

THE INFLUENCE OF MAGNETIC FIELD ON CRYSTALLIZATION FROM SOLUTIONS

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Abstract - The influence of magnetic field on some kinetic crystallization parameters of the systems zinc sulfate – water and copper sulfate – water were investigated in a series of controlled batch cooling experiments. The solutions were exposed to magnetic fields with different intensities, up to a maximum of 0.7 T. A clear influence of magnetic field on the zinc sulfate crystallization parameters was found: an increase in the saturation temperature, a decrease in the metastable zone width, and increased growth rate and average crystal size. The magnetic effect (“magnetic memory”) remained in the solution for at least 150 min after the magnetic exposure. These effects were observed for the diamagnetic zinc sulfate, but not in similar experiments with paramagnetic copper sulfate.

Keywords – magnetic field, batch crystallization, zinc sulfate, copper sulfate

INTRODUCTION

In the last 30 years many results about the effect of magnetic field on the crystallization and precipitation of organic and inorganic compounds have been presented in the scientific literature, but most of the experiments reported so far are rather qualitative and the results are sometimes contradictory.

Nývlt and Kricková¹ found that the magnetic field increased the nucleation kinetics during crystallization of MgSO₄ from aqueous solutions. Mitrovic et al.² showed that magnetic fields changed the growth rate distribution and slows the growth rate of the majority of small Rochelle salt crystals from aqueous solutions.

Higashitani et al.³ studied the effects of magnetic exposure on formation of CaCO₃ crystals from the reaction between solutions of CaCl₂ and Na₂CO₃. It was found that (1) the nucleation frequency of CaCO₃ crystals is suppressed but the growth of crystals is accelerated, if the exposed magnetic flux density is greater than about 0.3 T and the exposure time is larger than 10 min; (2) the magnetic effect on the formation of CaCO₃ is caused mainly by the effect on Na₂CO₃ solutions rather than CaCl₂; (3) solutions exposed to a magnetic field maintain the magnetic effect on the formation of CaCO₃ for at least 120 h. Recently, Barrett and Parsons⁴ published a report reproducing many of the results obtained by Higashitani et al.³ on the precipitation of the diamagnetic calcium carbonate.

Lundager Madsen⁵ investigated the influence of magnetic field on the precipitation of paramagnetic and diamagnetic inorganic salts, concluding that only phosphates and carbonates with diamagnetic metal ion are affected, through increased nucleation and growth rates. Sasaki et al.⁶ found that a high intensity magnetic field reduced the number of nuclei formed and modified the habit of protein crystals.

In this paper the influence of the magnetic field intensity on some crystallization parameters of the zinc sulfate-water and copper sulfate-water systems were investigated during batch crystallization under controlled cooling.

CRYSTALLIZATION MODEL

The determination of crystallization kinetic parameters in batch crystallizers is very attractive, due to the easy experimentation and simplicity of the experimental apparatus. On the other

hand, the evaluation of the experimental results is complex when compared to the simple mathematical description of continuous crystallizer experiments (constant supersaturation, constant suspension concentration and constant crystal surface area, under steady state).

Nevertheless, theoretical studies developed by Mullin and Nývlt⁷ and Nývlt et al.⁸, as well as model experiments described by Nývlt⁹, have shown that, under simplifying conditions, the cumulative crystal size distribution produced in a batch cooling crystallizer can be described by the same theoretical relations derived for continuous crystallizers (MSMPR).

At the end of each batch experiment, the measured cumulative crystal size distribution can be fitted by the equation (Nývlt et al.¹⁰):

$$M(L) = 100 \left(1 + z + \frac{z^2}{2} + \frac{z^3}{6} \right) \exp(-z) \quad (1)$$

where

$$z = 3 \frac{(L - L_N)}{(L_m - L_N)} \quad (2)$$

The distribution can be represented by a straight line in the z - L coordinate system and z values can be calculated for equation (1) from the corresponding value of cumulative weight fraction $M(L)$, solved by a numerical method. It is possible to obtain the values of L_m ($z = 3$ or $M(L) = 64.7\%$) and L_N ($z = 0$ or $M(L) = 100\%$) directly from a plot of z versus L . The metastable zone width and average growth rate are defined by the following equations (Nývlt et al.¹⁰):

$$\Delta T = T_{\text{sat}} - T_{\text{nuc}} \quad (3)$$

and

$$G = \frac{(L_m - L_N)}{t_c} \quad (4)$$

EXPERIMENTAL PROCEDURES

The solutions of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were prepared as follows: 92.84 g of reagent grade $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were mixed in 27.16 ml of pure water (resistivity ≈ 18 Mohm.cm) to produce a solution with a theoretical saturation temperature of 50°C , according to solubility data from Perry and Chilton¹¹. Since the sulfate is highly hygroscopic, great care is needed in keeping and handling the material in order to obtain a solution with the predicted saturation temperature.

Similarly, 47.49 g of reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, were mixed in 58.76 ml of pure water (resistivity ≈ 18 Mohm.cm) to produce a solution with a theoretical saturation temperature of 60°C , according to solubility data from Perry and Chilton¹¹.

Crystallization was performed in a 100 ml glass vessel. The crystallizer temperature was controlled by a water jacket connected to a thermostatic bath, monitored by a K-type thermocouple immersed in the suspension. The suspension was agitated by means of a stirrer with Teflon shaft and blades. The crystallizer was placed between the poles of an electromagnet, as shown in Figure 1. A DC magnetic field was applied and its intensity measured by a Hall probe gaussmeter.

The experimental saturation temperature was determined by the polythermal method proposed by Nývlt et al.¹⁰ under different magnetic field intensities, to evaluate its effects on solubility.

All experiments started by heating the solution up to 58°C in the case of zinc sulfate, and to 66°C for copper sulfate. The temperature was subsequently kept constant for 10 minutes. A given magnetic field intensity was applied and the solution was cooled to 30°C for the zinc

solution, and to 27°C for the copper solution, at 15°C/h. When the temperature was 2°C below the predetermined experimental saturation temperature (which was found to be dependent on the magnetic field intensity, in the case of the solution of zinc sulfate), two crystal seeds with an average size of 1 mm were added to the solution to keep it more stable and to induce nucleation.

The nucleation temperature was considered to be the temperature at which the first new crystals were visually observed.

At the end of each experiment the suspension was immediately vacuum filtered, the crystals were held for 12 h at ambient atmosphere and temperature for drying. The crystals size distribution was determined by sieving, with mesh apertures from 0.037 to 2.0 mm.

When the time dependence of the magnetic effect was measured, the solutions were exposed to a magnetic field intensity of 0.3 T for a period of 30 min (t_e) and then left standing for a given period (t_s) before they were allowed to cool to crystallize. Similar experiments without the magnetic exposure were also carried out as the control experiment.

RESULTS AND DISCUSSION

The empirical values of L_m and L_N were obtained for each experiment from the linearized crystal size distributions (in the z - L coordinate system), similar as is shown in figure 2 e 3.

Table 1 shows the effect of the magnetic field intensity on the experimentally measured saturation temperature, metastable zone width, average growth rate, and average crystal size of the zinc sulfate solutions.

The exposure of the solution to a magnetic field of 0.3 T, when compared to the “no field” condition, increased the experimental saturation temperature above the normal saturation value.

Table 1 – Results of the batch cooling crystallization experiments (Zinc Sulfate)

Experiment	B (T)	T_{sat} (°C)	ΔT (°C)	$G \cdot 10^8$ (m/s)	$L_m \cdot 10^4$ (m)	t_c (s)
1	0.0	50.0	5.5	8.32	5.03	5400
2			7.0	8.30	5.58	5760
3			8.5	6.89	4.75	5880
Average			7.0	7.84	5.12	
Confidence Interval ($\alpha_1 = 0.01$)			± 1.81	± 0.99	± 0.52	
4	0.3	53.7	4.7	10.40	7.14	6120
5			3.2	10.20	6.83	6000
6			4.2	12.50	7.20	5880
Average			4.0	11.03	7.06	
Confidence Interval ($\alpha_1 = 0.01$)			± 0.92	± 1.55	± 0.24	
7	0.5	52.5	2.0	10.40	6.54	6000
8			3.0	11.60	7.04	6000
9			4.2	11.00	6.89	5640
Average			3.1	11.00	6.82	
Confidence Interval ($\alpha_1 = 0.01$)			± 1.34	± 0.73	± 0.31	
10	0.7	53.5	3.2	12.80	7.96	5760
11			3.6	8.03	6.63	5940
12			4.4	9.91	7.74	5700
Average			3.7	10.25	7.44	
Confidence Interval ($\alpha_1 = 0.01$)			± 0.74	± 2.91	± 0.87	

Table 2 – Results of the batch cooling crystallization experiments (Copper Sulfate)

Experiment	B (T)	T_{sat} (°C)	ΔT (°C)	$G \cdot 10^8$ (m/s)	$L_m \cdot 10^4$ (m)	t_c (s)
1	0.0	61.5	5.0	6.64	5.84	8160
2			4.5	5.78	4.74	8160
3			5.0	5.45	4.60	8400
4			4.0	5.37	4.56	7920
5			4.5	5.74	5.41	7920
Average			4.6	5.80	5.03	
Confidence Interval ($\alpha_1 = 0.01$)			± 0.43	± 0.52	± 0.59	
6	0.3	61.5	5.0	5.63	4.86	8400
7			5.0	6.12	5.43	8160
Average			5.0	5.88	5.14	
Confidence Interval ($\alpha_1 = 0.01$)			...	± 0.45	± 0.52	
8	0.5	61.5	5.0	6.27	5.34	7440
9			4.5	6.47	5.65	8160
10			5.0	5.30	5.09	8160
Average			4.8	6.01	5.36	
Confidence Interval ($\alpha_1 = 0.01$)			± 0.36	± 0.76	± 0.34	
11	0.7	61.5	4.0	5.62	5.09	7920
12			4.5	4.59	4.09	8160
13			4.5	5.59	4.97	8160
Average			4.3	5.27	4.71	
Confidence Interval ($\alpha_1 = 0.01$)			± 0.36	± 0.71	± 0.66	

When a magnetic field of 0.3 T was applied, the average growth rate increased about 41% and the average crystal size was 38% higher, whereas the metastable zone width decreased by 43%.

A further increase in the magnetic field intensity from 0.3 to 0.7 T did not cause significant change in any of the measured parameters. Probably the effect of magnetic field reached saturation at some value below 0.3 T.

Figure 4 shows the dependence the metastable zone width (ΔT) on the standing period after the magnetic exposure (t_s). The magnetic effect remained in the solution for at least 150 min after cessation of the magnetic exposure. This effect is called the “magnetic memory”. A similar effect was also found for precipitation the CaCO_3 by Higashitani et al.³ and Barrett and Parsons⁴.

Table 2 presents the results for the copper sulfate solutions. It is interesting to note that no effect of the magnetic field was observed in the crystallization parameters of paramagnetic $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The fact that diamagnetic zinc sulfate is affected by magnetic exposure and paramagnetic copper sulfate is not affected is consistent with the findings of Lundager Madsen⁵ for some paramagnetic and diamagnetic salts.

CONCLUSIONS

Based on batch cooling crystallization experiments, we have found a clear effect of magnetic field of 0.3 T on the $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ crystallization parameters: an increase in experimental saturation temperature, an increase in average growth rate about 41% and the average crystal size was 38% higher, whereas the metastable zone width decreased by 43%.

As there is no significant change in these parameters when the magnetic field intensity is increased from 0.3 to 0.7 T, it is probable that the magnetic field effect reaches saturation at some value below 0.3 T.

These effects were observed with diamagnetic $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, but not in similar experiments with paramagnetic $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The magnetic effect ("magnetic memory") remained in the solution for at least 150 min after the magnetic exposure.

SYMBOLS

α_1	significance level
B	magnetic induction, tesla (T)
ΔT	metastable zone width, ($^{\circ}\text{C}$)
G	average growth rate, (m/s)
L	crystal size, (m)
L_m	average crystal size, (m)
L_N	minimum crystal size, (m)
$M(L)$	cumulative weight fraction, (%)
t_c	batch time, (s)
T_{sat}	experimental saturation temperature, ($^{\circ}\text{C}$)
T_{nuc}	nucleation temperature, ($^{\circ}\text{C}$)
z	dimensionless crystal size

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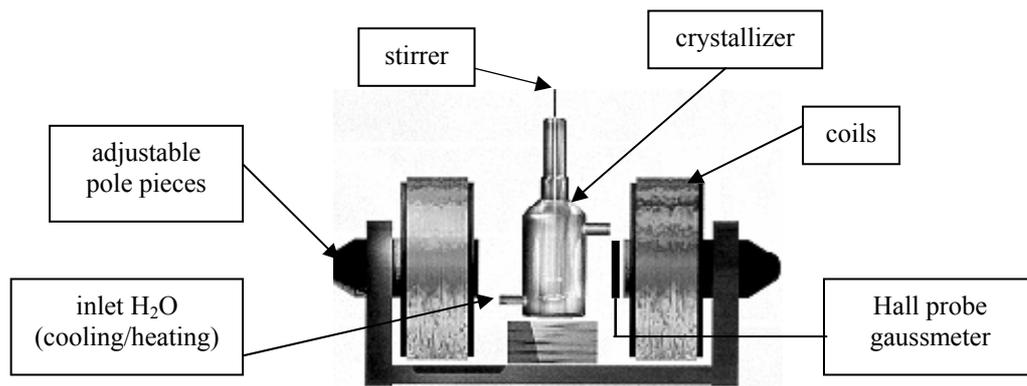


Figure 1. Experimental apparatus

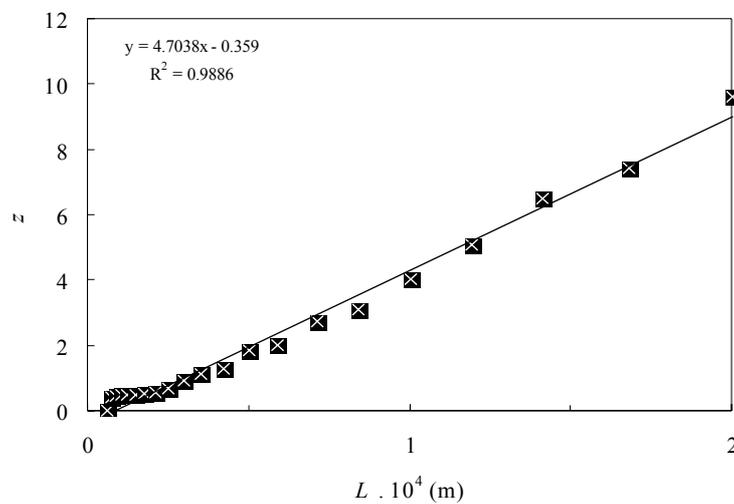


Figure 2. Linearization of the crystal size distribution from the experiment No. 4 (system zinc sulfate - water)

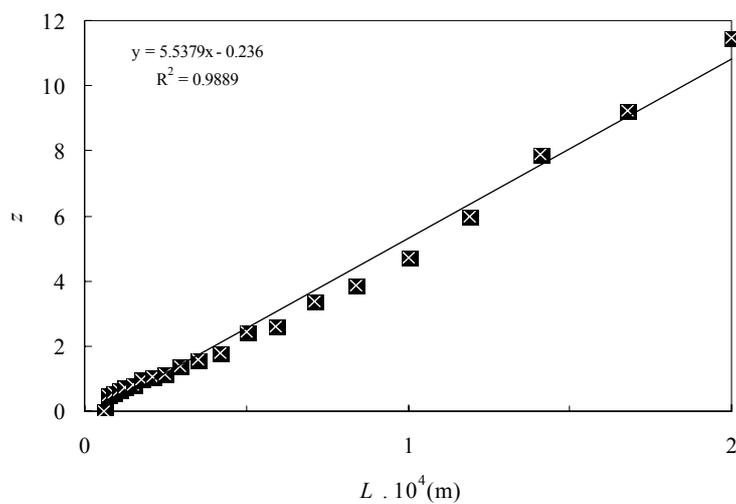


Figure 3. Linearization of the crystal size distribution from the experiment No. 1 (system copper sulfate - water)

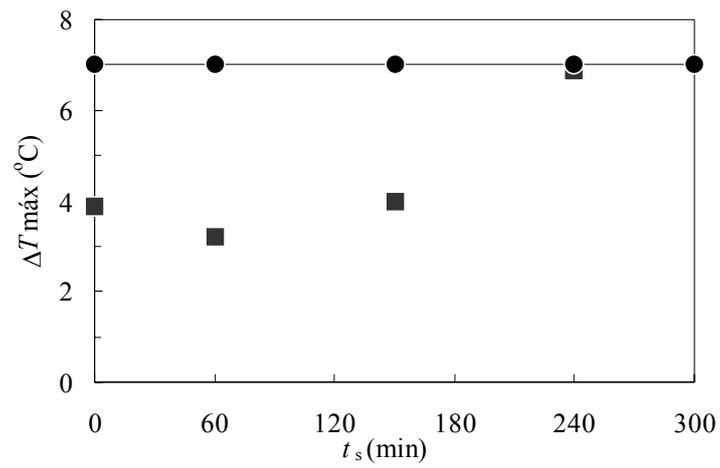


Figure 4 – Dependence of metastable zone width (ΔT) on the standing period after the magnetic exposure (t_s). (●) Non-magnetized solution, (■) magnetized solution at $B = 0.3 \text{ T}$ and $t_e = 30 \text{ min}$.