

## INVESTIGATION ON SOME OPERATING FACTORS INFLUENCING BATCH COOLING CRYSTALLIZATION

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The influence of batch time as well as the saturation temperature of stock solution on crystal size distribution has been examined. The results show that there is an optimal batch time,  $t_c$ , for which the mean crystal size of  $MgSO_4 \cdot 7 H_2O$  has a maximum. For  $MgSO_4 \cdot 7 H_2O$  and  $H_2C_2O_4 \cdot 2 H_2O$ , the mean crystal size of the product increased with increasing saturation temperature of the solution.

Secondary nucleation is the most important crystal-breeding mechanism under normal operating conditions of an industrial crystallizer. There are two known sources of secondary nucleation<sup>1-3</sup>. The first source is the so-called adsorption boundary layer whose structure is probably better ordered and more inhomogeneous than that of supersaturated solution. The second source is the actual surface of the crystal which exhibits a spectrum of roughness in microscopic and submicroscopic scales. With the assumption that these two sources are the prevailing mechanisms of secondary nucleation in the batch crystallizer Nývlt<sup>4,5</sup> showed that the mean crystal size of the product crystals depends on the batch time,  $t_c$ , and also on the ratio of the ostensible order of nucleation and the growth order,  $n_A/g$ . His theoretical considerations led to the relationship<sup>4</sup> which is plotted in Fig. 1, and has been confirmed only in the case of the crystallization of pentaerythritol<sup>6</sup>. The crystal size distribution depends on the saturation temperature of the stock solution. On the one hand, the width of the metastable zone is related to the saturation temperature of the solution<sup>7-9</sup>. On the other hand, crystallization from the more saturated solution yields more crystalline product (due to the greater difference between the saturation of stock solution and the final temperature) and that is why secondary nucleation increases with the increase of saturation temperature of stock solution.

### EXPERIMENTAL

Three series of experiments were carried out under the same hydrodynamical conditions with an agitation rate of 650 rpm. In each run approximately 1 l of aqueous stock solution was prepared by dissolving dry crystals in distilled water at about 10 K above that saturation temperature of the stock solution. The solution was then cooled quickly in the crystallizer to a temperature

equal to the saturation temperature of the stock solution. Further cooling was then commenced until the solutions had reached 15°C.

In the first series magnesium sulphate heptahydrate was crystallized from a stock solution whose saturation temperature was 35°C. The cooling rate was controlled by means of temperature programmer with cooling rates of 0.7, 1.1, 1.8, 4.3, 5.5, 6.5, and 15 K/h. In the second series magnesium sulphate heptahydrate was crystallized at 15°C from an aqueous solution which saturation temperature was variously 25, 30, 35, 40, and 45°C. In the third series crystallization was carried out by cooling oxalic acid aqueous solution saturated at 25, 30, 35, 40, and 50°C, down to 15°C. In both the second and the third series 3.4 K/h cooling rate was employed.

At the end of each run the slurry was discharged from the crystallizer and separated by filtration, washed with acetone, dried and analysed by sieving. The mean size of the crystal product was assumed as the criterion of crystal quality. Its values were calculated from the equation

$$\bar{L} = \sum_{i=1}^n M(L)_i \cdot \bar{L}_i,$$

where  $M(L)_i$  is the weight fraction oversize,  $\bar{L}_i$  is the mean crystal size of  $i$ -th fraction, and  $n$  is the number of sieves.

The apparatus shown schematically in Fig. 2, is composed of crystallizer (1) of capacity  $1.4 \cdot 10^{-3} \text{ m}^3$ , temperature programmer (3) coupled with thermostat (2). The crystallizer is a cylindrical glass vessel, fitted with a cooling jacket, four baffles, and an agitator.

## RESULTS AND DISCUSSION

The results of experiments are shown in Figs 3 and 4. The mean size of  $\text{MgSO}_4 \cdot 7 \text{ H}_2\text{O}$  crystals vs cooling rate and batch time is plotted in Fig. 3. Both curves plotted in Fig. 3 have distinct absolute maxima that are consistent with the theoretical hypothesis according to Nývlt<sup>4</sup>. On the basis of the curves shown in Figs 1 and 3,

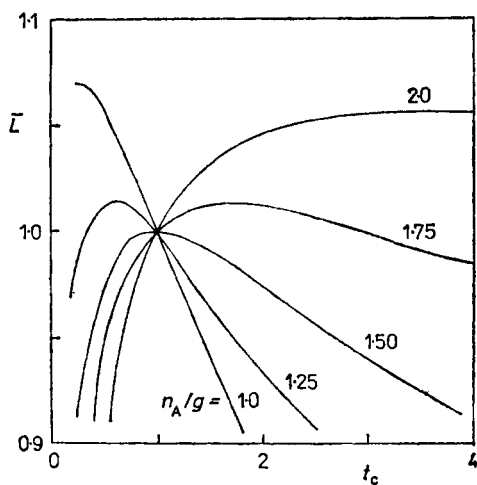


FIG. 1  
Dependence of mean crystal size on batch time<sup>4</sup>

it may be stated that for magnesium sulphate heptahydrate the quotient  $n_A/g$  is within the interval  $\langle 1, 2 \rangle$ . Consequently, there is an optimum of batch time  $t_{c,opt}$  for which the product obtained is characterized by the highest value of the mean crystal size. The actual value of  $t_{c,opt}$  probably depends on the hydrodynamic conditions in the crystallizer, the saturation temperature of the crystallizing solution and on the final temperature of the crystallization process. When  $t_c < t_{c,opt}$ , the value of  $\bar{L}$  decreased as the difference between  $t_c$  and  $t_{c,opt}$  increased. This was probably caused by primary nucleation predominating over secondary nucleation. For the value  $t_c > t_{c,opt}$ ,  $\bar{L}$  decreases with the increasing  $t_c$ . In this case the longer batch time ensures that secondary nucleation is predominant.

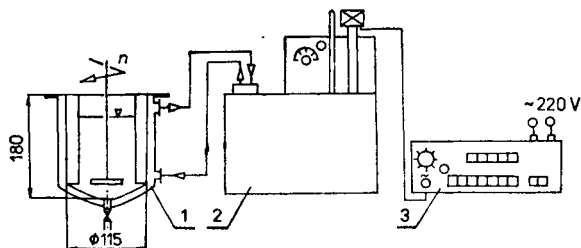


FIG. 2

Schematic diagram of experimental apparatus. 1 Crystallizer; 2 thermostat; 3 temperature programmer

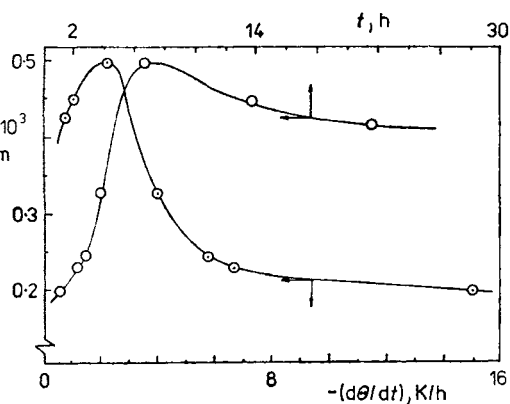


FIG. 3

Influence of batch time on mean size of  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  crystals

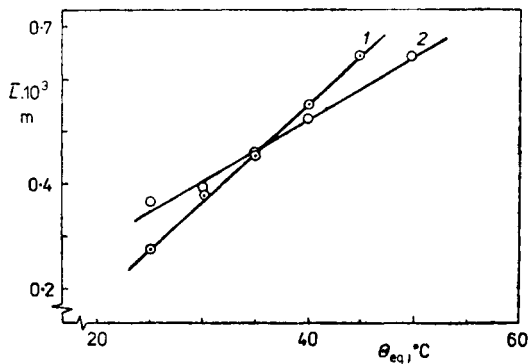


FIG. 4

Effect of saturation temperature of the solution on mean size of crystal product ( $-(d\theta/dt) = 3.4 \text{ K/h}$ ,  $n = 650 \text{ min}^{-1}$ ). 1  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ ; 2  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$

The mean size of magnesium sulphate heptahydrate and oxalic acid crystals *vs* the saturation temperature of their solution is plotted in Fig. 4. For both  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , the mean crystal size of the product increased with increasing saturation temperature of the solution. Experimental investigations have shown that the width of metastable zone decreases with the increasing saturation temperature of the oxalic acid solution<sup>7</sup> as well as of magnesium sulphate heptahydrate solution<sup>8</sup>. This conclusion is also confirmed by the experimental measurements of other substances by a number of other authors<sup>9</sup>. It follows that at a higher saturation temperature the intensity of spontaneous nucleation is lower and hence the mean size of the resulting product is larger. Crystallization from a more saturated solution generates slurry with a larger magma density which increases the secondary nucleation rate.

In conclusion, as the saturation temperature of the solution is increased, the effect of the decrease in the width of the metastable zone is greater than the effect of the increase of the magma density, and the mean crystal size increases.

#### LIST OF SYMBOLS

$g$	growth rate
$\bar{L}$	mean size of crystal product
$n_A$	ostensible order of nucleation
$t$	time
$t_c$	batch time
$\Theta$	temperature

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