

## EXPERIMENTAL SECONDARY NUCLEATION IN A BATCH CRYSTALLIZER

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The effect of the amount of seeded crystals on the result of crystallization of potassium sulphate, sodium nitrate and ferrous sulphate heptahydrate was studied experimentally on a laboratory model of a batch, stirred, cooled crystallizer. Estimate of kinetic parameters of crystallization and of the system constant was possible from the analysis of granulometric product composition. Nucleation exponents were determined from the dependence of the system constant on the production capacity of the crystallizer. It results, that the nucleation exponents depend on the amount of the crystals seeded and at their sufficient quantity the ratio  $n/g$  is approaching unity.

Formation and growth of crystals in crystallizers take place in relatively concentrated suspensions. While growth of a single crystal should be affected only minimally in the presence of other particles in the suspension, the problem of nucleation is much more complex. It is well known that the nucleation kinetics is considerably affected by the presence of even few individual crystals in the suspension<sup>1-5</sup> and thus the measurement and evaluation of the kinetics from the width of metastable region is always performed in the presence of few crystals. It has been also determined that in very diluted suspensions the result is independent of the number of added crystals. But a different situation may arise in the crystallizer where the concentration of the suspension reaches such value that the interaction of individual crystals cannot be neglected. And exactly these interactions are stipulating a new effect — the secondary nucleation. There exist quite a number of acceptable mechanisms which are explaining the secondary nucleation<sup>6,7</sup>. Here, an attempt has been made to find out if and how the secondary nucleation will affect the initial operation period of a batch crystallizer and how it will affect the shape of basic relations describing this process<sup>8-10</sup>.

### THEORETICAL

The mass of crystals obtained in a batch crystallizer can be expressed by a general relation

$$m_c = \int_0^{L_{\max}} n \alpha Q_c L^3 dL. \quad (1)$$

If the saturation (*e.g.* by cooling or evaporation) of the non-seeded solution is performed at a constant velocity, the initial supersaturation increases nearly linearly until the boundary of the metastable region corresponding to the conditions of the experiment is reached. When the boundary of the metastable region is reached crystal nuclei are formed which begin to grow and thus remove supersaturation from the solution. Under the assumption that an initial crystal area  $A_0$  has been formed by formation of crystal nuclei, then for the decrease of supersaturation can be written

$$\frac{d\Delta c}{dt} = s - k_G A(t) \Delta c^n. \quad (2)$$

Surface area of crystals in dependence on time can be expressed by the relation

$$A(t) = \int_{t_N}^{t_0} \beta n (\bar{L}t + L_N)^2 dt, \quad (3)$$

so that solution of the integro-differential Eq. (2) is very difficult. Nevertheless it can be assumed that a generalized solution can be approximated by a relation of the type

$$\Delta c(t) \sim at^b \exp(-ct),$$

or

$$\Delta c(t) \sim \Delta c_{\max} \exp(-dt), \quad [\Delta c \geq \Delta c_{\max}], \quad (4)$$

where  $a$ ,  $b$ ,  $c$ ,  $d$  are adjustable parameters which in general can also be a function of time,  $t$ . As the nucleation rate depends also on supersaturation

$$\dot{m}_N = k_N \Delta c^n \quad (5)$$

and thus

$$\dot{m}_N(t) = k_N \Delta c_{\max}^n \exp(-n dt), \quad (6)$$

the distribution function (crystal population density) can be approximated by the relation

$$n = n^0 \exp(-z), \quad (7)$$

where  $z$  is the dimensionless crystal size defined<sup>9,10</sup> as

$$z = 3(L - L_N)/(\bar{L} - L_N) \quad (8)$$

and the constant  $n^0$  represents the population density of crystal nuclei which is bound with the nucleation kinetics *via* the relation<sup>11-13</sup>

$$\dot{N}_N = n^0 \dot{L}, \quad (9)$$

or

$$\dot{m}_N = \alpha Q_c L_N^3 n^0 \dot{L}. \quad (10)$$

As Eq (7) is formally identical with the equation giving the crystal population density in a continuous ideally stirred crystallizer, the granulometric product composition from the batch crystallizer can be approximated under the above given conditions by the formally identical relation which is valid for the continuous crystallizer

$$M(z) = 100(1 + z + z^2/2 + z^3/6) \exp(-z). \quad (11)$$

So far we have considered only formation of crystal nuclei under the assumption that the original solution is not seeded. When the solution was at the beginning of the crystallization seeded by crystals whose dimensions were different from those of crystal nuclei,  $L_N$ , the distribution curve  $M'(z)$  would have two peaks and the given relations could not be applied to the direct experimental data. Thus let us assume that the crystals seeded as well as the newly formed nuclei behave more or less independently in the suspension and that the crystal size distribution can be described as a mixture of two fractions: of fraction 1 formed from the seeded crystal nuclei and fraction 2 originated from the newly formed crystal nuclei. For this case can be written<sup>14</sup>

$$M(L) = w_1 M(z_1) + (1 - w_1) M(z_2), \quad (12)$$

with quantities  $z_1$  and  $z_2$  defined by relationships

$$\begin{aligned} z_1 &= 3(L - L_0)/(\bar{L}_1 - L_0), & [L \geq L_0], \\ z_1 &= 0, & [L \leq L_0], \\ z_2 &= 3(L - L_N)/(\bar{L}_2 - L_N), & [L \geq L_N], \\ z_2 &= 0, & [L \leq L_N], \end{aligned} \quad (13)$$

while it holds (all crystals grow at the same conditions)

$$\bar{L}_1 - L_0 = \bar{L}_2 - L_N = 3\dot{L}t_c. \quad (14)$$

If the size distribution of seeded crystals differs considerably from the distribution of crystals which form spontaneously in the process *i.e.* if the seeded crystals were obtained by using a narrow fraction  $L_{01}$  to  $L_{02}$  of the screened product and if we, for the sake of mathematical simplicity, want to preserve the form of Eq. (12), we must assume that 99% of the fraction has the dimensions from  $L_{01}$  to  $L_{02}$  (value  $L_{01}$

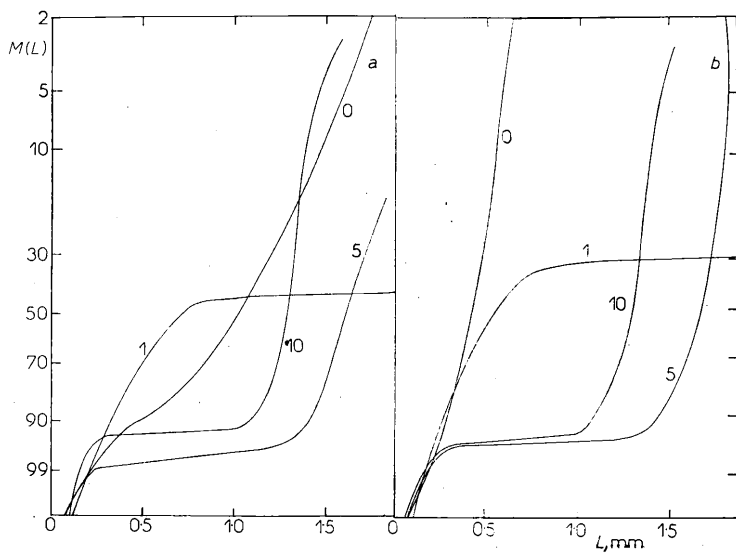


FIG. 1

Sieve Spectra of  $K_2SO_4$  in Experiments with Cooling Rates

a 5 K/h, b 20 K/h. Number with the curve is the content of solid phase.

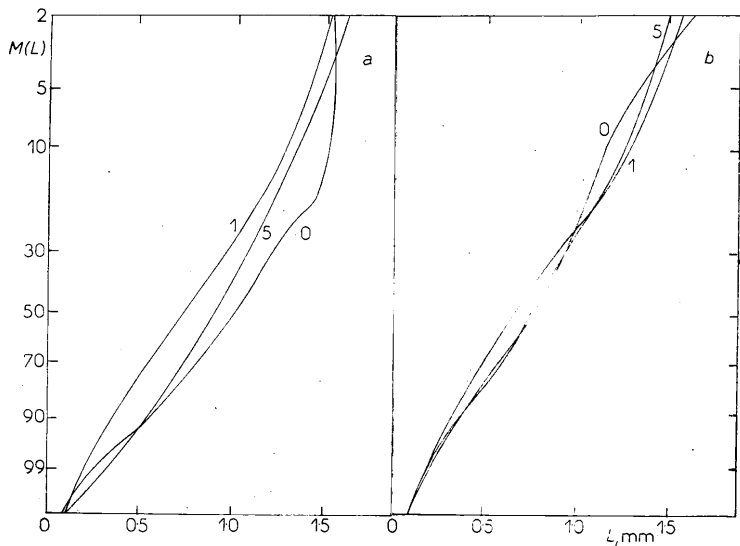


FIG. 2

Sieve Spectra of  $NaNO_3$  in Experiments with Cooling Rates

a 5 K/h, b 20 K/h. Number with the curve is the content of solid phase.

then corresponds to  $z_1 = 0$  and value  $L_{02}$  corresponds to  $z_1 = 10$ ), then it holds

$$\begin{aligned} z_1 &= 10(L - L_0)/(L_{02} - L_{01}), \quad [L \geq L_0], \\ z_1 &= 0 \quad [L \leq L_0]. \end{aligned} \quad (13a)$$

Under these conditions, Eq. (12) is satisfactorily expressing the crystal size distribution of the product from the seeded batch crystallizer. Evaluation of the experimental data can be advantageously performed on the computer<sup>15</sup>.

On combining Eqs (1), (7) and (8), the relationship (15) is obtained which enables calculation of the constant  $n^0$  from the direct experimental data

$$n^0 = \frac{m_c}{6\alpha Q_c} \left( \frac{3}{\bar{L} - L_N} \right)^4. \quad (15)$$

For the mean linear growth rate can be written<sup>9</sup>

$$\dot{L} \sim (\bar{L} - L_N)/3t_c \quad (16)$$

and as it holds<sup>5</sup>

$$\dot{L} = k_G \beta \Delta c^s / (3\alpha Q_c), \quad (17)$$

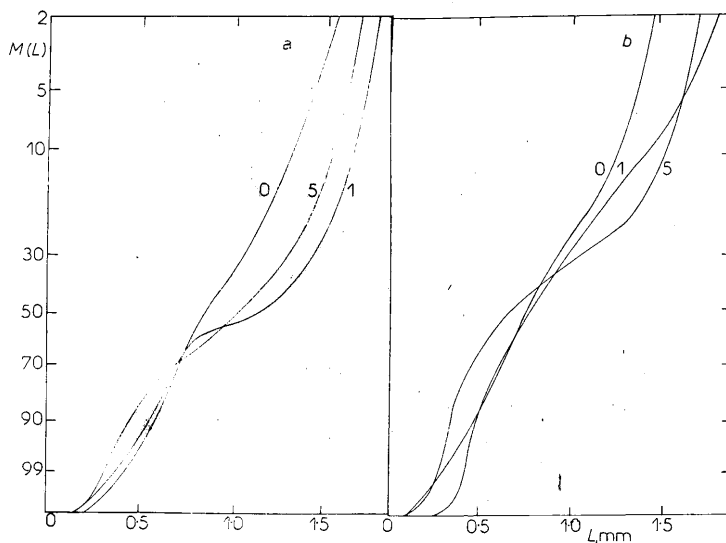


FIG. 3

Sieve Spectra of  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  in Experiments with Cooling Rates  
 a 5 K/h, b 20 K/h. Number with the curve is the content of solid phase.

the nucleation rate can be expressed by means of the linear growth rate under the same conditions

$$\dot{m}_N = (3\alpha\varrho_c k_N^{g/n} / k_G \beta)^{n/g} \cdot \dot{L}^{n/g} \quad (18)$$

TABLE I  
Characteristic Data of Individual Experiments;  $\alpha = 1$

No	Compound		
	K <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>	FeSO <sub>4</sub> ·7H <sub>2</sub> O
	$\varrho_c$		
	2 662	2 260	1 900
	$m_{H_2O}$		
1	2·074	1·042	1·505
2	1·778	1·622	1·462
3	1·893	1·528	1·180
4	2·275	1·671	1·525
5	2·094	1·600	1·185
6	1·943	1·642	1·795
7	1·510	—	—
8	2·230	—	—
	$m_0 \cdot m_{H_2O}$		
1	0	0	0
2	0·0030	0·0195	0·0130
3	0·0160	0·0930	0·0650
4	0·0390	0·0000	0·0000
5	0·0000	0·0190	0·0130
6	0·0032	0·0950	0·0700
7	0·0125	—	—
8	0·0390	—	—
	$m_c \cdot m_{H_2O}$		
1	0·0684	0·2287	0·2998
2	0·0634	0·3247	0·2946
3	0·0698	0·5049	0·2952
4	0·1070	0·3420	0·3086
5	0·0677	0·3466	0·2907
6	0·0721	0·4265	0·2968
7	0·0604	—	—
8	0·1017	—	—

It has been already proved<sup>8,9</sup> that the behaviour of the continuous and batch crystallizers can be satisfactorily characterised by the system constant

$$B = k_G \beta / 3 \alpha \rho_c k_N^{g/n} L_N \quad (19)$$

From Eqs (18) and (19) results the relation

$$B = \dot{L} / (L_N \dot{m}_N^{g/n}), \quad (20)$$

which enables determination of the ratio  $g/n$  from experimental data obtained at two different supersaturation rates.

TABLE II  
Evaluation of Sieve Spectra

$L$ , mm	$M(L)$ exper.	$M(L)$ calc.	$M_1(L)$	$M_2(L)$
Non-seeded solution of $\text{NaNO}_3$ ( $L_N = 0.1$ mm, $L_0 = 0.45$ mm, $\dot{L}t_c = 0.095; 0.095$ , $w_1 = 0.58$ , $\delta = 1.07$ )				
1.40	0.14	0.62	1.03	0.06
1.25	3.13	1.92	3.18	0.21
1.00	10.16	10.48	17.10	1.51
0.80	32.00	31.34	49.75	6.45
0.71	44.66	45.58	70.60	11.74
0.63	58.86	58.55	87.56	19.29
0.50	74.08	74.10	99.79	39.35
0.40	84.39	83.51	100.00	61.19
0.31	90.69	92.23	100.00	81.73
0.20	97.08	99.05	100.00	97.76
Seeded soln. of $\text{FeSO}_4$ ( $L_N = 0.1$ , $L_0 = 1.3$ , $\dot{L}t_c = 0.185; 0.03$ , $w_1 = 0.3$ , $\delta = 3.47$ )				
1.60	2.73	3.07	1.03	3.94
1.40	24.40	22.82	57.30	8.04
1.25	41.07	39.30	100.00	13.29
1.00	46.44	49.92	100.00	28.45
0.80	56.27	63.38	100.00	47.68
0.71	70.94	70.67	100.00	58.09
0.63	82.94	77.42	100.00	67.75
0.50	91.67	87.87	100.00	82.67
0.40	94.30	94.27	100.00	91.82
0.31	96.20	98.01	100.00	97.16
0.20	97.93	99.84	100.00	99.77

## EXPERIMENTAL

A series of experiments was performed with a batch crystallization of potassium sulphate, sodium nitrate and ferrous sulphate heptahydrate on the laboratory model described earlier<sup>9</sup>. The experiments were performed without seeding (only in the presence of 2 to 3 crystals) and with seeding at constant cooling rates 5 K/h and 20 K/h. The fraction of crystals from 0.6 to 0.9 or 1.00 mm was used for seeding in the amounts of about 0; 1; 5% and for  $K_2SO_4$  also 0% related to the total amount of the dissolved substance. The used chemicals were analytical grade reagents prepared by crystallization in distilled water. For  $FeSO_4$ , several drops of  $H_2SO_4$  were added into the solution to prevent the hydrolysis.

TABLE III  
Evaluation of Sieve Analysis

No	Seed %	$-\dot{T}$ K/h	$L_N$ mm	$L_0$ mm	$\dot{L}_c$	$(\dot{L}_c)_0$	$w_1$	$\delta$
$K_2SO_3$								
1	0	5	0.08	0.350	0.215	0.215	0.20	4.04
2	1	5	0.10	1.70	0.120	0.040	0.40	2.66
3	5	5	0.10	1.40	0.260	0.040	0.78	4.41
				1.30	0.175		0.93	5.19
4	10	5	0.10	1.05	0.05	0.040	0.93	2.12
5	0	20	0.08	0.280	0.080	0.080	0.00	5.31
6	1	20	0.10	1.95	0.060	0.040	0.25?	?
				1.60			0.28	9.61
7	5	20	0.10	1.35	0.095	0.040	0.93	2.81
8	10	20	0.10	1.05	0.050	0.040	0.93	1.61
$NaNO_3$								
1	0	5	0.10	0.400	0.190	0.190	0.30	1.28
2	1	5	0.10	0.900	0.090	0.030	0.33	4.94
3	5	5	0.10	0.900	0.160	0.030	0.25	4.87
4	0	20	0.10	0.450	0.095	0.095	0.58	1.07
5	1	20	0.10	0.900	0.100	0.030	0.28	4.13
6	5	20	0.10	0.900	0.145	0.030	0.10	2.93
$FeSO_4 \cdot 7 H_2O$								
1	0	5	0.10	0.250	0.170	0.170	0.55	4.16
2	1	5	0.10	1.300	0.185	0.030	0.30	3.47
3	5	5	0.10	1.300	0.170	0.030	0.23	2.45
4	0	20	0.10	0.300	0.165	0.165	0.03	3.14
5	1	20	0.10	1.450	0.155	0.030	0.05	2.66
6	5	20	0.10	1.350	0.150	0.030	0.10	7.31



Each experiment was three to six times repeated so that the representative resulting size distributions could be obtained. The freely dried product was weighed and the sieve analysis was undertaken. Obtained results of the sieve analysis were evaluated according to the published procedure<sup>16</sup> and the corresponding experiments were compared. From a series of obtained curves, that one had been selected which was a representative of the whole group, and the corresponding experiment was further analysed. The sieve analyses of products from these selected experiments are summarized in Figs 1 to 3. The characteristic data for these selected experiments are given in Table I. The results of sieve analyses of products from these experiments were analysed on the computer<sup>15</sup>. An example of such evaluation is given in Table II and in Figs 4 to 7. All results of evaluation of the experiments are summarized in Table III.

TABLE IV  
Kinetic Nucleation and Growth Parameters Calculated from Experimental Data

Seed %	$-\dot{T}$ K/h	$n^0 \cdot 10^{-10}$ $m^{-1}$	$N \cdot 10^{-8}$	$\dot{N} \cdot 10^{-3}$ $s^{-1}$	$\dot{m}_N \cdot 10^6$ $s^{-1}$	$\dot{L} \cdot 10^6$ m/s	$B$
<b>K<sub>2</sub>SO<sub>4</sub></b>							
0	5	0.08	1.50	11.9	31.7	14.9	0.35
1	5	0.67	10.19	55.6	148	8.3	0.42
5	5	0.01	1.67	1.8	4.8	18.1	0.66
10	5	3.44	10.39	120	319	3.5	110
0	20	5.16	9.00	1 145	3 048	22.2	0.36
1	20	13.48	29.84	2 250	5 990	16.7	0.43
5	20	0.22	5.35	58.1	155	26.4	0.67
10	20	3.33	6.64	463	1 233	13.9	113
<b>NaNO<sub>3</sub></b>							
0	5	0.87	12.35	115	260	13.2	0.99
1	5	15.07	59.52	949	2 145	6.3	5.82
5	5	2.79	20.78	310	701	11.1	4.71
0	20	7.78	27.76	2 054	4 642	26.4	0.98
1	20	11.50	30.13	3 197	7 225	27.8	6.65
5	20	3.90	63.62	1 572	3 553	40.3	4.42
<b>FeSO<sub>4</sub> · 7H<sub>2</sub>O</b>							
0	5	0.94	3.36	111	211	11.8	2.34
1	5	1.06	6.36	136	258	12.8	0.80
5	5	2.02	12.69	238	452	11.8	7.21
0	20	2.32	16.65	1 063	2 020	45.8	2.22
1	20	3.54	6.41	1 526	2 899	43.1	0.80
5	20	2.58	17.19	1 076	2 044	41.7	7.26

## DISCUSSION AND CONCLUSIONS

The nuclei population density,  $n_0$ , was evaluated from the experimental data for the fraction of fine particles,  $w_2$ , according to Eqs (9), (10), (15) and (16) together with the numerical nucleation rate  $\dot{N}$ , mass nucleation rate  $\dot{m}_N$  and linear growth rate  $\dot{L}$ . The mass of crystals in Eq. (15) was calculated as  $(m_c/m_{H_2O})(1 - w_1)$ . The total time of the experiments under cooling by 20 K at rates 5 K/h was 14400 s and at rates 20 K/h 3600 s. The nucleation rates  $\dot{m}_N$  and the linear growth rate  $\dot{L}$  from the comparable experiments (the same method of seeding, only different cooling rates) were plotted in logarithmic coordinates. If the nucleation rate is described by Eq. (18), the considered dependence must be represented by a straight line with the slope equal to  $n/g$ .

For individual pairs of experiments, the following approximate values were read off from the corresponding graph:  $K_2SO_4$  0% of solid phase:  $n/g = 12.0$ ; 1% of solid phase:  $n/g = 5.4$ ; 5% of solid phase:  $n/g = 9.4$ ; 10% of solid phase:  $n/g = 1.0$ .  $NaNO_3$ : 0% of solid phase:  $n/g = 4.1$ ; 1% of solid phase:  $n/g = 0.9$ ; 5% of solid phase:  $n/g = 1.2$ .  $FeSO_4$ : 0% of solid phase:  $n/g = 1.6$ ; 1% of solid phase:  $n/g = 2.0$ ; 5% of solid phase:  $n/g = 1.2$ .

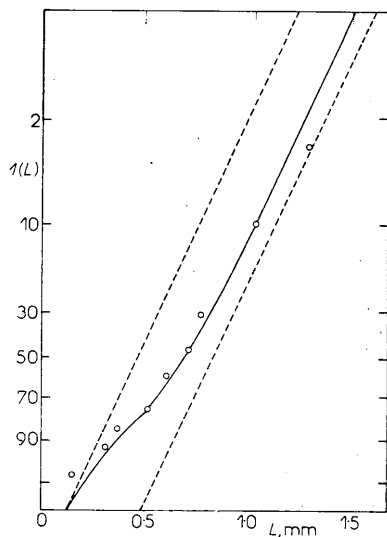


FIG. 4

Linearized Sieve Spectra of Experiments with  $NaNO_3$

20 K/h without seeding;  $L_N = 0.1$  mm,  $L_0 = 0.45$  mm,  $\dot{L}_e = 0.095$  mm,  $w_1 = 0.58$ .

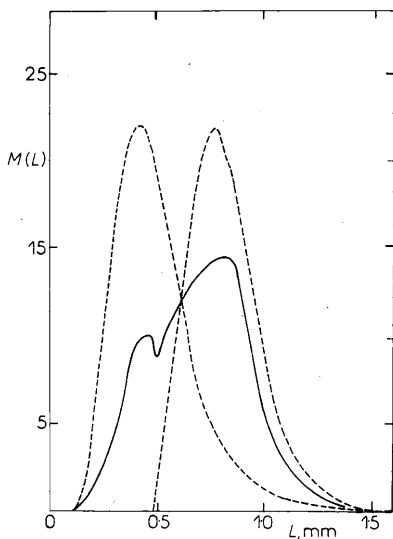


FIG. 5

Distributive Distribution Function of the Sample from Fig. 4

The system constants were evaluated by use of Eq. (20). All calculated results are summarized in Table IV.

First of all let us consider the results of  $n/g$  evaluated from kinetic data. We are well aware that these results are affected by a considerable error but nevertheless it is obvious that with increasing amount of seeded crystals the ratio  $n/g$  decreases from the initial higher value to the value close to one. If the ratios  $n/g$  are calculated from the published data<sup>17,18</sup> the following limiting values are obtained:

$$\text{K}_2\text{SO}_4: \quad n = 9.3, \quad g = 2.0, \quad n/g = 4.65;$$

$$\text{NaNO}_3: \quad n = 3.69, \quad g = 1.0, \quad n/g = 3.69;$$

$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}: \quad n = 2.30, \quad g = 1.0, \quad n/g = 2.30,$$

which are values close to those calculated in this study for zero (for  $\text{K}_2\text{SO}_4$  1%) amount of seeded crystals added. But of importance is the decrease of this value to 1 in cases when bigger amount of crystals was seeded, which demonstrates changes in mechanism of nucleation. Small nucleation exponents are in general characteristic for secondary nucleation and so validity of this mechanism has been clearly proved

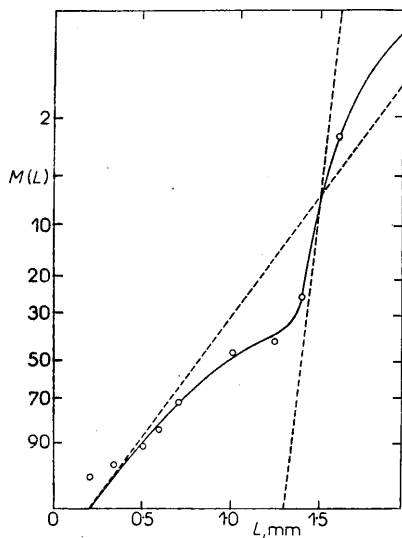


FIG. 6

Linearized Sieve Spectra of Experiments with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

5 K/h, seeding 1%;  $L_N = 0.1$  mm,  $L_0 = 1.3$  mm,  $\dot{L}t_c = 0.185$  mm,  $(\dot{L}t_c)_s = 0.03$  mm,  $w_1 = 0.30$ .

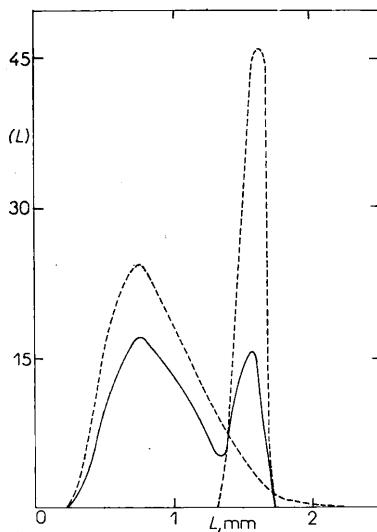


FIG. 7

Distributive Distribution Function of the Sample from Fig. 6

in the given experiments. The result is the more interesting that the amount of seeded crystals is quite negligible in respect to the total amount of product crystals at the end of the experiment. This speaks of considerable importance of initial periods in batch crystallization and that the kinetics of secondary nucleation was probably not determined by microabrasion of crystals in the considered cases but more probably by some of the mechanisms of adsorption layer; in the first case, the found dependence would not be so profound.

As concerns the growth and nucleation kinetics, it can be concluded that in agreement with the expectations an increase in the rates of both these processes takes place at higher cooling rates while dependence on the amount of seeded crystals has not a unique character.

With regard to necessary simplifying assumptions and approximations made in evaluation of experimental data from batch experiments, it was not reasonable to make a more detailed analysis of results which were affected by a considerable inaccuracy. But the present study is clearly demonstrating the role played by secondary nucleation in the initial periods of a batch process.

#### LIST OF SYMBOLS

$a, b, c, d$	constants
$B$	system constant defined by Eq. (19)
$c$	concentration (kg of crystallizing substance/kg of free solvent)
$\Delta c$	supersaturation (c)
$g$	order of kinetic equation of crystal growth
$k_G, k_N$	rate constant of growth and nucleation, respectively
$L$	size of crystals (m)
$L_N$	size of crystal nuclei (m)
$L_0$	size of smallest crystals in the coarse fraction (m)
$L_{01}, L_{02}$	size of seeded crystals (m)
$\bar{L}$	mean size of crystals (m)
$\dot{L}$	linear growth rate (m/s)
$M(L)$	cumulative distribution function (oversize)
$M'(L)$	distributive distribution function
$m_c$	mass of crystals in a unit amount of suspension (kg/kg <sub>H<sub>2</sub>O</sub> )
$m_{H_2O}$	mass of water in crystallizer (kg <sub>H<sub>2</sub>O</sub> )
$m_0$	mass of seeded crystals in a unit amount of suspension (kg/kg <sub>H<sub>2</sub>O</sub> )
$\dot{m}_N$	nucleation rate (kg kg <sub>H<sub>2</sub>O</sub> <sup>-1</sup> s <sup>-1</sup> )
$n$	nucleation order
$n$	crystal population density (m <sup>-1</sup> )
$n^0$	nuclei population density (m <sup>-1</sup> )
$N$	number of crystals in the product
$\dot{N}_N$	numerical nucleation rate (s <sup>-1</sup> kg <sub>H<sub>2</sub>O</sub> <sup>-1</sup> )
$-T$	cooling rate (K/h, K/s)
$t_c$	total cooling time (s)
$w_1$	mass fraction of coarse particle fraction
$z$	dimensionless crystal size

$\alpha$	volume shape factor
$\beta$	surface shape factor
$\delta$	mean quadratic deviation of experimental and smoothed values $M(L)$
$\rho_c$	density of crystals ( $\text{kg/m}^3$ )

## REFERENCES

1. Nývlt J., Gottfried J., Křičková J.: This Journal 29, 2283 (1964).
2. Nývlt J., Gottfried J.: This Journal 32, 3459 (1967).
3. Nývlt J.: J. Cryst. Growth 3, 4, 377 (1968).
4. Nývlt J., Rychlý R., Gottfried J., Wurzelová J.: J. Cryst. Growth 6, 151 (1970).
5. Nývlt J.: *Industrial Crystallisation from Solutions*. Butterworths, London 1971.
6. Asselbergs C. J., de Jong E. J.: *Secondary Nucleation, a Discussion at the Working Party on Crystallisation of the European Federation of Chemical Engineering*. Boekelo (the Netherlands) 1972.
7. Nývlt J.: Chem. Prům. 23, 417 (1973).
8. Nývlt J., Skřivánek J.: This Journal 33, 1788 (1968).
9. Nývlt J., Kočová H., Černý M.: This Journal 38, 3199 (1973).
10. Nývlt J.: Chem. Prům. 23, 343 (1973).
11. Randolph A. D., Larson M. A.: *The Theory of Particulate Processes*. Academic Press, New York 1971.
12. Nývlt J.: Chem. Prům. 21, 378 (1971).
13. Nývlt J.: Krist. Tech. 8, 595 (1973).
14. Nývlt J., Kožmín B.: Chem. Prům. 23, 173 (1973).
15. Nývlt J., Haas K.: *Crystal Size Distribution of the Products*. Rept. Res. Inst. Inorg. Chem., Ústí n. L. No 707 (1973).
16. Nývlt J.: Chem. Prům. 18, 579 (1968).
17. Kočová H., Nývlt H., Nývlt J.: Chem. Prům. 22, 165 (1972).
18. Wurzelová J., Nývlt J.: Chem. Prům. 23, 69 (1973).

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