KINETICS OF THE CRYSTALLIZATION OF POTASSIUM SULFATE

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The kinetics of the crystallization of potassium sulfate has been determined using the MSMPR technique. Values of the nucleation and crystal growth rates evaluated from the experimental data are compared with the corresponding literature data.

Potassium sulfate is one of the substances frequently used for testing crystallization apparatus and measurement methods. However, the literature data is not always consistent, because experiments have varied with respect to methods of measurement and/or the source and purity of the substances measured. The aim of this work was therefore to provide consistent kinetic data to be used for checking other methods of measurement[1].

THEORETICAL

In order to get reliable kinetic data from a MSMPR (Mixed Suspension–Mixed Product Removal) model crystallizer, several conditions must be met[2], namely establishment of a steady state and representative sampling. It has been shown that in a MSMPR crystallizer, the steady state is reached after six to ten times the mean retention time of the solution in the crystallizer[3]. A representative sample is understood to be one in which the suspension concentration and the distribution of particle sizes correspond to the average value in the whole crystallizer volume. Fulfillment of this condition must be confirmed for every particulate system using a wash-out test[4,5].

The kinetics of nucleation and of crystal growth can then be evaluated from the crystal size distribution of a product from a MSMPR crystallizer obtained under controlled conditions. From the linearized size distribution

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

where z is the dimensionless crystal size

$$z = L/\dot{L}\,\bar{t}_1\,, \tag{2}$$

the mean crystal size is obtained:

$$\bar{L} = 3\dot{L}\bar{t}_1 . \tag{3}$$

From the mean crystal size, the linear growth rate and nucleation rate can easily be obtained[6]:

$$\dot{L} = \bar{L}/(3\dot{L}\bar{t}_1) \tag{4}$$

TABLE I
Wash-out test and the results of its evaluation

t, min	m_c, g	m_{c1}, g	m_{c2}, g	m_1/m_2
0	24.00	12.00	12.00	1.00
7.5	19.64	9.60	10.04	1.15
15	14.62	7.00	7.62	1.07
22.6	10.82	5.11	5.71	0.99
30.1	8.42	3.96	4.46	0.92
37.6	6.62	3.06	3.56	1.00
45.2	5.185	2.335	2.85	1.02
52.7	4.095	1.755	2.34	1.14
60.3	3.315	1.365	1.95	1.00
67.8	2.70	1.055	1.636	0.99
	$\bar{t}_1 = 30.5$	$\bar{t}_{11} = 27.6$	$\bar{t}_{12} = 33.3$	

TABLE II
Parameters of MSMPR experiments

Experiment No.	T_{eq}, °C	T, °C	$\dot{V}$, cm^3 min^{-1}	$\bar{t}_1$, s	m_c, g/g$_{H_2O}$
1	67.1	49.2	10	2 400	0.0306
3	48.0	29.0	15	1 600	0.0352
4	47.9	28.9	10	2 400	0.0352
5	48.1	25.5	15	1 600	0.0419
6	48.6	29.0	15	1 600	0.0361

$$\dot{N}_N = 9\,\dot{m}_c/(2\,\alpha\,\rho_c\,\bar{L}^3)\,. \tag{5}$$

It is also possible to evaluate the MSMPR experimental data using the equation[6,7]

$$\bar{L}^{1+3g/n} = 3\,B_N\,m_c^{1-cg/n}\,\dot{m}_c^{(g/n)-1}\,, \tag{6}$$

TABLE III
Product crystals' size distributions (experiments 1, 3 – 6)

L, mm	1		3		4		5		6	
	$M(L)$	z	$M(L)$	z	$M(L)$	z	$M(L)$	z	$M(L)$	z
1.0	1.66	9.3								
0.75	5.21	7.7							1.02	10.0
0.6	15.54	5.9	4.03	8.1	1.58	9.4	0.94	10.1	4.86	7.8
0.5	27.7	4.9	11.24	6.5	3.52	8.4	2.75	8.6	15.17	6.0
0.4	48.7	3.7	31.49	4.7	17.01	5.8	12.78	6.3	36.91	4.3
0.3	61.72	3.1	46.3	3.9	35.19	4.4	26.3	5.0	56.1	3.4
0.2	78.37	2.4	72.23	2.7	66.47	2.9	58.4	3.3	79.45	2.3
0.1	87.77	1.9	86.42	2.0	84.73	2.1	79.88	2.3	91.05	1.7
0.08	91.79	1.6	91.71	1.6	90.87	1.7	88.22	1.9	94.97	1.4
$\dot{L}\,\bar{t}_1$, mm	0.101		0.076		0.063		0.059		0.079	
$\bar{L}$, mm	0.302		0.228		0.190		0.177		0.236	

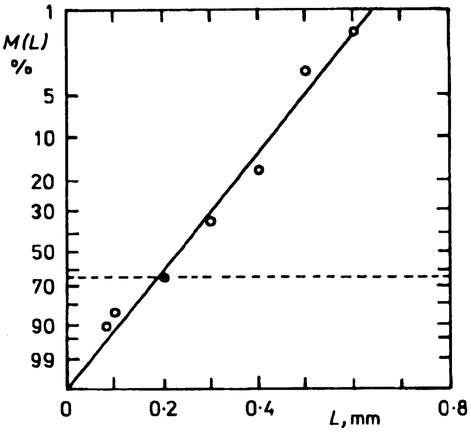

FIG. 1
Size distribution of crystals from experiment 4 plotted in the z–L coordinates. Dashed line denotes $\bar{L}$

where the system constant B_N can be calculated from experimental data using Eq. (*6*) or from kinetic data using

$$B_N = [4.5\, \dot{m}_c^c / (\alpha\ \rho_c\ \dot{N}_N)]^{g/n}\ \dot{L}\,. \tag{7}$$

The relative kinetic exponent g/n is obtained from at least two experiments carried out with identical suspension concentration but with different production rates:

$$\mathrm{d} \log \bar{L} / \mathrm{d} \log \dot{m}_c = [(g/n) - 1]/(1 + 3\, g/n)\,. \tag{8}$$

EXPERIMENTAL

The continuous model crystallizer used for our experiments has been described elsewhere[5]. Due to the relatively large size of the potassium sulfate crystals and the crystal/solution density difference, the crystals exhibited a tendency to settle down within the crystallizer, thus the agitator described[5] was exchanged for a propeller. Analytical grade potassium sulfate (Lachema, Brno) and distilled water were used to prepare solutions.

The wash-out test was performed using a mixture of two narrow K_2SO_4 crystal fractions (0.3 mm and 0.75 mm) in a weight ratio 1 : 1 introduced at time $t = 0$ into the crystallizer filled with K_2SO_4 solution just saturated at 30 °C and fed with an identical solution. Samples were taken in short constant intervals and the mass of crystals in both fractions was determined (m_1 and m_2). Through the subtraction of these values from the starting value the mass of crystals remaining in the crystallizer was calculated (m_c, m_{c1}, m_{c2}). The results are shown in Table I. The wash-out test equation

$$\ln m_c = \ln m_{c0} - t/\bar{t}_1 \tag{9}$$

TABLE IV
Kinetic parameters of crystallization of K_2SO_4 (experiments 1, 3 – 6)

Parameter	1	3	4	5	6
$\dot{m}_c \cdot 10^5$	1.275	2.200	1.467	2.619	2.256
$\dot{L} \cdot 10^8$	4.19	4.75	2.64	3.69	4.92
$\dot{N}_N$	783	3 138	3 615	7 983	2 902
$B_N \cdot 10^9$	1.90	1.71	0.924	1.15	1.80
c	1	1	1	1	1
g/n	0.187	0.187	0.187	0.187	0.187

TABLE V
Crystal growth rate of K_2SO_4 – literature data

T, °C	Δw, kg/kg$_{H_2O}$	$\dot{L}$. 10^8, m/s	g	Remark	Reference
	0.004	0.5	1.95	agitated	8
	0.008	5.5			
	0.012	12			
	0.01	4.7	2.0	face [001]	8
	0.01	8.6			
	0.01	7.8	1.4	face [100]	
	0.003	2			9
	0.001	1.69	2		10
	0.01	11.2			
20	0.005	2.30		fluid. bed	11
	0.015	20.7			
30	0.006	3.98			
	0.018	35.8			
40	0.007	6.60			
	0.021	59.4			
50	0.008	10.3			
	0.025	92.5			
30	0.006	2.88	2	fluid. bed	12
	0.013	11.5	2		
20	0.006	2.45 – 5.40		face [100],	
	0.019	22 – 48.6		u = (4 – 180) . 10^3 m/s	
20	0.008	2.86		fluid. bed	13
	0.016	14.8			
29	0.0006	0.3		MSMPR	15
	0.006	2.5			
30	0.0028	1.2		MSMPR	16
	0.0071	9.5			
~30	0.002	2		batch	1
	0.004	5			
	0.005	10			
	0.007	20			

plotted as ln m_c vs t, yielded almost identical straight lines for both of the fractions with the intercept ln m_{c0} and the slope $-t/\bar{t}_1$ corresponding to the starting conditions, so we may conclude that the sampling was indeed representative.

Five experiments with different starting parameters were carried out (Table II). The resulting crystal size distributions are shown in Table III, and the z–L plot of experiment No. 4 is presented in Fig. 1 as an example. (The z–L plot is based on Eq. (*1*): values of the dimensionless crystal size z are calculated from oversize fractions $M(L)$ using this equation and then plotted against corresponding crystal sizes, L. According to Eq. (*2*) the plot z vs L should be linear.)

RESULTS AND DISCUSSION

The kinetic parameters calculated using the equations above are summarized in Table IV. The values of the exponents g/n and c were determined using the method of least squares. If we take (ref.[1]) $g = 2$, the nucleation exponent found from these experiments would be $n = 10.7$. This value is unusually high but it is comparable to the value $n = 10.57$ found from the metastable zone width measurements[6] in the presence of crystals or to the nucleation exponent $n = 7.6$ published by Jones and Mullin[8] for MSMPR experiments.

Contradictory results are presented by Garside and Shah[14]: nucleation rate is here expressed as a power function of the growth rate, with the exponents ranging from −1 (ref.[15]) through 0 (ref.[16]) to 0.54 (ref.[17]). These results can be satisfactorily explained by strong secondary nucleation. Growth rates found in the literature are (after conversion to units employed here) shown in Table V, the nucleation rates for similar magma densities are nearly[14 - 16] 1 000 to 6 000 $\text{kg}_{\text{H}_2\text{O}}^{-1}\ \text{s}^{-1}$ which is also similar to the results presented in this paper.

SYMBOLS

B_N	system constant
c	exponent of secondary nucleation
g	growth rate order
L	crystal size
$\bar{L}$	mean crystal size
$\dot{L}$	linear crystal growth rate
$M(L)$	crystal size distribution
m_c	mass of crystals, suspension concentration
m_{c0}	initial mass of crystals
$\dot{m}_c$	specific production rate of the crystallizer
$\dot{N}_N$	nucleation rate
n	nucleation order
T	temperature
T_{eq}	temperature corresponding to just saturated solution
t	time
$\bar{t}_1$	mean retention time of solution
$\dot{V}$	volumetric feed rate

Δw	supersaturation
z	dimensionless crystal size
α	volume shape factor
ρ_c	crystal density

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