

SCALE-UP OF AGITATED CRYSTALLIZERS; COOLING BATCH CRYSTALLIZATION OF POTASSIUM ALUMINIUM SULPHATE

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The crystallization of potassium aluminium sulphate was conducted by cooling a solution saturated at 70°C to a temperature of 25°C at three various cooling rates. The measurements were performed on a small scale (160 cm³) and a large laboratory scale (0.021 m³). The mean size of product crystals was determined by sieve analysis, and the system constant, B_N , was calculated using previously derived relations. The B_N value is the same, within experimental error, for all the experiments and scales, indicating that agitated-vessel cooling crystallizers can be modelled successfully even on a very small laboratory scale.

The extent to which a crystallization process can be modelled is a question frequently discussed in the literature. Despite considerable theoretical and experimental difficulties encountered in modelling the process in a two-phase system, authors^{1,2} share the view that even approximate models may provide data adequate for crystallizer design if certain conditions are preserved, namely steady-state establishment³, ideal mixing of the suspension and representative sampling⁴⁻⁶. A question still unresolved is the confidence with which data obtained on a small laboratory models can be scaled up. Obviously, small-scale laboratory models are attractive because of the ease with which they can be controlled and kept in a required working regime. Moreover, they usually save time, and, last but not least, allow the consumption of chemicals to be minimized. On the other hand, there is a danger that the real hydrodynamic conditions will not be modelled appropriately in small-scale equipment. Furthermore, secondary effects such as the formation of incrustation may not be observed, and such factors as non-uniform distribution of temperatures, rates and concentrations occurring in large volumes cannot be involved.

The aim of this work was to establish, using a simple model system, whether results obtained on a small laboratory scale can be scaled up. The present communication, the first one of an intended series, deals with the comparison of two cooling batch-operated crystallizers of different capacity.

THEORETICAL

The crystal population density balance for a mixed-suspension continuous crystallizer with ideal mixing⁴,

$$n(L) = n^0 \exp(-t/\bar{t}_1) \quad (1)$$

was used to derive relations for the product crystal size distribution^{4,7},

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

where

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

and for the mean crystal size as a function of crystallization parameters^{7,8},

$$(\bar{L} - L_N)^{1+3g/n} f(z_N)^{g/n} = 3B_N m_c^{1-cg/n} (\dot{m}_c)^{g/n-1}, \quad (4)$$

where

$$f(z_N) = 1 + z_N + z_N^2/2 + z_N^3/6 \quad (5)$$

and

$$z_N = 3L_N/(\bar{L} - L_N). \quad (6)$$

According to Eqs (2) and (3), the size distribution of crystals leaving a continuous agitated crystallizer is determined uniquely by the mean crystal size, \bar{L} , and the initial crystal size, L_N . In the case of double-peak distributions, encountered frequently if the conditions during crystallization differ from those considered in deriving Eq. (1), the distribution can be expressed formally by the relation⁹

$$M(L) = w_1 M(z_1) + (1 - w_1) M(z_2), \quad (7)$$

where w_1 is the mass proportion of fraction 1, and the functions $M(z_1)$ and $M(z_2)$ are formally identical with Eq. (2) in which

$$\begin{aligned} z_1 &= (L - L_0)/\bar{L}i_1 & (L \geq L_0) \\ z_1 &= 0 & (L \leq L_0) \end{aligned} \quad (8)$$

$$\begin{aligned} z_2 &= (L - L_N)/\bar{L}i_1 & (L \geq L_N) \\ z_2 &= 0 & (L \leq L_N) \end{aligned} \quad (9)$$

For the purposes of crystallizer design, however, it is expedient¹⁰ to use, as an approximation, the simple Eq. (2) instead of experimental sieve analysis data represented by Eq. (7) even if the distribution deviates largely from the ideal shape.

As stated earlier^{11,12}, the above relations derived for continuous crystallizers can be applied, as an approximation, to batch-operated crystallizers if the specific output of the continuous crystallizer, \dot{m}_c , which loses its physical significance here, is replaced by the batch time¹³:

$$\dot{m}_c = m_c / \bar{t}_1 = 3m_c / t_c. \quad (10)$$

Eq. (4) then takes the form

$$(\bar{L} - L_N)^{1+3g/n} f(z_N)^{g/n} = 3B_N m_c^{(1-c)g/n} (t_c/3)^{1-g/n}. \quad (11)$$

EXPERIMENTAL

The crystallization of potassium aluminium sulphate was conducted by cooling a solution saturated at 75°C (containing 93.0 g $KAl(SO_4)_2 \cdot 12 H_2O$ in 100 g water¹⁴) at a constant preset rate to a final temperature of 25°C. The crystallizer employed in the first series of runs (I) consisted of a jacketed beaker of 250 cm³ capacity fitted with a perpendicular-blade stirrer, a top, and a baffle. The working volume of the crystallizer was 160 cm³. The stirrer speed was chosen to be about 700 rpm, permitting the suspension to be agitated appropriately even towards the end of the operation. The temperature in the crystallizer was regulated by passing water from a temperature-programmed thermostat through the jacket of the beaker. The second series of runs (II) was done in an analogous manner on a larger scale: the working volume of the crystallizer was 0.021 m³, and the propeller speed was 300 rpm.

In both cases the crystals obtained were filtered, washed with acetone, dried at ambient temperature, weighed and sieved. Six sieves in Series I and 14 sieves in Series II were used in the sieve analysis. The results, characterized by means of Eq. (7), are given in Table I, along with the parameters of the individual experiments. An example of the crystal size distribution, which was of similar character for all the runs, is illustrated⁹ in $z-L$ coordinates in Fig. 1.

RESULTS AND DISCUSSION

In order to evaluate the results by application of Eqs (4) or (11), we need to know the data on \bar{L} , L_N , m_c , and t_c for each run, and the values of exponents g/n and c . Although the crystal size distribution as shown in Fig. 1 is obviously non-linear and thus double-peaked, we shall approximate it for calculation purposes by Eqs (2) and (3). The least-squares approximation¹⁰ will be represented in the given diagram by a straight line (dashed line in Fig. 1) determining values of \bar{L} and L_N (included in Table I). The value of m_c , the suspension concentration, is obtained from the mass balance for the crystallizer; the theoretical value calculated on the basis of solubility data¹⁴, $m_c = 0.796$ kg of hydrate per 1 kg of free solvent. It is seen from the data on the yield (Table I) that the experimental values are sufficiently close to this theoretical value. Since all the experiments were carried out at the same concentra-

TABLE I
Results of batch crystallization experiments

Value	Serie I			Serie II		
	Experiment No					
	11	12	13	21	22	23
$-T$, K/h	27.9	6.75	3.75	15.0	10.0	5.0
t_c , s	5 800	24 010	43 200	10 800	16 200	32 400
Yield, kg	0.08015	0.08048	0.07905	10.87	10.64	10.80
m_c , kg/kg	0.8015	0.8048	0.7905	0.803	0.786	0.798
L_N , mm	0.01	0.01	0.01	0.01	0.01	0.01
L_0 , mm	0.255	0.302	0.370	0.386	0.413	0.565
\bar{L}_1 , mm	0.0700	0.0653	0.0575	0.090	0.093	0.060
w_1	0.790	0.862	0.934	0.786	0.800	0.950
L , mm	0.386	0.425	0.515	0.405	0.421	0.459
L_N , mm	0.1	0.1	0.1	0.1	0.1	0.1
$B_N \cdot 10^{12}$	2.22	1.76	2.55	2.05	1.98	2.00

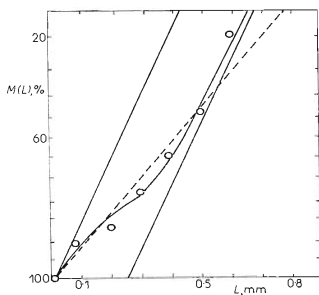


FIG. 1
Crystal size distribution in $z-L$ diagram
(Experiment No 11)

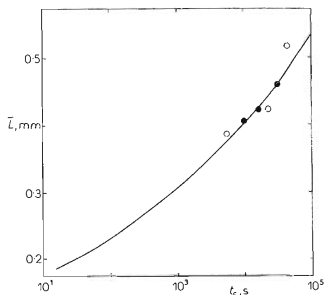


FIG. 2
Mean crystal size, L (mm), as a function of batch time, t_c (s). Curve — calculated from Eq. (11), experimental points \circ Series I, \bullet Series II

tion of suspension, m_c , it is not possible to determine the experimental value of the exponent c . As indicated by the analysis of the possibilities of its determination¹⁵, it is plausible, for calculation purposes, to adopt as an approximation the average value $c = 1$ representing the contacts crystal-crystallizer or crystal-stirrer, particularly in mechanically agitated concentrated suspensions. The value of g/n can be calculated from Eq. (11) rewritten for the given purpose in the form

$$\frac{d \log \bar{L}}{d \log t_c} = \frac{1 - g/n}{1 + 3g/n} \quad (12)$$

The g/n value was found to be 0.60 and 0.66 for Series I and II, respectively. These values are close enough to each other to be replaced by the average value $g/n = 0.63$. This value is somewhat lower than that calculated from separate measurements of nucleation and growth kinetics¹⁶, i.e. $g/n = 1.61/1.90 = 0.85$.

The values of the system constant, B_N , calculated from Eq. (11) for each run are listed in Table I. As is seen from the table, the calculated values are fairly close to one another, so that the potash alum crystallization by cooling can be characterized by an average value, $B_N = 2.09 \cdot 10^{-12}$. The dependence of the mean crystal size, \bar{L} , on the batch time, as expressed by Eq. (11), is represented for the experiments performed by the curve shown in Fig. 2.

The results show that Eq. (11) with the parameters $L_N = 1 \cdot 10^{-4}$ m, $g/n = 0.63$, $c = 1$, and $B_N = 2.09 \cdot 10^{-12}$ is satisfactory for representing the data from both series of measurements which differ in scale of the equipment used by more than two orders of magnitude. Thus, it might be expected that further scale-up based on the above equations would be sufficiently reliable, and that these equations constitute an adequate starting point for the crystallizer design.

LIST OF SYMBOLS

B_N	system kinetic constant of crystallization (m, kg, s)
c	secondary nucleation exponent
$f(z_N)$	function defined by Eq. (5)
g	kinetic exponent of growth
L	crystal size (m)
\bar{L}	mean crystal size (modus) (m)
L_N	initial crystal size (m)
L_0	size of the smallest crystals in coarse-grained fraction (m)
\dot{L}	linear crystal growth rate (m/s)
$M(L)$	oversize fraction (mass %)
m_c	suspension concentration (kg of crystals/kg of free solvent)
\dot{m}_c	specific output of crystallizer (kg/kg s)
n	kinetic exponent of nucleation
$n(L)$	crystal population density ($m^{-1} kg^{-1}$)

n^0	nuclei population density ($m^{-1} kg^{-1}$)
t	time (s)
t_c	batch time (s)
\bar{t}_1	mean residence time of solution (s)
w_1	mass proportion of coarse-grained fraction
z	dimensionless residence time of crystals
z_N	dimensionless initial crystal size

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