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EFFECTS OF ADMIXTURES ON THE CRYSTALLISATION RATE OF GYPSUM: A BATCH CRYSTALLISATION STUDY

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Abstract

This paper describes a study on the effects of admixtures on the crystallization rate of gypsum. Two different types of biodegradable admixtures commonly used as flotation agent in copper/zinc concentrate production, namely, sodium isopropyl xanthate (= SIPX) and isopropyl thionocarbamate were investigated in this study. A laboratory batch crystallizer was used in this study, and the experiments were run using seeded method. The rate of desupersaturation or the time required to reach the equilibrium concentration was compared for varying admixture concentrations. It was discovered that the added seed crystals started growing immediately upon addition into the supersaturated solution, i.e. there was no induction time.

Results of this batch crystallization study suggest that addition of admixtures individually or in combination, significantly affects the crystallization kinetics and in particular, reduces the rate of crystallization of gypsum. Activation energies were determined using three different temperatures, and the values obtained mostly agreed with other published values, i.e. 60.00 ± 3.00, 57.39 ± 2.87, and 37.65 ± 1.88 kJ/mol, for pure gypsum, isopropyl thionocarbamate, and SIPX, respectively.

Keywords: *activation energy; admixtures; $CaSO_4.2H_2O$; crystallization, gypsum; reaction rate.*

Introduction

During a crystallization process, admixtures play an important role. They can act as growth modifiers, growth inhibitors or nucleation controllers. Admixtures are sometimes added to the crystallizing solution to produce end products with predetermined qualities. It is common practice to alter the shape of crystals using admixtures so that flow ability and/or filterability of the crystals can be improved (Weijnen and van Rosmalen, 1984). Since admixtures (= additives) can be selected and added in precise amount, they are also able to control the change of shape of the crystals. Admixtures can also be added with the purpose of restraining the growth of crystals. This is the case when fouling or scaling on pipes or other equipment is to be prevented. By adding admixtures it is hoped that the shape of the crystals will change so as to lessen the tendency of the crystals to agglomerate. Then, the crystals will not attach to the surface of equipment or pipes, but will float freely in solution and can be swept away by the flowing fluid easily. In addition, admixtures can also reduce scaling by decreasing crystal growth rates.

In an attempt to better understand the retarding effect of admixtures on gypsum scale formation found in mineral processing industries, for example in flotation water piping system, crystallization of gypsum was investigated in the present study, in which two biodegradable admixtures normally used in copper/zinc concentrate production were investigated. A laboratory batch crystallizer was used in this study to obtain the experimental data. The data were subsequently used to determine the mean residence time and other parameters for a continuous crystallization experiment with the intention to study the effects of various admixtures on gypsum reported in a similar study (Muryanto, 2002).

Detailed description of gypsum crystallization from solutions is well documented (Liu and Nancollas, 1970; Liu and Nancollas; 1973, Amjad, 1985) and shows that the gypsum forming components react according to the following reaction equation.

$$CaCl_2.2H_2O + Na_2SO_4 \rightarrow CaSO_4.2H_2O + 2\,NaCl$$

Moreover, investigation on the effects of organic admixtures on gypsum crystallization kinetics (Smith and Alexander, 1970; Sarig *et al*, 1975; Amjad and Masler, 1985; Al-Sabbagh *et al*, 1996; Oner *et al*, 1998) clearly indicated that the effects were largely physical in nature, i.e. the admixtures adsorbed on the growth sites of the crystal surfaces. Hence the admixtures would hinder/stop the growth of the crystal surfaces. Hence the admixtures would hinder/stop the growth of the crystals without reaction with the crystal lattice ions.

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Experimental Design

The experimental design used for this study is the "One-factor-at-a-time" method (Davies, 1978) since literature search revealed that batch crystallization operating conditions for gypsum vary widely (Weijnen and van Rosmalen, 1984; Liu and Nancollas, 1970; Liu and Nancollas, 1973; Brandse and van Rosmalen, 1977; Amjad, 1988; White and Mukhopadhyay, 1990; Witkamp *et al*, 1990; He *et al*, 1994). Based on previous projects (Murray, 1997; Northwood, 1995; Headley *et al*, 2001) the fixed variable values were selected as detailed in the Experimental section. Meanwhile, the manipulated variables used for each crystallization run, which included admixture concentrations and crystallizer temperature are shown in Table 1.

Determination of the reaction rate constant for subsequent crystal growth determination in solutions can be explained by using the diffusion model of Chernov (Myerson, 1993). The model proposes that the diffusion of solute or growth units in the boundary layer and the thickness of the boundary layer are important aspects in controlling the growth. In crystallization from solutions containing equimolar lattice ions, which is the case of the present work, it is expected that the crystallization rate follows **Eq. (1)** (Liu and Nancollas, 1970) and is written as

$$\frac{dm}{dt} = K_G A\left(C - C_{eq}\right)^g \qquad (1)$$

where the exponent ***g***, has values between **1** and **2**.

Furthermore, many crystallization studies replace the constant K_G, and the surface area, ***A***, by a single value ***k***, which is termed the crystallization rate constant (Myerson, 1993). In many gypsum crystallization systems (Liu and Nancollas, 1970; Liu and Nancollas, 1973; He *et al*, 1994; Amjad and Hooley, 1986; Amjad and Masler, 1985; Christoffersen *et al*, 1982; Klima and Nancollas, 1987; Nancollas *et al*, 1979), especially when induction period was not observed, the value of ***g*** in **Eq. (1)** was taken as equal to **2**, and that value was used in this study In addition, the surface area term, ***A***, was assumed to be relatively constant. With equimolar concentrations of lattice ions in the crystallization solution, **Eq. (1)** can be represented as **Eq. (2)** as follows:

$$-\frac{dCa}{dt} = k\left(Ca_t - Ca_{eq}\right)^N \qquad (2)$$

where

- $-dCa/dt$ = rate of lattice ion concentration decrease due to crystallization, (ppm. min^{-1})
- Ca = lattice ion concentration of the crystallizing solution (concentration of Ca^{2+}, ppm)
- Ca_t = lattice ion concentration of the solution at time t, ppm
- Ca_{eq} = lattice ion concentration at equilibrium, (lattice ion concentration of the solution at t = 90 minutes, ppm)
- k = crystallization rate constant, $ppm^{-1}.min^{-1}$
- N = reaction order 2.

Upon integration, with **N = 2**, **Eq. (2)** yields the following :

$$\frac{1}{Ca_t - Ca_{eq}} - \frac{1}{Ca_0 - Ca_{eq}} = kt \qquad (3)$$

where,

- Ca_0 = lattice ion concentration of the solution at t = 0, (ppm)
- t = crystallization time, (minutes).

Concentrations of the lattice ions were calculated as the concentrations of Ca^{2+} in the crystallizing solution. Atomic absorption spectrometry (AAS) was used to calculate the concentrations as required. Using **Eq. (3)**, concentrations of Ca^{2+} obtained from AAS determination were then plotted versus time of crystallization, which (in order for the chosen reaction order, **N = 2** to be warranted) should result in a straight line having slope equals to **k**, which is the reaction rate constant of the crystallization process.

Experimental

A crystallizer operating in a batch mode was utilized in this study. It has a working volume of two liters, made of stainless steel with four internal baffles to prevent vortex. The crystallizer was agitated using a variable speed 45^0 pitched blade impeller and was placed in a thermostatically controlled water bath. The experiment was carried out using seeded growth technique as it was found that the technique is highly reproducible (Gill and Nancollas, 1980; Liu and Nancollas, 1970). For the crystallizing solution, a synthetic gypsum solution was used, made by dissolving calcium chloride dehydrate ($CaCl_2.2H_2O$) and anhydrous sodium sulfate (Na_2SO_4) in equimolar amounts in distilled water, respectively. Gypsum crystals sized 53 to 90 µm were used as seeds.

Table 1. Manipulated variables used in the seeded batch crystallization experiments

Run	SIPX concentration, (g/L)	Isopropyl thionocarbamate concentration, (g/L)	Crystallizer temperature, (^{0}C)
1	0.00	0.00	25
2	0.00	0.00	25
3	0.05	0.00	25
4	0.10	0.00	25
5	0.20	0.00	25
6	0.20	0.00	35
7	0.20	0.00	45
8	0.30	0.00	25
9	0.40	0.00	25
10	0.00	0.0175	25
11	0.00	0.035	25
12	0.00	0.07	25
13	0.00	0.07	35
14	0.00	0.07	45
15	0.00	0.14	25
16	0.00	0.21	25
17	0.20	0.07	25
18	0.05	0.035	25

Stirring rate was fixed at a speed of 125 rpm as it was found that this speed was sufficient to make the seed crystals evenly suspended in the solution. The initial concentration of the synthetic gypsum solution in the crystallizer was 2,000 ppm of Ca^{2+}. One liter each of 0.1 M calcium chloride solution and sodium sulfate solution were prepared and subsequently placed in the crystallizer.

The impeller was started and the whole system was left to equilibrate to the designated temperatures: 25, 35 or 45^{0}C. Having reached the designated temperature, a 20 ml solution sample (which corresponds to t = 0 or zero time) was taken and prepared for atomic absorption spectrometry (AAS) analysis. Sixteen grams of gypsum seed crystals were added into the crystallizer and the timer was started. During the experimental run, solution samples (each of 20 ml volume) were withdrawn from the crystallizer at 2, 5, 10, 15, 20, 30, 40, 60 and 90 minutes, respectively after the seed addition, filtered through 0.22-μm filter paper (Millipore™ Corp.), and stored in vials ready for AAS analysis.

After the completion of one experiment, the crystallizer and its accessories were cleaned and prepared for the next run.

Extreme care was taken to keep the solutions from dust, other particulate matter, and so on.

Results and Discussion

The typical curves for desupersaturation of Ca^{2+} against crystallization time are shown in Figure 1 below:

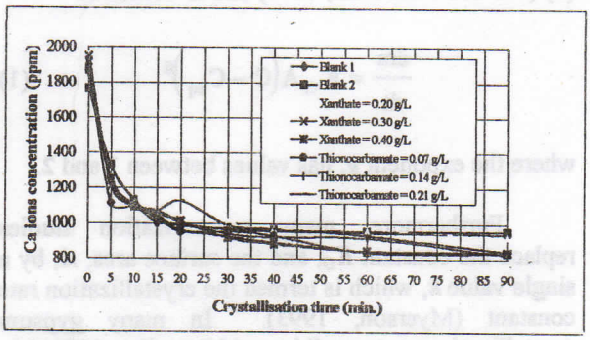

Figure 1. Typical desupersaturation curves for Ca^{2+} vs. crystallization time

As can be seen, in each case the reduction of calcium ion concentrations takes place rapidly in the first 5 to 10 minutes of the run.

It is very likely that the added seed crystals start growing immediately upon addition into the supersaturated solution; i.e. there is no induction time.

A sample calculation for the determination of the reaction rate constant is presented below for the condition of crystallization run with no admixtures. Plotting **Eq. (3)** with the desupersaturation data as shown in **Table 2** will result in a graph as shown in **Figure 2**, where **F** or the **Y** axis represents the left hand side of **Eq. (3)**. The slope of the straight line is 0.0014. Hence the value of the reaction rate constant (in the absence of admixtures), k, is 0.0014 ppm^{-1} min^{-1}.

Table 2 Desupersaturation data for crystallisation run without admixtures

Sampling time (minutes)	$[Ca^{2+}]$ (ppm)	$1/[Ca_t - Ca_{eq}]$ (ppm^{-1})	$1/[Ca_0 - Ca_{eq}]$ (ppm^{-1})
0	1901	0.00104	0.00104
2	1251	0.00321	0.00104
5	1112	0.00581	0.00104
10	1093	0.00653	0.00104
15	1004	0.01562	0.00104
20	995	0.01818	0.00104
30	965	0.04000	0.00104
40	957	0.05882	0.00104
60	949	0.11111	0.00104
90	940	∞	0.00104

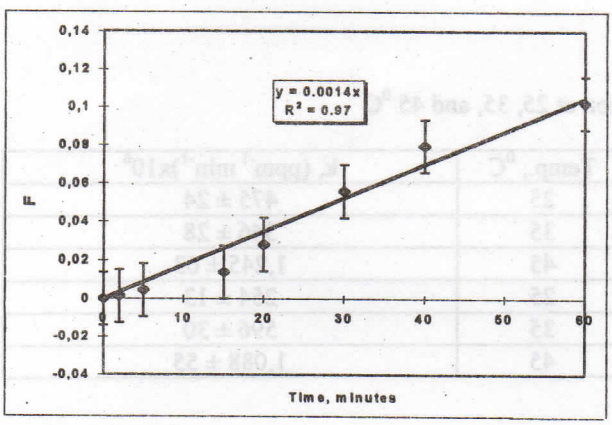

Figure 2. Typical plot of the determination of a second order reaction rate constant

Effects of admixture concentrations on reaction rate constant

Results of this study show that higher concentrations of admixtures decrease the rate constant. This is seen clearly in **Table 3** where admixtures drastically suppress the rate constant. For both admixtures, increasing the dosage will result in further suppression. At a plant dosing level of 0.20 g/L, SIPX decreases the rate constant to about one-third of that without admixtures. It is obvious from the table that the isopropyl thionocarbamate has higher inhibition effect than SIPX. The plant dosing level of isopropyl thionocarbamate is 0.070 g/L and can already control the rate constant to become around half that of SIPX (= SIPX at a plant dosing level, which is 0.20 g/L). Increasing the dosage, that is, the plant dosing level, however, does not result in further significant reduction of rate constant. This could be caused by preferential adsorption of admixture molecules onto the crystal surfaces. At the beginning there are a lot of kink sites at the surface of the crystals where the molecules of admixtures tend to bond as kink sites have the highest binding energy.

As a growth site, the crystal surface is usually classified into three regions: terraces, steps, and kinks (Myerson, 1993). Terraces have the highest, while kinks have the lowest bonding energy. Consequently, kink sites offer the most favorable sites for unit growth or particle attachment.

However, in a seeded growth technique, the large number of kinks, if any, will soon disappear due to the rapid 'self healing' of the surface (Nancollas, 1979). Consequently, the rate constant will not change as the rest of the admixture molecules stay in the bulk solution and do not attach to the crystal surfaces.

Table 3 Second order rate constant of gypsum crystallisation at 25^0C

Type of Admixtures	Admixture concentration, (g/L)	2^{nd} Order rate constant, ($ppm^{-1} . min^{-1}$) x 10^6
No admixture	0.000	1,405 ± 71
No admixture	0.000	1,561 ± 79
SIPX	0.050	871 ± 44
SIPX	0.100	568 ± 29
SIPX	0.200	475 ± 24
SIPX	0.300	440 ± 22
SIPX	0.400	365 ± 19
Isopropyl thionocarbamate	0.0175	830 ± 42
Isopropyl thionocarbamate	0.035	487 ± 25
Isopropyl thionocarbamate	0.070	254 ± 13
Isopropyl thionocarbamate	0.140	191 ± 10
Isopropyl thionocarbamate	0.210	171 ± 9

Effects of crystallization temperature on reaction rate constant

Table 4 and **Figure 3** demonstrate that the rise in temperature enhances the rate constant, but at higher temperatures the effect of the two admixtures on the rate constant is almost the same. It appears that both admixtures have approximately the same effect on the rate constant at intermediate temperature of 35^{0}C. At lower and higher temperatures, however, the isopropyl thionocarbamate seems to be more effective in reducing the value of the rate constant.

Effects of admixture combinations on reaction rate constant

The effects of admixture individually or in combination are shown in **Table 5**. As can be seen, there seems to be a masking effect of isopropyl thionocarbamate on SIPX when these two admixtures are combined. Combination of SIPX and isopropyl thionocarbamate shows that only the effect of isopropyl thionocarbamate is obvious, that of SIPX seems to disappear. It is likely that the masking effect is due to the difference in molecular weight and the structure of the two admixtures. The molecular weight of SIPX ($C_4H_7OS_2Na$) is 158 whereas that of isopropyl thionocarbamate (as thiocarbamic acid, $C_{10}H_{16}Cl_3NOS$) is 304.68 (Howard and Neal, 1972). The longer C chains of isopropyl thionocarbamate as the "backbone" of the molecular structure might have acted as a fence to block the growth sites and thus stopping the propagating steps (Amjad, 1988; Oner *et al*, 1998).

Table 4 Second order rate constant of gypsum crystallisation at 25, 35, and 45 ^{0}C

Admixtures	Admixture conc., g/L	Temp., ^{0}C	k, (ppm^{-1} min^{-1})x10^6
SIPX	0.20	25	475 ± 24
SIPX	0.20	35	546 ± 28
SIPX	0.20	45	1,245 ± 63
Isopropyl thionocarbamate	0.07	25	254 ± 13
Isopropyl thionocarbamate	0.07	35	596 ± 30
Isopropyl thionocarbamate	0.07	45	1,088 ± 55

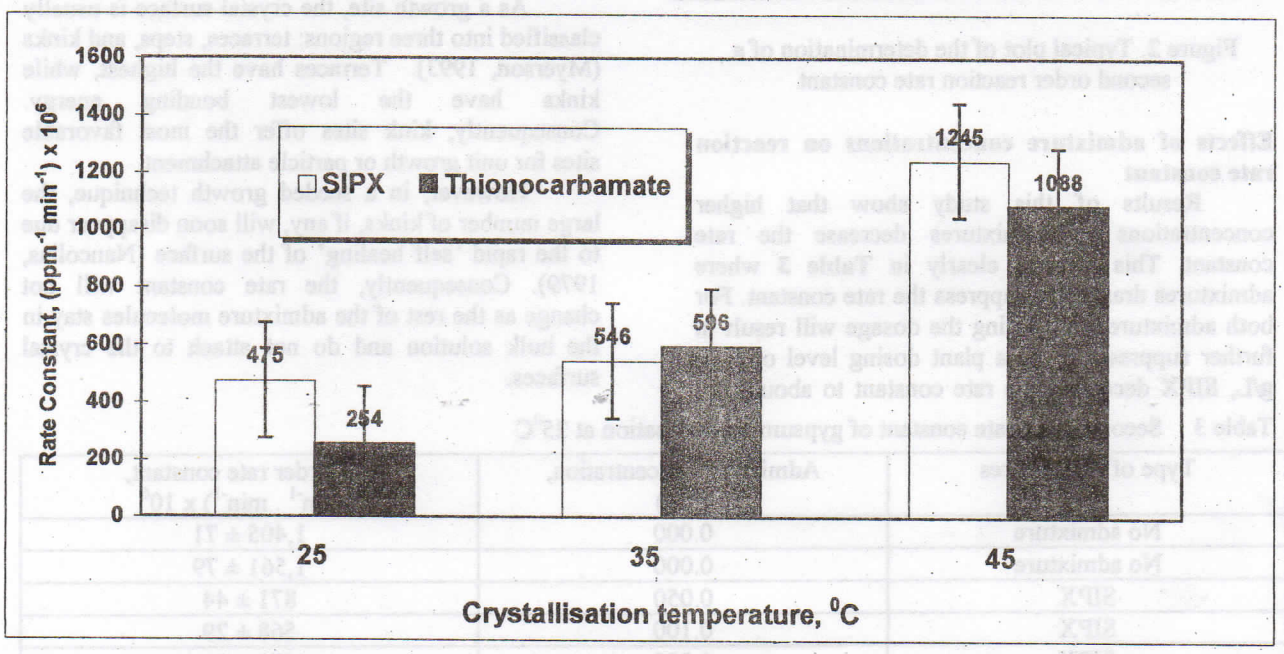

Figure 3 Reaction rate constants for the two admixtures at three different crystallization temperatures

Table 5. Second order rate constant of gypsum crystallization at 25^{0}C using SIPX, isopropyl thionocarbamate and combination of the two admixtures

Admixtures	k, (ppm^{-1} min^{-1})x10^6
0.050 g/L SIPX	871 ± 44
0.035 g/L isopropyl thionocarbamate	487 ± 25
0.050 g/L SIPX + 0.035 g/L isopropyl thionocarbamate	482 ± 24
0.200 g/L SIPX	475 ± 24
0.070 g/L isopropyl thionocarbamate	254 ± 13
0.200 g/L SIPX + 0.070 g/L isopropyl thionocarbamate	244 ± 13

Determination of activation energy

For the experimental data obtained in this batch crystallization by varying crystallizer temperature, with admixture dosing fixed at normal plant conditions, the Arrhenius parameter of the reaction has been determined. Three different temperature levels were used for this purpose, and this was done by utilizing both **Eq. (4)** and its logarithmic form as shown in **Eq. (4.a)**.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

or in logarithmic form

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4a)$$

where,

k = reaction rate constant, (the units of which depend on reaction order)
A = Arrhenius parameter (total number of effective collisions of molecules per second)
E_a = activation energy, kJ/mol
R = universal gas constant, 8.31 (kJ)/(mol)(^{0}K)
T = absolute temperature, ^{0}K.

Plotting the natural logarithm of the rate constants at varying temperatures against the inverse of the absolute temperature (1/T) results in a straight line. The slope of this line is $-E_a/R$ and the intercept is the natural logarithm of the pre-exponential factor, A, where E_a is the activation energy and R is the universal gas constant. Typical plots of 1/T versus ln (k) are shown in Figures 4 and 5, respectively.

The value of the activation energy, E_a, obtained for the isopropyl thionocarbamate admixture at plant dosing level of 0.07 g/L can be calculated from **Figure 4**. The slope of the line in **Figure 4** = $-E_a/R$ = - 6903.4. Hence, E_a = 6903.4 x **R**, where **R** = universal gas constant = 8.314 x 10^{-3} kJ/mol. Thus, the activation energy, E_a = 6903.4 x 8.314 x 10^{-3} kJ/mol = 57.39 ± 2.87 kJ/mol.

As discussed later, the activation energies calculated for both pure gypsum and the system with isopropyl thionocarbamate show that the use of the reaction order **N = 2** can be warranted. The system with SIPX, however, shows a discrepancy with published values and, therefore, some arguments were advanced.

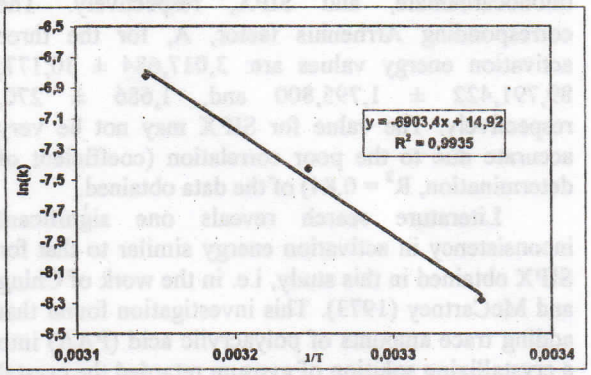

Figure 4. Plot of Arrhenius parameter for 0.07 g/L isopropyl thionocarbamate at 25, 35, and 45^{0}C, respectively

The activation energy values, E_a, for the three conditions: pure gypsum, in the presence of SIPX and in the presence of isopropyl-thionocarbamate, respectively, are calculated from a similar graph as depicted in **Figure 5**.

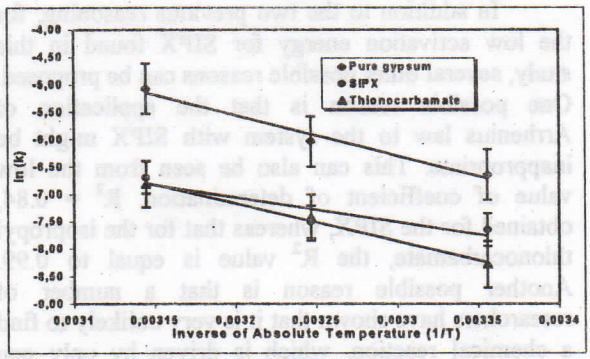

Figure 5. Plot of Arrhenius parameter for pure gypsum, SIPX and isopropyl thionocarbamate at 25, 35, and 45^{0}C, respectively

The activation energy for the pure gypsum solution calculated from Figure 5 is 60.00 kJ mol^{-1}. This value is in very good agreement with similar experiments carried out previously (Liu and

Nancollas, 1970; Nancollas and Reddy, 1974). Isopropyl thionocarbamate addition also yielded reasonable results compared with other published values for gypsum crystallization system with admixtures (He *et al*, 1994; White and Hoa, 1977).

It would be expected that the activation energy calculated for SIPX would also be in the same range as that of isopropyl thionocarbamate since both of them are found as inhibitors for gypsum growth.

It turned out, however, that the value of the activation energy for SIPX was lower, which should be contrary to the fact that SIPX hindered the growth. Overall, the activation energy values calculated from Figure 5 are: 60.00 ± 3.00, 57.39 ± 2.87, and 37.65 ± 1.88 kJ/mol, for pure gypsum, isopropyl thionocarbamate, and SIPX, respectively. The corresponding Arrhenius factor, A, for the three activation energy values are: 3,017,684 ± 30,177; 89,791,422 ± 1,795,800 and, 1,686 ± 270, respectively. The value for SIPX may not be very accurate due to the poor correlation (coefficient of determination, $R^2 = 0.84$) of the data obtained.

Literature search reveals one significant inconsistency in activation energy similar to that for SIPX obtained in this study, i.e. in the work of Ching and McCartney (1973). This investigation found that adding trace amounts of polyacrylic acid (PAA) into a crystallizing solution of gypsum retarded the crystal growth but decreased the activation energy. They assumed that such a decrease was probably due to the defect or imperfection of the crystal surface, hence caused easier incorporation of ions into the crystal lattice, which resulted in lower activation energy.

The work of He *et al.* (1994) on seeded gypsum crystallization also shows such inconsistent activation energies when impurities present in the crystallizing solution at certain concentrations. It was thus postulated that the activation energy could be solution composition dependent.

In addition to the two previous reasoning, for the low activation energy for SIPX found in this study, several other possible reasons can be proposed. One possible reason is that the application of Arrhenius law to the system with SIPX might be inappropriate. This can also be seen from the low value of coefficient of determination, $R^2 = 0.84$, obtained for the SIPX, whereas that for the isopropyl thionocarbamate, the R^2 value is equal to 0.99. Another possible reason is that a number of researchers have shown that it is very unlikely to find a chemical reaction, which is driven by only one single step process. In other words, two or more competing/opposing reactions might occur that results in inconsistency of the activation energy value (Masel, 2001). Still another possible reason is the dependence of mechanism of crystal growth on super saturation level. At low super saturation levels, diffusion mechanism is the dominant mechanism while at higher levels the principal mechanism is surface reaction (Nancollas, 1979). It could be assumed therefore, that a combination of mechanisms might be operative or competing in a system with intermediate super saturation levels (as used in the present study), which may lead to the lowering of the activation energy. In a previous investigation on the rate of precipitation of gypsum under the influence of certain inorganic electrolytes, Mile *et al.* (1982) found that the low activation energy value might result from competition between the surface integration and diffusion processes. The same phenomenon was also found in a batch crystallization system of another sparingly soluble salt ($BaSO_4$) carried out by Taguchi *et al.* (1996).

Conclusions

The effects of admixtures, namely sodium isopropyl xanthate (SIPX) and isopropyl thionocarbamate on the crystallization rate of calcium sulfate dehydrate or gypsum have been investigated using a laboratory seeded batch crystallizer and by measuring the rate constant. It was found that adding the admixtures individually or in combination significantly affected the crystallization kinetics and in particular reduced the rate of the crystallization of gypsum. The effect was measured using a second order kinetic model, that is, using the difference between the initial and the equilibrium calcium ion concentrations. The mechanism of inhibition or reduction in the rate constant by both admixtures was assumed to be one of adsorption of admixtures onto the gypsum crystal surface, thus blocking the active sites of the crystals. The effect of combinations of admixtures was seen to be equal to the effect of using only isopropyl thionocarbamate.

Therefore, it was assumed that isopropyl thionocarbamate "overrode" the effect of SIPX by preferentially being adsorbed onto the gypsum crystal faces. Activation energies were calculated using data from three different temperatures with admixture levels fixed at typical plant values.

Both the pure (gypsum) system and the system with isopropyl thionocarbamate as admixtures yielded high activation energies (Ea > 40 kJ/mol), which is indicative of a surface reaction process. Hence, it was concluded that the use of the second order kinetics (N=2) model is warranted. In the presence of SIPX, the growth of the gypsum crystals was inhibited, but the activation energy decreased, which is contrary to expectation. It was assumed that this discrepancy was probably caused by the nature of both the crystallizing solutions and, and the occurrence of different types of reaction mechanisms taking place simultaneously (Muryanto, 2002).

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