIMENTAL

The batch crystallizer was simulated mathematically on the computer TESLA 200 for conditions which corresponded to various cooling modes of the solution of sodium thiosulphate from 40 to 30°C. For calculation, the following values of constants were used:

Nucleation[6] $n = 3.71$; k_N (30°C) $= 0.362$; k_N (40°C) $= 0.0169$; $L_N = 9.6 \cdot 10^{-5}$, from that $k_{NO} = 1.34 \cdot 10^{-41}$ (for the length of time interval 12 s), $E_N = -57693$.

Growth[7]: $g = 1.0$; k_G (30°C) $= 0.313 \cdot 10^{-2}$; $\alpha = 0.45$; $\beta = 3.80$; $\varrho_c = 1685$, estimate $E_G = 3000$ (for assumption that growth is controlled by diffusion); from here $k_{GO} = 5.48$ (for the length of time interval 12 s).

Solubility: w_{hyd} (30°C) $= 2.460$, w_{hyd} (40°C) $= 3.888$; from here $w_0 = 4.15 \cdot 10^6$, $E_w = 8624.7$.

Mode of cooling[3]: time of experiment was chosen 2 and 4 h. For non-controlled cooling (in the mathematical model for input $x = 0$):

$$T = T_w + (T_0 - T_w) \exp\left(-Kt\right). \tag{6}$$

The chosen temperature of cooling water $T_w = 25°C$, from here $K = 1.863 \cdot 10^{-3}$ (for time 2 h which corresponds to 600 time steps).

The controlled cooling is determined by the equation of the cooling curve

$$\frac{T - T_e}{T_0 - T_e} = \left(\frac{t}{t_e}\right)^x. \tag{7}$$

For the experiments values $x = 1$ (linear cooling), $x = 3$ (theoretical cooling curve for the seeded solution without nucleation) and $x = 4$ (theoretical cooling curve for non-seeded solution and constant nucleation rate), were chosen.

Seeding: the size of seeded crystals was chosen $L_0 = 5 \cdot 10^{-4}$ m. The amount of seed crystals for the idealised case (negligible nucleation) and for the assumed growth by 1 mm can be calculated from the relation[4]

$$m_0 = \frac{L_0^3}{L_e^3 - L_0^3} \cdot \Delta m, \tag{8}$$

while the amount of crystallized substance is

$$\Delta m = w_{hyd}(T_0) - w_{hyd}(T_e). \tag{9}$$

For the specified conditions the value $m_0 = 0.055$ is obtained from Eq. (8). For calculation four

values were used $m_0 = 0$, $m_0 = 5 \cdot 10^{-3}$, $m_0 = 5 \cdot 10^{-2}$, $m_0 = 5 \cdot 10^{-1}$. The experiments realized on the computer are summarized in Table I.

As was demonstrated in our last study the crystallisation process is considerably affected by initial supersaturation (which in all given experiments is chosen as $\Delta w_0 = 0$), therefore the experiments were extended by three experiments with the non-zero initial supersaturation: Exp. No 421a $w_0 = 0.016$; No 422a, 0.016; Exp. 423a, 0.007.

RESULTS AND DISCUSSION

The theoretical analysis[3] has demonstrated that the product CSD from a non-seeded batch crystallizer with the exponential decrease of supersaturation should give a straight-line dependence in the coordinate system derived for continuous crystallizers[8]. For verification of this assumption and also for verification of the model the experiment No 010 was performed. The time dependence of supersaturation from this experiment with the non-controlled cooling (Fig. 1) demonstrates that in the first 7 to 8 min the supersaturation formed was so high that it reached the limit of the metastable region and after this period the decrease in supersaturation was actually approaching an exponential. In agreement with this result is also the linear dependence of oversize fractions on the size of product crystals which is plotted in the given coordinate system.

The results of other experiments are plotted in Figs 2 and 3 (the dependence of supersaturation in dependence on time) and in Figs 4 and 5 (CSD). In Fig. 6

TABLE I

Initial Parameters of Individual Experiments

Experiment	x	t_e	m_0	Experiment	x	t_e	m_0
010	0	118	0	320	3	240	0
110	1	120	0	321	3	240	0.005
111	1	120	0.005	322	3	240	0.05
112	1	120	0.05	323	3	240	0.5
113	1	120	0.5	410	4	120	0
120	1	240	0	411	4	120	0.005
121	1	240	0.005	412	4	120	0.05
122	1	240	0.05	413	4	120	0.5
123	1	240	0.5	420	4	240	0
310	3	120	0	421	4	240	0.005
311	3	120	0.005	422	4	240	0.05
312	3	120	0.05	423	4	240	0.5
313	3	120	0.5				

are being compared the corresponding dependences for the experiments with the non-zero initial supersaturation.
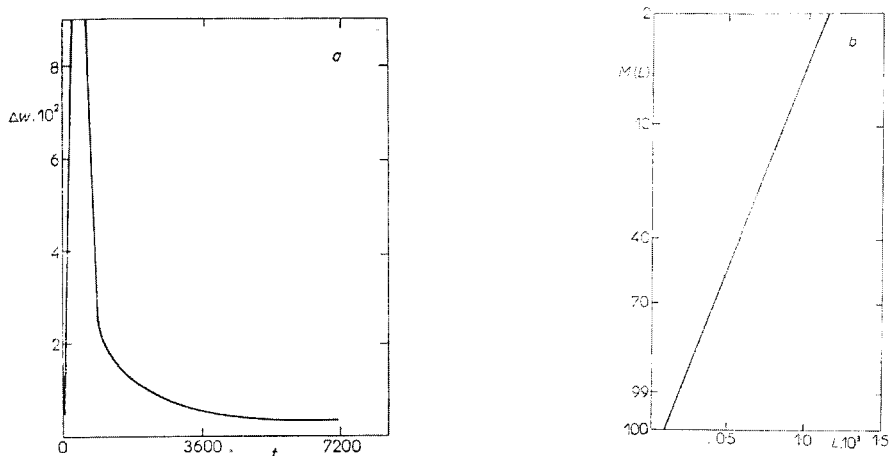

FIG. 1

Supersaturation in Dependence on Time for Non-controlled Cooling (*a*) and the Product CSD (*b*) from Experiment 010
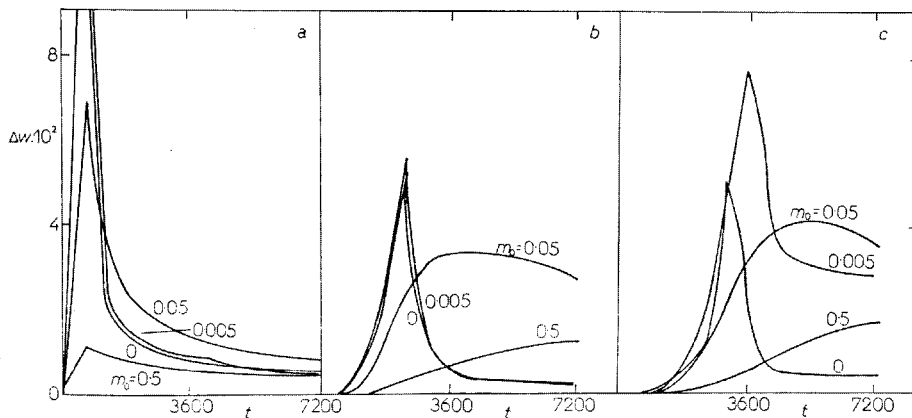

FIG. 2

Supersaturation in Dependence on Time for the 2 h Experiments
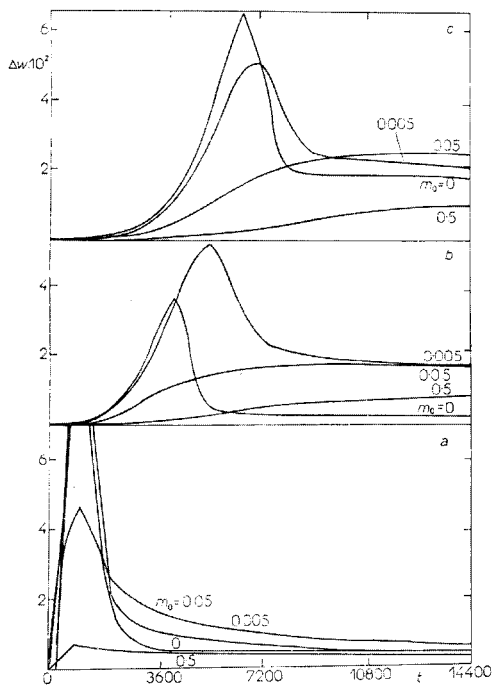   *a* $x = 1$ (exp. 110—113); *b* $x = 3$ (exp. 310—313); *c* $x = 4$ (exp. 410—413).

Fig. 3

Fig. 3

Supersaturation in Dependence on Time for the 4 h Experiments

a $x = 1$ (exp. 120—123); b $x = 3$ (exp. 320—323); c $x = 4$ (exp. 420—423).
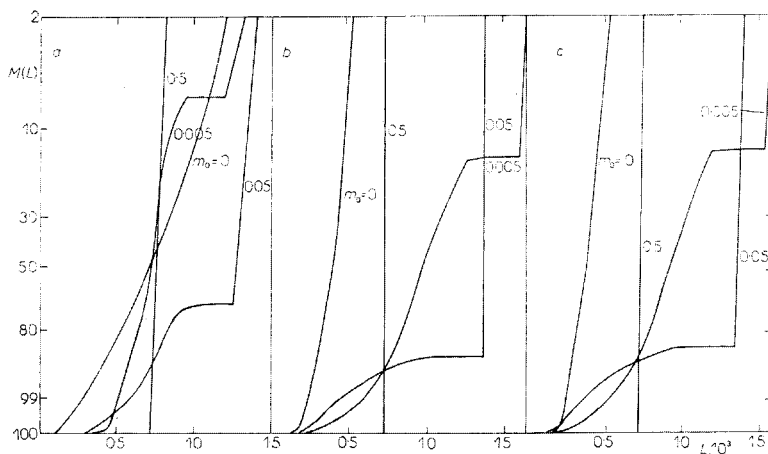

Fig. 4

The Product CSD

a Exp. 110—113; b 310—313; c 410—413.

On basis of the above given graphs, the following conclusions can be made: With the increasing amount of seeded crystals the maximum supersaturation reached during the experiment is considerably diminishing. In the experiments with linear cooling, the position of maximum on the supersaturation curve is not affected by the amount of seed crystals. In the experiments with controlled non-linear cooling the position of maximum on the supersaturation curve is shifted toward longer times; in the
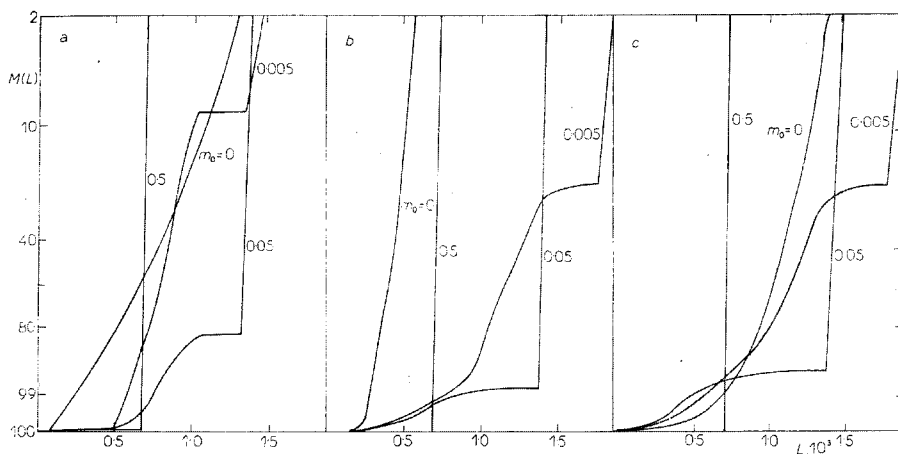

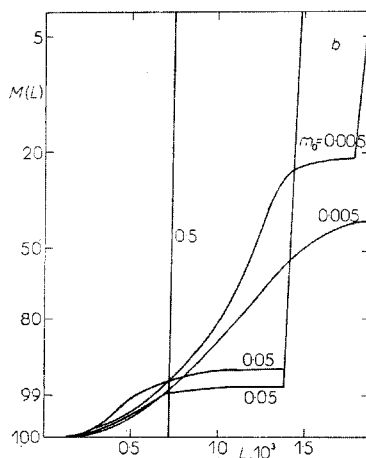FIG. 5

The Product CSD
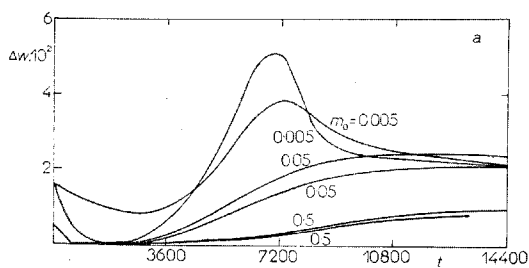
a Exp. 120—123; b 320—323; c 420—423.

FIG. 6

The Effect of Initial Non-Zero Super-saturation on Supersaturation in Dependence on Time (a) and on the Product CSD (b) (Exp. 421, 421a, 422, 422a, 423, 423a).

experiments with controlled cooling, the supersaturation curve is, after reaching the maximum and the following decrease, more or less steadied on some value which depends on the amount of seeded crystals; in the non-seeded experiments it is the lowest value, with increasing amount of seeds it increases up to the value of theoretical amount of crystals seeded. When this value is reached, in a number of cases a relatively high supersaturation in the crystallizer is steadied. A greater amount of seeds results in the supersaturation curve which has only an inexpressive maximum or, during the experiment, it monotonously increases and the maximum value is reached at the end of the experiment. The non-zero supersaturation at the beginning of operation is decreasing (too slow rate of supersaturation, supersaturation in the solution is removed by the crystals present) the rest of dependence is similar to that characterized in the case of controlled cooling described above.

The CSD has in all studied cases a similar character: in the non-seeded experiments shape is slightly curved, in the experiments with the controlled non-linear cooling in the region below 99% of oversize fraction it is nearly a straight line. With the increasing amount of seeds there appears on the curves a steep change or the CSD remains constant which appears for small amounts of seed crystals (10% of calculated amount) in the range from 5 to 25% of the oversize fraction, in the case of the theoretical amount in the range from 70 to 98% of the oversize fraction and finally in the case of seeding by a tenfold of calculated amount in vicinity of the 100% of the oversize fraction, *i.e.* practically the whole crystal matter has grown on the present seed crystals. The maximum size of product crystals is according to expectations decreasing with the increasing amount of seeds as the same mass of crystallized substance is distributed to a greater number of particles which are of course smaller in size; the largest crystals are obtained under cooling which corresponds to the theoretical cooling curve. With reduced time of the experiment, also the maximum size of product crystals is decreasing according to expectations. With regard to the non-linear dependence of the CSD (oversize fraction on size of crystals) plotted in a suitably selected scales[8] it has no sense to define the mean size of crystals; the product is here characterized by the size of largest crystals and by the oversize fraction which corresponds to the growth on the seeded crystals. There seems to be an alternate possibility to evaluate the data on product CSD by their separation into the fraction corresponding to the seed and to the fraction corresponding to nucleation[5].

LIST OF SYMBOLS

A surface area of crystals (m^2/kg_0; kg_0 is representing 1 kg of free solvent)

E_N activation energy of nucleation   (kcal/kmol)

E_G activation energy of crystal growth   (kcal/kmol)

E_w parameter of energy characterizing the temperature dependence of solubility   (kcal/kmol)

g order of the kinetic equation of growth

k_N rate constant of nucleation $(kg_0^{n-1} \, kg^{1-n} \, s^{-1})$

k_G rate constant of growth $(kg^{1-g} \, m^{-2} \, s^{-1} \, kg_0^g)$

k_{NO} constant in Eq. (3) $(kg_0^{n-1} \, kg^{1-n} \, s^{-1})$

k_{GO} constant in Eq. (4) $(kg^{1-g} \, m^{-2} \, s^{-1} \, kg_0^g)$

K constant characterizing the heat transfer

L size of crystals   (m)

L_0 size of seed crystals   (m)

L_N size of original crystals   (m)

$M(L)$ oversize fraction   (%)

Δm amount of matter crystallized in the batch (kg/kg_0)

m_0 mass of seed crystals

$\dot{m}_G$ mass rate of crystal growth $(kg \, kg_0^{-1} \, s^{-1})$

$\dot{m}_N$ mass rate of nucleation $(kg \, kg_0^{-1} \, s^{-1})$

n order of kinetic equation of nucleation

R gas constant   (kcal/kmol K)

t time   (s)

t_e total time of the batch   (s)

T temperature   (°C)

T_0 initial temperature   (°C)

T_e final temperature   (°C)

T_w temperature of cooling water   (°C)

w_{hyd} concentration (kg/kg_0)

w_0 constant in Eq. (5) (kg/kg_0)

Δw supersaturation (kg/kg_0)

Δw_0 initial supersaturation (kg/kg_0)

w_{eq} solubility (kg/kg_0)

x exponent in the equation of cooling curve (7)

α volume shape factor

β surface shape factor

ϱ_c density of crystals (kg/m^3)

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