KINETICS OF TRANSFORMATION OF CALCIUM SULPHATE HEMIHYDRATE INTO THE DIHYDRATE IN A SYSTEM CONTAINING PHOSPHORIC AND SULPHURIC ACIDS

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The kinetics of the conversion of calcium sulphate hemihydrate into the dihydrate were determined by measuring the time dependence of the activity of a solution of calcium sulphate labeled by the ^{45}Ca radioisotope in phosphoric and sulphuric acids. The measured data were verified independently on a pilot plant crystallizer.

One of important methods for the production of phosphoric acid consists in decomposition of natural phosphate by sulphuric acid, by the so-called extraction or wet process. Decomposition of fluoroapatite is effected by a mixture of sulphuric and phosphoric acids. The separation of thus formed calcium sulphate and possibilities of its utilization depend on its crystalline form. In dependence on temperature and concentration of phosphoric acid there are crystallizing either anhydrous calcium sulphate (anhydrite) or crystallohydrates: $CaSO_4.0.5 H_2O$ (hemihydrate), or $CaSO_4.2 H_2O$ (dihydrate). In the studied temperature and concentration range (25—32% P_2O_5, 50—70°C) the calcium sulphate precipitates in a metastable form of hemihydrate which is transformed with various rates into the stable dihydrate. The hydratation rate is dependent on temperature, concentration of phosphoric acid and on the concentration of other components present[1−10]. The hydratation time can be subdivided into two periods: *1.* latent period during which no observable change takes place and *2.* period of hydratation.

The published papers dealing with the course of hydratation[4,6−8], are mostly limited to purely mathematical expression of experimental curves without considering mechanism of the mentioned reaction. Obtaining the kinetic data on this phase transformation under conditions corresponding to the process technology has been the aim of this work and an effort has been made on their physico-chemical interpretation.

THEORETICAL

The kinetics of transformation of the calcium sulphate hemihydrate into dihydrate can be measured for example by the Birss–Thornwaldsen method[11]. At the beginning of measurements, the system is formed by inactive saturated solution of calcium sulphate whose concentration corresponds to the solubility of hemihydrate, in which

active hemihydrate labeled by radioisotope ^{45}Ca is suspended. Since the hemihydrate is a metastable phase, it is more soluble than the stable dihydrate and the solution is thus with regard to the dihydrate supersaturated for a concentration difference

$$\Delta c_0 = c_{1/2} - c_2 . \tag{1}$$

Independent experiments[10] have shown that the hemihydrate dissolves very quickly and so it can be assumed that, provided sufficient quantity of hemihydrate crystals is present in the system, the value of supersaturation Δc_0 remains constant.

After elapse of the latent period of time ($t = 0$) the first crystal nuclei of the dihydrate are formed. For the overall surface area of the dihydrate crystals in the suspension, after elapse of time t from origination of the first nuclei, we can write[12]

$$A = \beta \dot{N}_n L_n^2 (1 + \lambda t + \lambda^2 t^2 / 3) , \tag{2}$$

where

$$\lambda = \dot{L}/L_n , \tag{3}$$

and the linear crystallization rate[12]

$$\dot{L} = k_g \beta \, \Delta c / (3\alpha \varrho_c) . \tag{4}$$

The amount of dihydrate which is precipitated from the solution due to growth of nuclei, is directly proportional to the surface area of the crystals[12]:

$$\dot{m}_g = k_g A \, \Delta c_0 . \tag{5}$$

This amount is compensated by dissolving the active hemihydrate so that the mass of dissolved hemihydrate in time t will be also equal to $\dot{m}_g$. The total increase of the dihydrate mass is given by the sum of increase of mass of nuclei and the increase of mass of the crystals[12] present

$$\dot{m} = \mathrm{d}m/\mathrm{d}t = \dot{m}_g + \dot{m}_n = k_g A \, \Delta c_0 + \dot{m}_n . \tag{6}$$

If we substitute into this equation the surface area of crystals given by relation (2), we obtain[12] with regard to Eq. (4)

$$\mathrm{d}m/\mathrm{d}t = \dot{m}_n (1 + \lambda t)^3 , \tag{7}$$

or, for the amount of dissolved hemihydrate

$$m = \dot{m}_n t (1 + 3\lambda t / 2 + \lambda^2 t^2 + \lambda^3 t^3 / 4) . \tag{8}$$

In the experiment the activity of the solution is followed. For the activity balance we can write the differential equation

$$da_s = a_c \, dm - a_s/g \, dm \,, \qquad (9)$$

in which the expression $a_c \, dm$ denotes the increase in activity of the solution caused by dissolving of the active hemihydrate, and the expression $a_s/g \, dm$ corresponds to the decrease in activity of the solution due to dihydrate crystallization. All quantities are expressed in relation to one form of the calcium sulphate, e.g. $CaSO_4$. Eq. (9) can be also transformed into

$$dm = \frac{da_s/a_c}{(1 - a_s/a_c g)} \,. \qquad (10)$$

After integration within the limits $t = 0$ to t and $a_s = a_{s0}$ to a_s and after substitution into relation (8), we obtain

$$\varphi(a_s) = \log \frac{a_c g - a_{s0}}{a_c g - a_s} = \frac{\dot{m}_n}{2 \cdot 3 \, g} \, t(1 + 3\lambda t/2 + \lambda^2 t^2 + \lambda^3 t^3/4) \,. \qquad (11)$$

According to this equation the solution activity increases, at the verified assumption of very rapid dissolving of hemihydrate, to the moment of dissolving of all the solid hemihydrate. Then only growth of the present dihydrate crystals takes place according to equation[12]

$$dm/dt = k_g A \, \Delta c \,, \qquad (12)$$

while the supersaturation decreases according to the analogous equation

$$d\Delta c/dt = - k_g A \, \Delta c \,, \qquad (13)$$

down to the solution concentration corresponding to the solubility of dihydrate. As the surface area of crystals does not substantially change during their growth, it holds

$$\log (\Delta c_0/\Delta c) = k_g A t/2 \cdot 3 \,. \qquad (14)$$

At the assumption that the isotope ^{45}Ca precipitates into the crystals at a rate proportional to the concentration in the solution, Eq. (14) can be transformed into the form

$$\log \psi = \log \frac{a_{s \, max} - a_{s\infty}}{a_{st} - a_{s\infty}} = k_g A t/2 \cdot 3 \,. \qquad (15)$$

According to this equation the activity of the solution decreases exponentially with time until it steadies at the value $a_{s\infty}$. The dependence of activity of the solution on time is thus characterized by an expressive maximum because both branches of the curve represented by Eq. (11) and (15) are convex.

EXPERIMENTAL

Preparation of Solutions

The method is based on studying the activity of solution after adding the hemihydrate labelled by radioisotope ^{45}Ca to the inactive solution saturated in respect to the hemihydrate. The saturated solution was prepared by dissolving inactive hemihydrate in a mixture of sulphuric and phosphoric acids of required concentration. It is assumed that the equilibrium is reached very quickly. The data in Table I prove that the equilibrium is reached within 5 minutes after addition of the solid phase.

The equilibrium can be reached even more quickly by cooling the solution prepared at a higher temperature. This way of preparing the solution has another advantage in prolonging the time of hydratation by increasing the temperature. The time of preparation of saturated solutions by dissolving the hemihydrate at a higher temperature than is the temperature of the experiment does not affect therefore substantially the hydratation time. Equilibrium is reached at the temperature decrease very quickly, practically instantly.

Preparation of Hemihydrate

The hemihydrate prepared according to Birss[11] by drying the dihydrate at 85°C for 8 hours, or according to Harry[9] by drying the dihydrate at 130°C for 2 hours, always contained, according to analyses made thermogravimetrically and by difraction of X-rays, a certain quantity of dihydrate within the range of 1—3%. The hemihydrate without the dihydrate was therefore prepared by precipitation from solutions of calcium phosphate. To verify the effect of conditions of precipitation on the form and size of crystals the precipitation of hemihydrate was made by sulphuric acid from solutions of concentrations 25, 28, 32 and 35% P_2O_5 at 70°C. Instantly after precipitation the hemihydrate was filtrated and washed by methyl alcohol. The drying lasted 2 hours at 80°C. From microfilm pictures of these samples has been found that in the mentioned

TABLE I

Equilibrating Rate

t, min	imp./g min	% $CaSO_4$	t, min	imp./g min	% $CaSO_4$
0·5	480	0·385	4	795	0·640
1	595	0·480	4·5	805	0·645
2	700	0·560	5	805	0·645
2·5	740	0·595	5·5	810	0·650
3	770	0·620	10	808	0·648

concentration range is the size of crystals the same, in the range from 20 to 40 μm. Thermogravimetrical and X-ray difraction analyses have proved the purity of hemihydrate obtained in this way.

Further, the dependence of the size of hemihydrate crystals on the crystallization time was determined. The conditions of precipitation were: 32% P_2O_5, 70°C. Values obtained by evaluation of microfilm pictures show that after 2 hours the size of crystals does not change any more and attains the average value of 150 μm. To eliminate the effect of the crystal size, crystals of hemihydrate crystallized for 4 hours at the mentioned conditions were used both for measurement of the time of hydratation as well as for measurement of solubility. Precipitation was made by drops using solution of 50% sulphuric acid.

The active hemihydrate was prepared in the same way with addition of isotope [45]Ca in the form of $CaCl_2$ before precipitation.

Apparatus and Methodics

To follow the rate of hydratation of calcium sulphate to dihydrate, the apparatus shown schematically in Fig. 1 was used.

The experiments were made in 250 ml three-necked flasks. Into these flasks, there was pipetted from the stock solutions 50 ml of a solution of a chosen concentration of P_2O_5 and H_2SO_4, heated up to a temperature higher by 10°C than was the temperature of the proper experiment and saturated by inactive hemihydrate for a period of 5 minutes. The system was then quickly cooled down to the required temperature and the active hemihydrate was added.
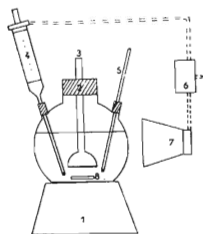

FIG. 1

Apparatus for Measuring the Hydratation Rate

1 Electromagnetic stirrer, 2 flask 250 ml, 3 fritted glass S 5, 4 contact thermometer Vertex, 5 thermometer, 6 mercury relay, 7 infralamp, 8 stirrer.

The temperature was kept constant by an infralamp controlled by a contact thermometer with an accuracy ± 0.1°C and was measured by the thermometer with 0.1°C scale. Mixing was made by an electromagnetic stirrer. Sampling of the solution was made with the use of a fritted glass S 5 (Kavalier) which had a form of a small flask with a stem. Into this fritted glass the solution was sucked with an injection syringe and samples of volume of 0.2 ml were taken by a micropipette into an aluminium bowl into which there was beforehand pipetted 1.8 ml of water to keep the calcium sulphate in solution. The activity measurement was made after thoroughfull mixing.

Dosimetry of Radioisotope [45]Ca

Radioisotope [45]Ca is a pure β-emitter with its half-life period of disintegration 163 days and radiating energy 0.254 MeV. The disintegration constant has the value $4.922 \cdot 10^{-8}$ s^{-1}.

The dosimetry was carried out by GM tubes made by Vakutronik (GDR) with mica view slit with a square weight 2 mg/cm^2 (type VA-2-300). Lead cover of the tube and the counter of pulse rate were also products of the company Vakutronik. The dead time was for used device 3 . 10^{-5} min and with most of measurements (up to 2 000 pulses/min) only correction for the background was made. Efficiency of GM tube was measured in measuring the liquid samples on aluminium plates at the distance 1 cm from the view slit. The sample of volume 1 ml with calculated total activity 6 . 10^{-2} μC had in the given arrangement an average counting rate of 1 150 pulses/min, *i.e.* the measuring efficiency approx. 1%. Measurements of liquid samples were carried out on aluminium plates of 30 mm diameter and 5 mm depth which were coated with a thin layer of epoxide resin to prevent corrosion. Without this arrangement there occurred, at longer lasting measurements, a leakage of hydrogen from the plate bottoms and a contamination of the mica

TABLE II

Solubility of Hemihydrate and Dihydrate in Mixtures of Phosphoric and Sulphuric Acids (weight % CaSO$_4$)

% P$_2$O$_5$	% H$_2$SO$_4$	CaSO$_4$.0·5 H$_2$O	CaSO$_4$.2 H$_2$O	Δc_0
		50°C		
28	0	1·03	0·63	0·4
	1·5	0·54	0·30	0·24
	3	0·32	0·15	0·17
	5	0·21	0·07	0·13
		60°C		
25	0	1·50	1·17	0·33
	1·5	0·75	0·51	0·24
	3	0·54	0·32	0·22
	5	0·41	0·21	0·20
28	0	1·32	1·06	0·26
	1·5	0·65	0·48	0·17
	3	0·47	0·31	0·16
	5	0·35	0·20	0·15
32	0	1·21	0·99	0·22
	1·5	0·58	0·45	0·13
	3	0·33	0·24	0·04
	5	0·22	0·15	0·07
		70°C		
28	0	1·45	1·22	0·23
	1·5	0·83	0·65	0·18
	3	0·58	0·44	0·14
	5	0·43	0·31	0·12

view slit due to entrained activity. Distance of the plates from the view slit of the GM tube was 1 cm. The volume of the measured active solution after dilution was 2 ml which was sufficient for ensuring a saturated layer. With solutions of concentration 2·5—5% H_3PO_4, the saturated layer corresponds to approx. 2 mm. The depht of liquid layer of measured samples was approx. 3 mm.

With β^- emitting of radioisotope ^{45}Ca which has relatively low energy, a considerable self-absorption of radiation takes place in the studied layer. Therefore, there was verified the effect of the solution density on the activity measurement in the assumed range of concentrations of the phosphoric acid, *i.e.* in the range 2·5—5% H_3PO_4 (the presumed range of measurement 25—50% H_3PO_4, dilution 1 : 10). The results obtained have shown that in the given concentration range at the required measuring accuracy $\pm 3\%$ rel., the effect of solution concentration on the accuracy of measurements can be neglected.

Solubility of Calcium Sulphate in Mixtures of Sulphuric and Phosphoric Acids

To evaluate the kinetic data, the solubilities of hemihydrate and dihydrate must be known. The solubility was measured by measuring the rate with which the system is reaching the equilibrium, by the radio-chemical method using the active hemihydrate labeled by ^{45}Ca.

To a solution with a chosen concentration of P_2O_5 and H_2SO_4 the active hemihydrate was added at a temperature higher by 10°C than that at which the measurement itself was carried out. The temperature was decreased to a required value after 10 minutes and, by use of the fritted glass, samples were taken of approx. 2 ml solution which were weighed into 10 ml measuring flasks and filled up with water. Activity was measured in 2 ml of this solution. Samples for determination of solubility of dihydrate were withdrawn after 24 hours which was the sufficient time for reaching the equilibrium. Solubility was determined from the ratio of specific activities of the measured samples and the specific activity of a standard solution in which the active hemihydrate was dissolved and the concentration of $CaSO_4$ was determined chelatometrically[13]. The same apparatus was used as for measuring the hydratation kinetics. Results of measurements of solubility of the calcium sulphate are summarized in Table II.

RESULTS AND DISCUSSION

By the method presented in previous paragraphs, there has been obtained the solution activity dependence on time for the experimental parameters given in Table II. Typical course of such a dependence is plotted in Fig. 2.

As can be seen from Fig. 2, the activity of the solution increases at first very slowly because of the isotope exchange, and that practically linearly with time. Only when first crystal nuclei of the dihydrate are formed, the activity begins to increase non-linearly. In the graphical plot of individual experiments, we can thus determine the initial point of re-crystallization as the time at which the first observable deviation of the curve from the initial linear course takes place. Summary of periods thus obtained is given in Table III.

Evaluation of measured curves was done according to Eq. *(11)*. Initial activity a_{s0} was equal to the value measured in the initial moment of re-crystallization t_0. The value g was calculated from the solubility and weight of the solution. Value c was calculated from the suspension activity and weight of the active hemihydrate corrected

by the excessive inactive hemihydrate. As this value is affected by a considerable experimental error (difficulties in sampling suspensions for measurements), it was considered to be only an estimate. The accuracy of estimation is verified directly by Eq. (11): by graphic presentation of the dependence $\varphi(a_s)/t$ on t and by extrapolation to the value $t = 0$ was on the axis $\varphi(a_s)/t$ determined the intercept $\dot{m}_n/2\cdot3$ g, from which it was possible to calculate directly the nucleation rate $\dot{m}_n$. Eq. (11) was

TABLE III

Summary of Latent Periods

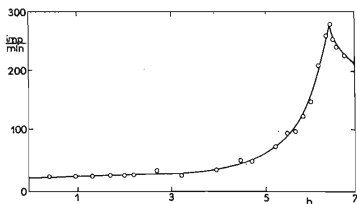| % P_2O_5	% H_2SO_4	t, min	% P_2O_5	% H_2SO_4	t, min
	50°C			60°C	
28	0	150	32	0	300
	1·5	60		1·5	180
	3·0	—		3·0	210
	5·0	—		5·0	205
	60°C			70°C	
25	0	30	28	0	180
	1·5	—		1·5	240
	3·0	—		3·0	190
	5·0	—		5·0	120
28	0	240			
	1·5	70			
	3·0	35			
	5·0	45			

FIG. 2

Examples of the Activity Dependence on Time (60°C, 28% P_2O_5, 5% H_2SO_4)

further arranged into the form

$$y = \frac{\varphi(a_s)}{\dot{m}_n/2\cdot3g} - 1 = 3\lambda t/2 + \lambda^2 t^2 + \lambda^3 t^3/4 \qquad (16)$$

and calculation was made for several different values of t. The values complying to relation (16) and to experimental points were read off the Fig. 3 representing the right-hand side of Eq. (16). Constancy of the found values of λ for different chosen values of t proved the accuracy of estimate of a_c. The results are given in Table IV.

By substituting the calculated values $\dot{m}_n$ and λ into Eq. (11), the theoretical course of dependence of activities on time was calculated. An example of comparison of calculated and measured data of activities for the case $60°C$, $28\% P_2O_5$, $1\cdot5\% H_2SO_4$ is given in Table V, from which a very good agreement of measured and calculated values is obvious.

TABLE IV

Values of log λ in Dependence on Parameters of Experiments

| % H_2SO_4 | 50°C | | 60°C | | 70°C |
	28% P_2O_5	25% P_2O_5	28% P_2O_5	32% P_2O_5	28% P_2O_5
0	−1·7	−2·25	−2·3	−2·4	−2·2
1·5	−2·2	−1·7	−2·0	−2·7	−2·1
3·0	−2·1	−1·9	−2·2	−2·1	−2·2
5·0	−2·2	−2·1	−1·5	−1·9	−2·2

TABLE V

Comparison of Calculated and Experimental Activities ($60°C$, $28\% P_2O_5$, $1\cdot5\% H_2SO_4$)

| t, min | a_s | |
	calculated	experimental
5	65	63
20	73	78
60	122	120
80	160	172
100	208	215
120	260	280

TABLE VII

Values of Nucleation Constants m and k_n at $60°C$ and $28\% P_2O_5$

% H_2SO_4	m	k_n
1·5	4·0	$5\cdot4 \cdot 10^{-4}$
3·0	3·5	$1\cdot05 \cdot 10^{-3}$
5·0	3·2	$1\cdot40 \cdot 10^{-3}$

As can be seen from Table IV, the average value of log λ is about $-2\cdot0$; the deviations can be ascribed neither to the temperature effect nor to the composition of the solution. That is why the evaluation of experiments has been repeated for the constant value $\lambda = 10^{-2}$ and from thus obtained values were calculated the smoothened values $\dot{m}_n$. These values were transformed into usual units $\dot{m}_n(g/l\ min)$. The results are summarized in Table VI, which also gives the values of supersaturation Δc_0 (in g $CaSO_4/100$ g of solution).

TABLE VI
Values $\dot{m}_n$ and Δc_0

°C		% P_2O_5	% H_2SO_4	$\dot{m}_n \cdot 10^3$	Δc_0
50		28	0	12·0	0·4
			1·5	12·4	0·24
			3·0	10·6	0·17
			5·0	19·2	0·13
	Average value			*13·6*	
60		25	0	16·6	0·33
			1·5	14·8	0·24
			3·0	15·2	0·22
			5·0	14·4	0·20
	Average value			*15·2*	
		28	0	10·6	0·26
			1·5	10·2	0·17
			3·0	11·0	0·16
			5·0	10·0	0·15
	Average value			*10·4*	
		32	0	2·14	0·22
			1·5	3·62	0·13
			3·0	2·28	0·09
			5·0	1·90	0·07
	Average value			*2·56*	
70		28	0	5·46	0·23
			1·5	7·20	0·18
			3·0	4·20	0·14
			5·0	8·40	0·12
	Average value			*6·40*	

Nucleation rate $\dot{m}_n$ can be expressed[14] by equation of the type

$$\dot{m}_n = k_n \, \Delta c_0^m \, , \tag{17}$$

or

$$\log \dot{m}_n = \log k_n + m \log \Delta c_0 \, . \tag{18}$$

If we plot $\log m_n$ as a function of $\log \Delta c_0$, we get the straight lines with the slope m, and from it we can calculate from experimental points the values of nucleation constant k_n using Eq. (18), (Table VII).

After dissolving all the hemihydrate the solution is still supersaturated with respect to the stable dihydrate, and supersaturation Δc decreases from the initial value c_0 down to the zero value corresponding to the equilibrium solubility of dihydrate. To this stage corresponds the descending part of the curve $a_s(t)$, expressed by Eq. (15).
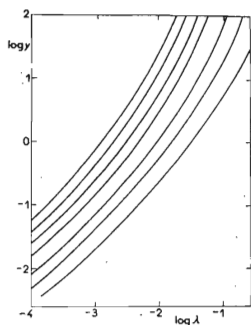

Fig. 3

Dependence of $\log y$ on $\log \lambda$ for Different Time Periods

Curves numbered from bottom to top: 1 15 min, 2 30 min, 3 50 min, 4 100 min, 5 150 min, 6 240 min, 7 360 min.

TABLE VIII

Values of k_g, A and t_n at 60°C

% P_2O_5	% H_2SO_4	$\dfrac{k_2}{l\,cm^{-2}\,min^{-1}}$	$\dfrac{A_1}{cm^2\,l^{-1}}$	$L_n \cdot 10^3$ mm
25	0	$5 \cdot 5 \, . \, 10^{-7}$	33 000	2·3
	3	$1 \cdot 25 \, . \, 10^{-6}$	42 000	3·5
	5	$1 \cdot 5 \, . \, 10^{-6}$	46 000	3·8
28	1·5	$5 \cdot 5 \, . \, 10^{-7}$	46 000	1·4
	3·0	$7 \cdot 5 \, . \, 10^{-7}$	43 000	1·5
32	3·0	$8 \cdot 5 \, . \, 10^{-7}$	48 000	1·0
	5·0	$1 \cdot 07 \, . \, 10^{-6}$	51 600	0·96

The surface area of crystals A is expressed by the relation

$$A = \beta N L^2 = \beta m / \alpha \varrho_c L, \qquad (19)$$

in which the shape coefficient β/α has for prism crystals with the length 10 times larger than thier thickness the value $\beta/\alpha = 42$ and the average crystal size is 100 μm. From Eq. (15) the values k_g and A were calculated; at the same time the values k_g were recalculated to usual units ($l \, cm^{-2} \, min^{-1}$). With the use of relations (3) and (4) the values of L_n were then also calculated (Table VIII). By use of the thus calculated kinematic constants of the crystal growth of dihydrate were back calculated the dependence of the solution activities on the time, t, and compared with the experimental values. Example of comparison for the conditions of 60°C, 28% P_2O_5 and 1·5% H_2SO_4 is given in Table IX.

TABLE IX
Comparison of Calculated and Experimental Activities

t, min	a_s	
	calculated	experimental
5	303	307
10	291	297
25	265	262
40	248	245

Pilot Plant Verification of Calculated Kinetic Constants

The pilot plant experiments[15] were carried out in a cascade of four crystallizers in which the crystals of the size 45 μm were obtained. Parameters were as follows: 28% P_2O_5, 1·5% H_2SO_4, 60°C; $\beta/\alpha = 16$ (crystals of ratio of the length to width 3·5 : 1), m_1 82 g/l, specific production rate of the crystallizer $s = 0·68$ g/l, the residence time of the solution in the crystallizer $\bar{t}_s = 120$ min, solution density 2·2 g/cm³.

For calculation of the average size of crystals from the cascade k of agitated crystallizers, the relation

$$\bar{L}_k / \bar{L}_1 = (k + 2)/3k \qquad (20)$$

was derived[16] in which the mean crystal size obtained from simple agitated crystallizer

with corresponding parameters was given by the relation[17]

$$\left(\frac{\bar{L}_1}{L_n}\right)^{1+3/m} - \left(\frac{\bar{L}_1}{L_n}\right)^{3/m-2} = \frac{k_g \beta m_1}{k_n^{1/m} \alpha \varrho_c L_n} s^{1/m-1} . \qquad (21)$$

After substitution of corresponding values into the relations (20) and (21) there was calculated $L_1 = 88\cdot5$ μm and $L_4 = 44\cdot2$ μm, which represents a very good agreement with the experimental values.

LIST OF SYMBOLS

A	surface area of crystals (cm^2)
a_s	activity of solution (imp./min)
a_{s0}	activity of solution in time t_0 (imp./min)
$a_{s,max}$	maximum activity of solution (imp./min)
$a_{s\infty}$	final activity of solution (imp./min)
a_{st}	activity of solution in time t (imp./min)
Δc	supersaturation (g/l)
Δc_0	supersaturation defined by Eq. (1) (g/l)
$c_{1/2}$	solubility of hemihydrate (g/l)
c_2	solubility of dihydrate (g/l)
g	amount of $CaSO_4$ in solution (g)
k	number of crystals in the cascade $(-)$
k_g	rate constant of crystal growth (l cm^{-2} min^{-1})
k_n	rate constant of nucleation (g^{1-m} l^{m-1} min^{-1})
L	crystal size (cm)
$\bar{L}_1$	mean size of product crystals from the simple stirred crystallizer (cm)
$\bar{L}_k$	mean size of product crystals from the cascade of k stirred crystallizers (cm)
L_n	size of crystal nuclei (cm)
$\dot{L}$	linear crystallization rate (cm/min)
m	nucleation order $(-)$
m	amount of dissolved hemihydrate (g), mass of crystals (g)
$\dot{m}$	rate of crystallization (g/min)
$\dot{m}_g$	rate of crystal growth (g/min)
$\dot{m}_n$	nucleation rate (g/min)
N	number of crystals $(-)$
$\dot{N}_n$	rate of formation of crystal nuclei (min^{-1})
s	specific production rate of the crystallizer (g l^{-1} min^{-1})
t	time (min)
y	function defined by Eq. (16) $(-)$
α	shape factor based on volume $(-)$
β	shape factor based on surface area $(-)$
λ	parameter defined by Eq. (3) (min^{-1})
$\varphi(a_s)$	function defined by Eq. (11) $(-)$
ψ	function defined by Eq. (15)
ϱ_c	density of crystals (g/cm^3)

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