

CRYSTALLIZATION

An Interesting Experience in the ChE Laboratory

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The economy of Chile is strongly based on metallic mining activity. However, large reserves of salt and brines available in northern Chile have led to a significant increase in the amount of research effort expended on non-metallic mining exploitation and processing. Wealthy reserves of lithium, potassium, nitrates, sulphates, boron, etc., including varied crystalline forms, are found there.

The Universidad de Antofagasta has played an important role in the development of these non-metallic mining research projects. Crystallization has been one of the chosen subjects and has been taught during the last three terms in the department of chemical engineering.

Crystallization is offered as a four semester-hour course, including lecture and laboratory work which consists of four experiments. The one described in this paper is aimed at the study of sodium-sulphate crystallization in a MSMPR continuously-agitated crystallizer tank. It is intended for the study of crystallization kinetics of decahydrated sodium sulphate.

The nucleation growth rate kinetics were evaluated by measuring the crystal size distribution (CSD) and using the mass, energy, and population balances.

CRYSTALLIZATION KINETICS

Industrial crystallization is defined as a technique aimed at producing crystals with specific characteristics of purity and size distribution. Crystallization is an extremely complex process which is affected by a number of variables, such as supersaturation level, temperature, agitation, impurities, mechanical effects, etc. Important advances related to analytical description and process understanding

have been achieved since the 1960s.

The population-balance approach to the description of crystal size distribution is the most widely accepted approach, and it has proved to be the most fertile in germinating new developments for describing and modeling crystallizers.

The population-balance equations were first formalized by Randolph and Larson.^[1] They allowed us to get the nucleation and crystalline growth kinetics. Two phenomena are involved in the crystallization process: the formation of new particles by nucleation processes and crystal growth processes. They both depend on supersaturation, but in different manners.

During nucleation, small regions are formed within the homogeneous phase that consist of variable numbers of ordered atoms or molecules, called clusters or embryos. Some of these are in equilibrium with the mother liquor. This cluster, termed a critical nucleus, is converted during further growth into a macrospecies which forms the new phase.

Kinetics data on crystallization processes are of basic importance for the design of industrial crystallization equipment. These data determine the size of the crystallizer and the crystal size of the product.



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POPULATION BALANCE

A population balance general relationship valid in a crystal size range L_1 to L_2 (ΔL) and in the period of time Δt , is the starting point in the analysis.

N of crystals entering the reactor with size ΔL + N of crystals entering range ΔL because of growth = N of crystals exiting the reactor with size ΔL + Crystals exiting the range ΔL because of growth

- a) The number of crystal seeds entering the crystallizer having a size range ($L_1, L_1 + \Delta L$) during Δt interval, is given by

$$Q_1 \cdot n_s \cdot \Delta L \cdot \Delta t \quad (1)$$

where n_s is the population density at the inflow, $n_s \Delta L$ represents the fraction of crystals with size ΔL , and Q_1 is the volumetric inflow.

- b) The number of crystals entering to ΔL range in the Δt interval due to G_1 growth is given by

$$V \cdot G_1 \cdot n_1 \cdot \Delta t \quad (2)$$

where V is the volume of the crystallizer. The growth function of G_1 crystals is represented as a supersaturation and crystal size function.

$$G = G(L, \Delta C) \quad (3)$$

$$G = G_c(C) \cdot \phi(L) \quad (4)$$

- c) The number of crystals having a size range ($L_1, L_1 + \Delta L$) which are removed from the reactor during Δt interval are given by

$$Q_2 \cdot n \cdot \Delta L \cdot \Delta t \quad (5)$$

where n is the population density at the exit and Q_2 is the volumetric exit flow.

- d) The number of crystals growing outside the size range ($L_1, L_1 + \Delta L$) at Δt interval is

$$V \cdot G_2 \cdot n \cdot \Delta t \quad (6)$$

Then the population balance [using Eqs. (2) to (5) in the size range ($L_1, L_1 + \Delta L$)] is

$$V G_1 n_1 \Delta t + Q_1 n_s \Delta L \Delta t = V G_2 n \Delta t + Q_2 n \Delta L \Delta t \quad (7)$$

Carrying out the appropriate arrangements in Eq. (7) and considering that there are no crystals in the feeding, yields

$$-\frac{d(Gn)}{dL} = \frac{Q_2}{V} n \quad (8)$$

Defining the half-time residence as

$$\tau = \frac{V}{Q} \quad (9)$$

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and assuming steady state

$$\frac{d(Gn)}{dL} + \frac{n}{\tau} = 0 \quad (10)$$

Integrating Eq. 10, by separation of variables when $G \neq G(L)$, yields

$$n = n_0 \exp(-L / G\tau) \quad (11)$$

in which n_0 is the nuclei population density.

Therefore Eq. (7) represents the crystal size distribution (CSD) of the process, where the distribution function n represents the number of particles having a certain size range per unit volume and a characteristic size.

$$n(L) = \frac{\text{Number of particles with size between } L \text{ and } (L + \Delta L)}{(\text{Volume})(\Delta L)} \quad (12)$$

This size distribution function can be directly obtained by determining the number of particles associated to each size range, as

$$\Delta N = \frac{\text{Mass of crystals retained in a sieve} / \rho_c}{(\text{average size particle volume})(\text{volume})} \quad (13)$$

where ρ_c is the crystal density. Using an average size

$$L = \frac{L_1 + L_2}{2} \quad (14)$$

and defining the particle volume as

$$V_p = k_v L^3 \quad (15)$$

in which k_v is the crystal shape factor

Also

$$\Delta L = L_2 - L_1 \quad (16)$$

where L_1 is the lower mesh opening (through which the particles enter) and L_2 is the retaining mesh opening of the sieve. Therefore

$$n = \frac{\Delta N}{\Delta L} \quad (17)$$

$$n = \frac{W}{\rho_c k_v L^3 \Delta L V_s} \quad (18)$$

where V_s is the volume occupied by the solution. Then it is possible to interpret the population

density of zero particle size, or nuclei number density, n^0 , as

$$n^0 = B/G \quad (19)$$

resulting in Eq. (11)

$$\ln(n) = \ln \frac{B}{G} - \frac{1}{G\tau} L \quad (20)$$

This equation is very important, since by using experimental distribution functions (obtained through screening tests) it is possible to find the adequate system kinetic model. Representing graphically $\ln(n)$ versus L we obtain a straight line of slope $-1/G\tau$ and intercept B/G from which the growth velocity G can be determined at specific values of τ . In addition, it is possible to obtain the value of nucleation velocity B .

EXPERIMENT

The experimental equipment used in this study (see Figure 1) was a translucent acrylic MSMPR crystallizer, cylindrical in shape and 15.2 cm diameter by 39 cm height. Inside the tank there were three baffles and a 10 cm diameter by 15.2 cm height concentric tube, located at 6.5 cm distance from the bottom of the tank. The overflow volume is 3.250 ml. The system was provided with agitation similar to a perfect mixed crystallizer proposed by Randolph.^[3]

Due to the significant decrease in solubility exhibited by decahydrated sulphate sodium solution with decreasing temperature, the crystallization was carried out by cooling. The feeding solution was pumped from a storage container provided with a heater (25 ± 0.1 C) to the crystallizer (using a double-head peristaltic pump in order to obtain a perfectly regulated flow). The crystallizer was maintained at 18 C inside a 20 l thermostatic bath, obtaining the supersaturation by cooling. The feeding flow was monitored with a Gilmont rotameter provided with a precision valve.

One of the experiments was carried out at 500 rpm for a residence time of 0.62 hours. The solution flow for this experiment was established measuring the solution density in order to reach the steady state. After steady state was reached, the outlet flow was vacuum-filtered and the product was washed with acetone to eliminate residual water and avoid agglomeration of crystals. After the drying stage the crystals were screened in a Rotap provided with standard Tyler sieves with mesh of 16, 18, 20, 30, 40, 50, 70, 100, and 140, by which the crystal size distribution was obtained.

RESULTS

Table 1 shows the experimental steady-state data for an experiment at 500 rpm with a residence time of 0.62 hours and the conditions mentioned in the previous section.

Equations (13) to (18) were used in order to obtain the values of the crystal size distribution function. The former results were plugged into the population balance from which the experimental results, plotted in Figure 2, were obtained.

To determine the crystal shape factor under the conditions used in this work, small samples of known crystal size were counted and weighted, determining the shape factor by the relation

$$k_v = \frac{W}{\rho_c(L)^3 \Delta N} \quad (21)$$

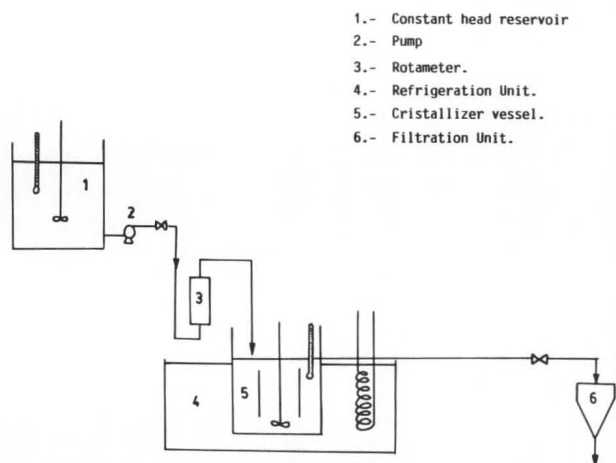


Figure 1. Experimental equipment

TABLE 1
Experimental Data

VOLUMETRIC FLOW Q_A (cc/min)	CRYSTAL DENSITY ρ_c (g/cc)	OPERATION TIME top (min)
102	1.464	15
Mesh	Sieve Opening L (mm)	Sieve Mass (g)
16	1.180	9.12
18	1.000	32.12
20	0.850	39.82
30	0.600	235.42
40	0.425	89.14
50	0.300	54.42
70	0.212	22.02
100	0.150	7.22
140	0.106	1.22
BED	-	0.50

Sample Mass M_c (g) = 490.99

where ΔN is the number of crystals in the sample of mass W . An average shape factor of 0.553 was obtained.

From the data plotted in Figure 2, we obtain the slope and interception values by applying a linear regression method to Eq. (20), obtaining

$$\frac{1}{G\tau} = 4.9951 (1/\text{mm})$$

$$B/G = 2.7154 \times 10^7 (\text{crist./1 mm})$$

with a correlation factor = 0.979.

Clearing the equation, we obtain the growth and nucleation velocity

$$G = 0.3216 (\text{mm/h})$$

$$B = 1.04451 \times 10^7 (\text{crist./1 h})$$

CONCLUSIONS

The laboratory experiment described above allows a good understanding of the crystallization process. The key factors affecting this process (*i.e.*, agitation, size distribution, nucleation) are better grasped by the student when theoretical equations are worked out together with real-life processes.

Even though this work presented only one set of experimental data, the experiment itself is very flexible since it is possible to work out various situations under different conditions (temperature, concentra-

tion, spatial time, agitation velocity, etc.). For instance, the parameters affecting the B and G values can be determined by testing B and G under different operating conditions. Thus the students can find a kinetic equation of the studied system, through $B = k(G)^b$. Furthermore, it also allows the student to understand the influence that each variable has in the crystallization process, *i.e.*, agitation velocity. In industrial processing this has great importance since a homogeneous crystal size distribution is required by connecting processes such as centrifugation, among other things.

Due to its simple phase diagram, the $\text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ system is a good example for experimental study and teaching purposes. In fact, this system exhibits direct and reverse solubility between 0 and 60 C with formation of different hydrates. For the reason stated below, the experiment allows a good versatility in crystallization products when working under different operating conditions.

The graphical representation of the equilibrium phases as well as the distribution of crystal size is an effective way to understand the phenomenon from a physical point of view. Also, the solubility diagram allows the student to calculate theoretical output by means of simple material balances.

By analyzing the experimental data (presented in Table 1) the crystal mass turned out to be 490.95 g, and the predicted value was expected to be 500 g. This result means a 2% accuracy when the crystal performance is considered. The resulting difference may be due to the fact that some of the crystals produced remain attached to the crystallizer walls and to the losses in the drying and filtration processes.

Since in the former graph a linear relationship was obtained, it can be stated that the experiment was performed under the basic assumptions of crystal growth independent of its size and steady-state conditions.

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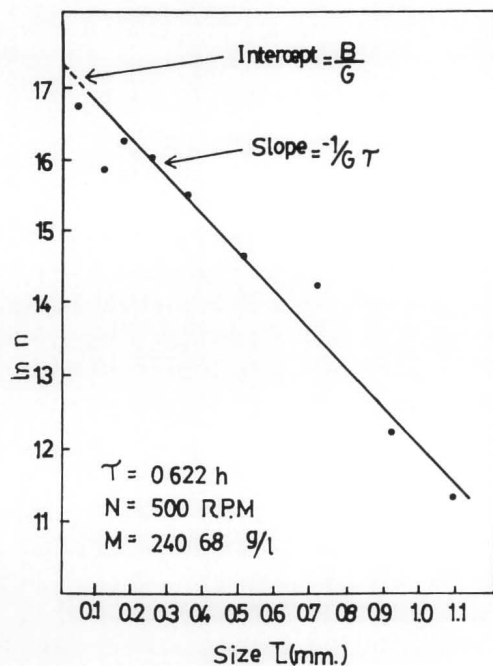


Figure 2. Crystal size distribution obtained from a laboratory-scale MSMCR crystallizer