

## THE EFFECT OF THE COOLING MODE ON THE KINETIC PARAMETERS OF CRYSTALLIZATION

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Received January 20, 1989  
Accepted February 16, 1989

*Dedicated to late Academician Eduard Hála.*

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The effect of different cooling regimes (natural, linear, and programmed cooling according to a theoretical curve) on the kinetic parameters of crystallization and on the mean product crystal size is demonstrated by an example of batch cooling crystallization of ammonium aluminium sulphate dodecahydrate. The kinetic exponent  $g/n$  determined on the basis of model experiments does not depend on the cooling regime, the system constant  $B_N$  is highest for the programmed cooling. If this constant is to be a basis for the design of a cooling crystallization equipment, it is necessary to carry out its experimental determination under the same temperature regime.

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The design of industrial crystallizers not always respects the crystallization properties of a system. At the given composition of entering solution, the required crystallizer capacity and the known temperature of cooling water, the cooling crystallizer is, for instance, often chosen in a simplified way so that it should be possible to cool the solution in it in the time which is available, to the required final temperature. The design itself is then rather a question to solve the hydrodynamics and heat transfer. In the last resort, the maximum possible cooling surface is inserted into the crystallizer with the aim to reduce as much as possible the batch cooling time.

Even in such a crystallizer designed likewise it is possible, in some cases, to grow crystals of sufficient size which do not make difficulties in further treatment, especially in separating them. However, the product is usually too small, its fine crystals pass through the centrifuge and so cut down the equipment output. A problem occurring very often in case of intense or uncontrolled cooling is the formation of incrustations on the cooling surfaces which greatly worsen the overall heat transfer coefficient and thus extend unbearably the overall cooling time.

Therefore, when designing a crystallizer, it is necessary to consider also the crystallization parameters of the given system and to adapt the crystallizer and the crystallization regime so that the product should be of better quality at an acceptable batch time. One of the possible ways of increasing the crystal size is the adaptation of the

cooling regime of solution<sup>1-5</sup>. The consequences of such an adaptation can be estimated by means of the kinetic system constant of crystallization  $B_N$  found out on the basis of the laboratory model experiments under different cooling regimes.

## THEORETICAL

### *Cooling Rate*

The actual temperature course in an industrial cooling crystallizer may be usually approximated by one of relations derived for the maximum cooling rate under different regimes:

*Natural (uncontrolled) cooling (regime 1)*. Under this regime, the flow rate of cooling water of temperature  $T_w$  is constant and sufficiently large. Then the temperature difference between the solution or suspension in crystallizer and the cooling water is maximum, and therefore also the cooling is the most rapid at the beginning. The cooling rate drop is due to the temperature difference drop and the deterioration of the overall heat transfer owing to the overgrowing the heat exchange surface with incrustations. The batch temperature change can be described in this regime by the relation<sup>6</sup>

$$T = T_w + (T_0 - T_w) \exp(-kt). \quad (1)$$

When calculating, with respect to the incrustation growth, it is necessary to choose the overall heat transfer coefficient involved in constant  $k$  to correspond to the less favourable conditions at the end of cooling. The incrustation formation can be reduced to a certain extent, and the quality of the product can be improved by controlled cooling.

*Linear cooling (regime 2)* is the most easily feasible mode of the cooling control which partly eliminates the undesirable high initial supersaturation of solution. The temperature of crystallizing solution is described by the equation

$$T = T_0 - (T_0 - T_e) (t/t_c)^X \quad (2)$$

with exponent  $X = 1$ .

The linear temperature drop with time in crystallizer requires the control of temperature or the cooling water flow rate. It is possible to find experimentally such a temperature difference between the cooling and cooled medium at which the formation of incrustations on the cooled surface does not take place yet. Unless this maximum temperature difference is exceeded, the overall heat transfer coefficient remains approximately constant for all the cooling time, and so it is possible to reach higher cooling rates and thus even to reduce the batch time.

*Programmed cooling* (regime 3). For the maximum cooling rate of seeded solution in which nucleation does not take place, and where the originated supersaturation is drawn off only by the growth of crystals present, the equation was derived<sup>7</sup> which is formally identical with Eq. (2) in which  $X = 3$  holds. In this case, the rate of cooling is minimum in the beginning and its highest value is reached in the batch end when the present crystal surface is maximum.

#### *Crystal Size and System Constant of Crystallization*

Besides the batch time in a batch cooling crystallizer (equipment capacity), the mean product crystal size  $L_m = L(M(L) = 64.7\%)$  is as well an important quantity which can be calculated from experimental data on using the cumulative distribution function<sup>8</sup>

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

where

$$z = 3L/L_m. \quad (4)$$

The number and size of crystals in the resulting product result from the simultaneous effect of the crystal formation rate and the crystal growth rate which are functions of the instantaneous supersaturation. However, since the time dependence of supersaturation has usually complicated character in the course of batch crystallization, we use the mean linear crystallization rate defined as<sup>9</sup>

$$r_L = L_m/t_c, \quad (5)$$

and the mean nucleation rate for which holds<sup>9</sup>

$$r_N = 27m_c/2\alpha Q_c L_m^3 t_c. \quad (6)$$

The interrelation between the mean product crystal size and the equipment capacity is expressed by the equation

$$L_m^{1+3g/n} = 3B_N m_c^{(1-c)g/n} (t_c/3)^{1-g/n}, \quad (7)$$

where the system kinetic constant of crystallization

$$B_N = 4 \cdot 5^{g/n} k'_G / (\alpha Q_c k'_N)^{g/n} \quad (8)$$

is the basic quantity for the description of the crystallization kinetics and for designing crystallizers. To calculate it according to Eq. (7), it is necessary to know, besides the direct experimental values of  $L_m$ ,  $m_c$ , and  $t_c$ , also the kinetic exponent  $g/n$  and the exponent of secondary nucleation  $c$ . These exponents of kinetic equations for

the numerical nucleation rate

$$r_N = k'_N m_c^c \Delta w^n \quad (9)$$

and for the linear rate of crystal growth

$$r_L = k'_G \Delta w^g \quad (10)$$

can be determined by the separate measurement of the crystal growth kinetics and the nucleation kinetics.

To calculate the system constant, it is, however, more advantageous its determination from the model experiments in which the growth and nucleation take place simultaneously under the conditions close to the real crystallization. To do so, it is necessary to carry out a set of experiments with different batch time  $t_c$  but with the same suspension density  $m_c$ . Then we can rearrange Eq. (7) into the form<sup>1</sup>

$$\log L_m = K \log t_c + k, \quad (11)$$

where

$$K = (n/g - 1)/(n/g + 3), \quad (12)$$

and calculate the slope  $K$  of line (11) from a pair of experimental values of  $L_m$  and  $t_c$  by the least-squares method according to the relation

$$K = \frac{\sum \log t_c \sum \log L_m - p \sum \log L_m \log t_c}{(\sum \log t_c)^2 - p \sum \log^2 t_c}. \quad (13)$$

From Eq. (12) we then get directly

$$n/g = (1 + 3K)/(1 - K). \quad (14)$$

By using an analogous procedure, it is possible to determine also the coefficient of secondary nucleation  $c$  if we carry out a series of model experiments with constant batch time  $t_c$  and varying suspension concentrations  $m_c$ . The presumption is a sufficient difference of values  $m_c$  on which depends the accuracy of the determined value of  $c$ . The practically attainable differences in suspension concentrations are, however, usually too small, and therefore it is, as a rule, necessary to choose the values of  $c$  according to an assumed mechanism of secondary nucleation<sup>10</sup>.

The estimation of parameters in Eq. (7) for calculating the system constant from the batch model experiments stems from the formal analogy with the description of continuous crystallization<sup>9</sup> for which a constant supersaturation of solution is assumed. In batch set-up, it is possible to reach the constant supersaturation, e.g., by cooling the seeded solution according to a temperature curve described by Eq. (2) with exponent  $X = 3$ .

On an industrial scale, however, such requirements are difficult to perform, and therefore it is necessary to verify the applicability of the system constant found out in this way even under other temperature regimes of crystallization.

## EXPERIMENTAL

*Equipment:* Glass jacketed kettle KAVALIER from borosilicate glass SIMAX of 10 dm<sup>3</sup> volume with hemispherical bottom and lower discharge hole, closed with a cover. Three plane blade stirrer with blades inclined at 45°, frequency of revolution 150 min<sup>-1</sup>. The temperature of cooling water flowing in the closed circuit thermostat-kettle jacket was controlled by an electronic controller so that the batch temperature decreased according to the regime chosen.

*Substances used:* Distilled water and ammonium aluminium sulphate dodecahydrate (therein-after alum). On using the AAS, RTG, and spectral analysis methods, it was found out that the overall admixture contents of inorganic nature did not exceed 0.05 mass %. Organic admixtures were not found.

*Procedure:* According to the data on solubility<sup>11</sup> in the system studied, 5 435 g water was put into the crystallizer and 4 565 g alum was dissolved in it at 70°C. The concentration was checked by measuring the temperature of saturation<sup>12</sup> in the solution sample. Then the batch was tempered to 67.0°C (temperature of saturation), the cooling controller was set on, and 50 g small alum crystals ( $L_m = 0.18 \cdot 10^{-3}$  m) were added. The cooling was finished at 25.0°C. The batch was stirred 20 min more to draw off the supersaturation and discharged to a centrifugal filter where the crystals were held back on a cotton filter cloth. The separated alum crystals were dried up at laboratory temperature in the air stream and sieved.

*Experimental arrangement:* The batchwise model experiments were carried out for three different cooling regimes described in the theoretical part (Fig. 1). 1) The temperature course during natural cooling is described by Eq. (1). When calculating the cooling curve according to this equation, the value of  $k = 4 \cdot 10^{-4}$  was used for the constant characterizing the overall heat transfer, which corresponded to the given temperature interval and the cooling time  $t_c$ . 2) During the linear cooling, the temperature change with time is given by Eq. (2) in which  $X = 1$ . 3) For the programmed cooling, Eq. (2) was employed with exponent  $X = 3$ , cor-

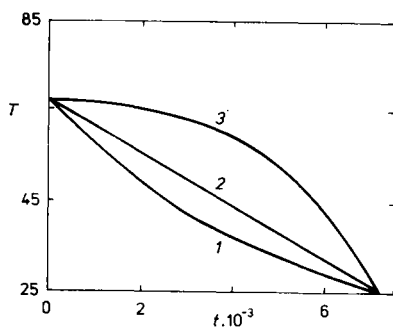


FIG. 1

Cooling curves for the cooling regimes studied. 1 Natural cooling (Eq. (1)); 2 linear cooling (Eq. (2),  $X = 1$ ); 3 programmed cooling (Eq. (2),  $X = 3$ )

responding to the growth of seeded crystals with negligible nucleation. Under all the regimes investigated, the total cooling times  $t_c$  were 7 200 and 16 200 s, in case of linear cooling, moreover, 11 700 s.

## RESULTS AND DISCUSSION

Altogether seven experiments were carried out for three regimes of cooling. From the results of sieve analyses, the mean crystal sizes  $\bar{L}_m$  were calculated from relations (3) and (4). On the basis of repeating two experiments, the error of determination of mean size was estimated to be  $\pm 0.02 \cdot 10^{-3}$  m. The values of  $L_m$  along with mean rates  $r_L$  and  $r_N$  calculated from Eqs (5) and (6) are given in Table I. When calculating  $r_N$ , the polished values of  $\alpha = 0.471$  (ref.<sup>13</sup>) and  $\rho_c = 1\,640$  kg/m<sup>3</sup> (ref.<sup>11</sup>) were used.

Table I shows that the mean linear crystallization rate is highest at programmed and lowest at natural cooling. With respect to the temperature dependence of the crystallization rate, the explanation of this fact can be sought in higher mean crystallization temperature under the programmed cooling regime (Fig. 1). The decrease in nucleation rate with higher degree of cooling control is in agreement with the model pattern according to which at intense initial cooling, a number of new nuclei is formed whereas at low cooling rate at the beginning of experiment, the supersaturation generated is drawn off above all by the growth of the crystal surface present. The higher crystal growth rate along with the lower nucleation rate during the cooling control lead then to the increase in the product crystal size.

The values of kinetic exponent of crystallization  $g/n$  were determined on using relations (13) and (14) for each cooling regime studied. They are given in Table II.

It is evident that the differences between the coefficients calculated for single regimes are insignificant. The mean value of  $g/n = 0.617 \pm 0.004$ , which will be used further, is besides in a very good agreement with the value of  $g/n = 0.608$  calculated from the separately measured values of  $g = 1.66$  (ref.<sup>14</sup>) and  $n = 2.73$  (ref.<sup>15</sup>). It follows from the results given that the value of kinetic exponent  $g/n$  does not depend on the cooling regime in our case.

The mean values of system constant  $B_N$  for the individual cooling regimes are given in Table II. Constant  $B_N$  was calculated for each experiment on using the mean value of  $g/n = 0.617$  and the suspension concentration at the end of experiment  $m_c = 0.39$  according to Eq. (7). With respect to the high content of the solid phase in suspension and intensive stirring it is to be assumed that in the course of crystallization, the secondary nucleation took place brought about mostly by the interactions of the crystal-crystal type. The value of exponent  $c = 2$  is recommended for such conditions of secondary nucleation.

As it could be expected, the system constant  $B_N$  depends on the cooling regime. Thereto the difference of values  $B_N$  for the natural and linear cooling is greater than between the regimes 2 and 3.

From the system constants presented follows that unlike the measurement of kinetic exponent  $g/n$ , to obtain reliable values of  $B_N$ , in model experiments it is necessary to approach, in the highest possible degree, the real temperature regime expected in the industrial crystallizer.

The practical consequence of these differences can be documented, e.g., by calculating the total time necessary for preparing a product of mean crystal size  $L_m = 0.65 \cdot 10^{-3}$  m at different cooling regimes. The calculated values of  $t_c$ , which are given in Table II, are the distinct evidence of the fact how, at the given product crystal size, it is possible to influence the batch time through the cooling regime and consequently also the capacity of batch cooling crystallizer.

It follows from the batchwise model experiments carried out under various cooling regimes (natural, linear, programmed) that the kinetic exponent  $g/n$  of the crystallization of ammonium aluminium sulphate dodecahydrate does not depend on the temperature regime whereas the system constant  $B_N$  is a function of cooling regime

TABLE I  
Experimental and calculated crystallization parameters

Cooling regime	Cooling time, $t_c$ s	$L_m \cdot 10^3$ m	$r_L \cdot 10^{10}$ m s <sup>-1</sup>	$r_N^{-1} s^{-1}$ kg <sub>o</sub> <sup>-1</sup>
1	7 200	0.567	788	5 193
	16 200	0.631	390	1 675
2	7 200	0.628	872	3 822
	11 700	0.667	570	1 963
	16 200	0.701	433	1 221
3	7 200	0.656	911	3 353
	16 200	0.733	453	1 068

TABLE II  
Kinetic exponent and system constant

Cooling regime	$g/n$	$B_N \cdot 10^{12}$	$t_{c,calc}$ s
1	0.622	5.24	20 040
2	0.616	7.00	9 410
3	0.612	7.98	6 680

and acquires its highest value in case of programmed cooling according to the curve derived theoretically.

## SYMBOLS

$B_N$	system constant, $m^{1+3g/n} \text{ kg}^{(c-1)g/n} \text{ kg}_0^{(1-c)g/n} \text{ s}^{g/n-1}$
$c$	exponent of secondary nucleation
$g$	kinetic order of crystal growth
$k$	coefficient characterizing overall heat transfer, $\text{s}^{-1}$
$k'_G$	rate constant of growth, $\text{m kg}^{-g} \text{ kg}_0^g \text{ s}^{-1}$
$k'_N$	rate constant of nucleation, $\text{kg}^{-c-n} \text{ kg}_0^{c+n-1} \text{ s}^{-1}$
$L_m$	mean particle size, m
$M(L)$	cumulative mass distribution function
$m_c$	suspension concentration, $\text{kg/kg}_0$
$n$	nucleation equation order
$r_L$	mean linear crystallization rate, $\text{m s}^{-1}$
$r_N$	mean nucleation rate, $\text{kg}_0^{-1} \text{ s}^{-1}$
$T$	instantaneous temperature, K
$T_e$	end cooling temperature, K
$T_0$	initial cooling temperature, K
$T_W$	cooling water temperature, K
$t$	time interval, s
$t_c$	cooling time, s
$w$	concentration (kg of crystallizing substance/kg of water), $\text{kg/kg}_0$
$z$	dimensionless crystal size
$\alpha$	volume shape factor
$\rho_c$	crystal density, $\text{kg m}^{-3}$

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Translated by J. Linek.