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Growth Kinetics of Calcium Sulfate Dihydrate in the Presence of Oxalic Acid

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Abstract: This study is focused on the crystallization kinetics of calcium sulfate dihydrate. The reactive crystallization of calcium sulfate dihydrate in the absence and presence of 250 ppm, 1000 ppm, and 2500 ppm oxalic acid concentrations was carried out in a mixed-suspension-mixed-product-removal (MSMPR) type crystallizer. The growth kinetic of calcium sulfate dihydrate crystals was analyzed in accordance with size-independent and size-dependent growth models. It was found that the growth rates of calcium sulfate dihydrate crystals depend on the particle size and the kinetic parameters were evaluated according to Bransom, MJ2, and MJ3 models. Also, the relative coefficient, mean square error, and the mean square deviation were determined for each model and the results showed that MJ3 model was the best fitting model to the experimental data.

Keywords: Calcium sulfate dihydrate; crystallization kinetic models; oxalic acid.

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INTRODUCTION

Calcium sulfate dihydrate ($CaSO_4.2H_2O$) is one of the most common components encountered in several industrial and environmental precipitation processes. It is a by-product of both the production of phosphoric acid from phosphate rock and the production of boric acid from colemanite ore. In both processes, the most important point is separation of the calcium sulfate dihydrate crystals via filtration. It is well known that achieving good filtration process depends on the produced crystals having homogeneous crystal size distribution [1]. The crystal size distribution depends on the nucleation and growth rate as well as residence time in the crystallizer. It is possible to investigate all of these functions for both steady and unsteady state functions by population balance theory. The continuous mixed-suspension mixed-product-removal (MSMPR) types are the most suitable crystallizers in order to apply population balance theory [2]. There are some assumptions to analyze the MSMPR crystallizer based on the population balance theory. These assumptions are (a) steady-state operation, (b) no particles in the feed, (c) no attrition of the particles [3]. As a result of these assumptions, the general population balance equation is demonstrated in Eq. (1).

$$\frac{\mathrm{d[G(L)n(L)]}}{\mathrm{dL}} + \frac{\mathrm{n(L)}}{\tau} = 0 \qquad (1)$$

G(L) is the crystal growth rate, L is the crystal size, n(L) is the population density at and τ is the residence time of suspension in the crystallizer [4]. As considering the crystal growth rate obeys the McCabe ΔL law, the growth of crystals rate is size independent. That is dG(L)/dL=0 and G(L)=G=constant. The population density distribution in MSMPR crystallizer could be presented as shown in below.

$$\mathrm{n(L)} = \mathrm{n_0}\exp\left(-\frac{\mathrm{L}}{\mathrm{G}\tau}\right) \qquad (2)$$

n_0 is the $\lim_{L\to 0} n(L)$, the zero size population density. In this situation, if the graph of ln (n) versus L is drawn, a straight line is produced with the intercept n_0 and the slope $-1/(G\tau)$ and from which the crystal growth rate could be calculated [5].

A non-linearity in ln (n) vs. L plot has been observed in many crystallization systems. Such curvature can result from various reasons such as secondary nucleation, size-dependent growth, abrasion, growth rate dispersion, agglomeration, and breaking. If the crystal growth rate does not obey the McCabe ΔL law and the line deviates from linearity, this case indicates to the existence of size dependent growth. Therefore, the population density distribution will not follow the simple exponential relationship given by Eq. (2). The relationship between crystal size and growth rate has been studied by a number of authors and certain models have been offered such as Bransom, Canning and Randolph (C-R), Abegg Stevens and Larson (ASL) two parameter (MJ2) and three parameter (MJ3) size dependent growth models [6]. While C-R and ASL models can be reduced to Bransom models, MJ2 and MJ3 are the latest proposed models. Therefore, in the literature mostly and notably Bransom, MJ2, and MJ3 models are preferred. Several

examples are given in the literature in which small amount of carboxylic acids alter the crystal growth, shape of the crystals and their agglomeration or dispersion behavior, yet the exact role of carboxylic acids is not yet fully disclosed. Furthermore, the effects of oxalic acid containing two carboxyl functional groups on calcium sulfate dihydrate crystallization has not been investigated and there is no kinetic study about calcium sulfate dihydrate crystallization in the presence of oxalic acid in the literature. Therefore, this study is focused on the examination of the crystallization kinetics of calcium sulfate dihydrate crystal produced in the absence and presence of oxalic acid using Bransom, MJ2 and MJ3 size dependent growth models.

Bransom Model. The growth rate equation of this size dependent model proposed by Bransom is written as

$$\mathrm{G(L)} = \mathrm{a}L^{b} \tag{3}$$

Using the Eq. (3), Eq. (1) can be integrated to obtain the population balance equation

$$\mathrm{n(L)} = n_0 \exp\left[\frac{1}{\mathrm{a\tau(b-1)}}\left(\mathrm{L}^{1-\mathrm{b}} - \mathrm{L}^{*(1-\mathrm{b})}\right) - \ln\left(\frac{\mathrm{L}}{\mathrm{L}^{*}}\right)^{\mathrm{b}}\right] \tag{4}$$

MJ2 Model. The MJ2 model was suggested by Mydlarz and Jones with two parameters and the equation is shown as

$$G(L) = G_m[1 - \exp(-aL)] \tag{5}$$

$$b = a\tau G_m$$

The population balance equation in accordance with MJ2 model can be defined as

$$n(L) = n^{*} exp[a(L - L^{*})]\left(\frac{\exp(aL) - 1}{\exp(aL^{*}) - 1}\right)^{\frac{(-1-b)}{b}} \tag{6}$$

MJ3 Model. Mydlarz and Jones three-parameter model (MJ3) was improved from MJ2 model, the equation is

$$G(L) = G_m\left[1 - \exp[-a(L + c)]\right] \tag{7}$$

$$\mathrm{b} = \mathrm{a\tau G_m}$$

By replacing Eq. (9) into the general population equation, the following population balance equation is obtained as

$$n(L) = n_0 \exp(aL)\left(\frac{\exp[a(L + c)] - 1}{\exp(ac) - 1}\right)^{\frac{(-1-b)}{b}} \tag{8}$$

a, b, c are the growth model parameters. G_0 is the growth rate of nuclei, G_m is the limiting growth rate of large crystal, L* is the chosen crystal size, and n* is population density at L*[2-9]. In this study, the modified procedure of models was used and the experimental data concerning crystallization kinetics of calcium sulfate dihydrate were presented. The kinetic parameter values were evaluated according to size-independent and size-dependent growth models.

MATERIALS AND METHODS

Chemicals

The solution of calcium carbonate ($CaCO_3$) and sulfuric acid (H_2SO_4) were prepared with distilled water. Calcium carbonate and sulfuric acid were used to prepare formation of calcium sulfate dihydrate crystals ($CaSO_4.2H_2O$) and were supplied by Merck Company. In addition, oxalic acid ($C_2H_2O_4$) was used as additive in this study.

Experimental procedure

Calcium carbonate solution (20% w/w) was reacted with sulfuric acid (20% w/w) solution in 1-liter double jacketed glass crystallizer in pure media and in the presence of oxalic acid at a residence time of 0.5 h, 2.5 pH and 65°C to carry out calcium sulfate dihydrate crystallization. The experiments were conducted at three different oxalic acid concentrations as 250 ppm, 1000 ppm and 2500 ppm. The exact control of temperature within the crystallizer was achieved using a thermostatted system. During the experiments, pH in the crystallizer was kept at 2.5 by feeding concentrated sulfuric acid solution. Stirring of the solution was performed via a three-blade propeller located in the center of crystallizer including three flow breakers and one draft-tube. The feed solutions were continuously fed into the crystallizer using peristaltic pumps. At the end of each experiment, the crystals were separated from suspension via vacuum filtration and washed with saturated calcium sulfate solution. Then the crystals dried at room temperature to constant weight. The obtained crystals were subjected to morphology observation by scanning electron microscopy (SEM) to investigate the change of crystal habit and the zeta potential of the produced crystals were also measured. The crystal size distribution was gathered via laser diffraction particle size analyzer. Furthermore, the values of kinetic parameter were calculated in accordance with size-independent and size-dependent growth models.

RESULTS AND DISCUSSION

In this study, the effect of oxalic acid over the growth rate of calcium sulfate dihydrate was investigated and the kinetic parameters were evaluated according to size-independent growth model and size-dependent growth models using population balance theory. Figure 1 demonstrated both linear regression between population density ln (n) and crystal size (L) and the relation of different models estimation with experimental data. When Figure 1 was examined, the deviation was observed from McCabe's ΔL law and the size independent growth rate model was not appropriate for describing the crystal growth of calcium sulfate dihydrate. In the present study, the size dependent growth was considered and Bransom, MJ2, and MJ3 size dependent growth models were utilized to describe the growth rate of calcium sulfate. The kinetic parameters of these models were determined using modified population balance equations and the parameters values were given in Table 1.

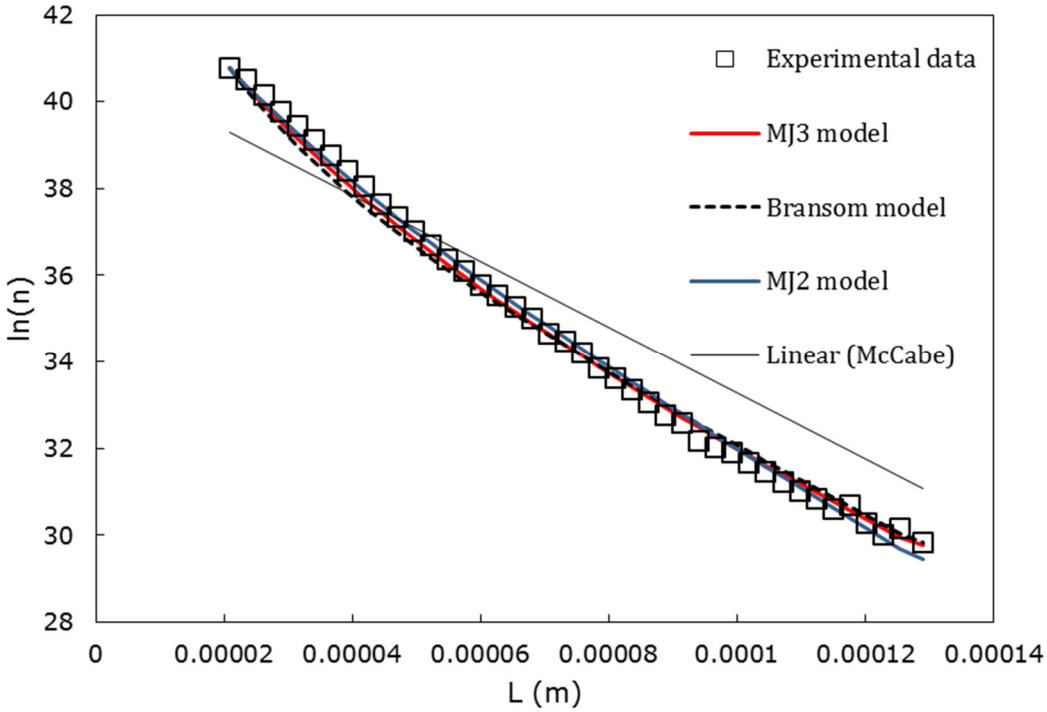

Figure 1. Population density evaluation according to the size-independent and size dependent models for calcium sulfate dihydrate obtained in the presence of 1000 ppm oxalic acid.

Table 1. Kinetic parameters of Bransom, MJ2 and MJ3 models.

Oxalic Acid Concentration	Model	Model parameters			
		$a \times 10^6$ (m^{-1})	b	$c \times 10^6$ (m)	$G_m \times 10^{-8}$ ($m.s^{-1}$)
Pure media	Bransom	4	0.456	-	-
	MJ2	0.020	0.402	-	1.117
	MJ3	0.005	0.201	40.8	2.233
250 ppm	Bransom	3.8	0.400	-	-
	MJ2	0.031	0.480	-	0.860
	MJ3	0.016	0.219	40.2	0.760
1000 ppm	Bransom	5	0.340	-	-
	MJ2	0.029	0.380	-	0.728
	MJ3	0.024	0.280	39	0.648
2500 ppm	Bransom	3.2	0.500	-	-
	MJ2	0.031	0.380	-	0.681
	MJ3	0.018	0.130	37.0	0.040

In order to find the model which best fitted the experimental data, relative coefficient, mean square error and mean square deviation of each model were evaluated and the results were presented in Table 2. By comparison, it was found that the MJ3 size-dependent growth model was the best model to characterize the experimental data with high relative coefficient and small square deviation.

Table 2. R, MSE and variance values for the kinetic models.

Oxalic Acid Concentration	Model	R	MSE	Variance
Pure media	McCabe ΔL	0.9758	-	-
	Bransom	0.9989	0.4072	0.0171
	MJ2	0.9984	0.4744	0.0242
	MJ3	0.9991	0.3496	0.0128
250 ppm	McCabe ΔL	0.9742	-	-
	Bransom	0.9984	0.5817	0.0416
	MJ2	0.9986	0.4743	0.0242
	MJ3	0.9992	0.3442	0.0124
1000 ppm	McCabe ΔL	0.9882	-	-
	Bransom	0.9978	0.0571	0.7898
	MJ2	0.9984	0.0725	0.7765
	MJ3	0.9991	0.0330	0.5402
2500 ppm	McCabe ΔL	0.9759	-	-
	Bransom	0.9995	0.7003	0.0522
	MJ2	0.9988	0.4849	0.0278
	MJ3	0.9997	0.3178	0.0130

The MJ3, a three-parameter growth rate model, also satisfied all essential size dependent growth model conditions because of predicting zero-size crystal growth. Therefore, the MJ3 size dependent growth rate model could predict the calcium sulfate dihydrate growth rate well all through the entire size range. Application of MJ3 model to the experimental data, nucleation rates was calculated range from 2.8×10^{9} to 7.8×10^{9} $m^{-3}.s^{-1}$ and as the concentrations of oxalic acid increased, the nucleation rates of crystals decreased. It was determined that oxalic acid as additive in the media affected the calcium sulfate dihydrate growth rate. In other words, growth mechanism of the crystals was changed in the presence of oxalic acid. This situation was supported by SEM analysis and zeta potential measurements.

The SEM image of the calcium sulfate dihydrate crystals obtained in pure media was given in Figure 2. As can be clearly seen in Figure 2, calcium sulfate dihydrate crystals were of needle-like shape in pure media. While the calcium sulfate dihydrate crystals produced in the presence of 2500 ppm oxalic acid preserved basically the same needle-like form, the length/width ratio of the crystals decreased compared to the crystals obtained in the pure media. That is oxalic acid favored the formation of needle shaped crystals smaller, thinner, and weaker than the crystals obtained in pure media. This kind of weak structures could be broken easily by the hydrodynamic conditions of the media [10].

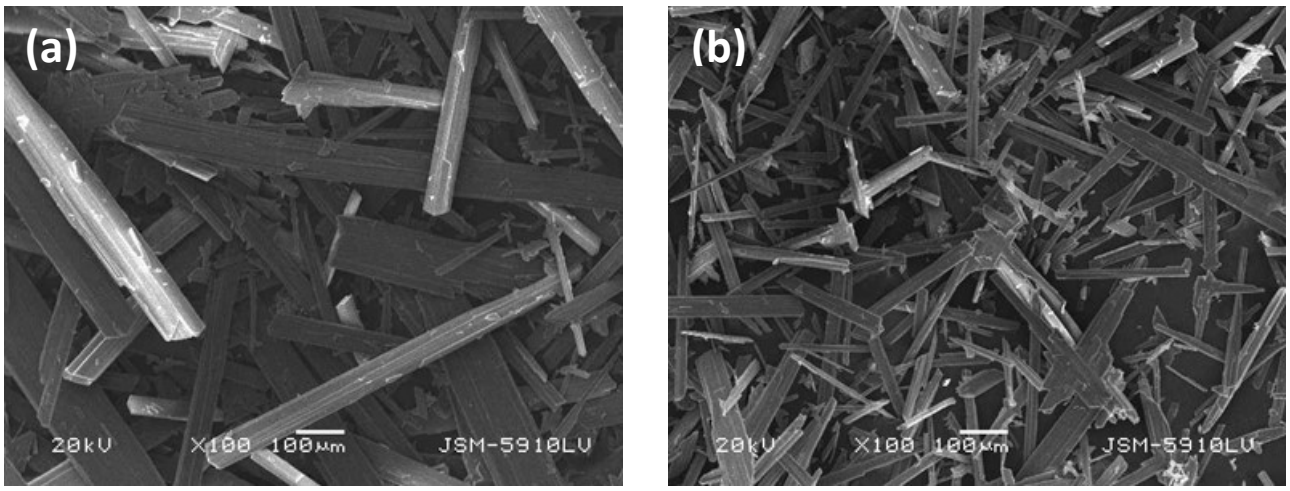

Figure 2. SEM images of the calcium sulfate dihydrate crystals. (a) Pure media (b) 2500 ppm oxalic acid.

The results of zeta potential measurements were given in Figure 3. As seen on Figure 3, calcium sulfate dihydrate crystals produced in pure media had a -13.3 mV surface charge in its own saturated solution.

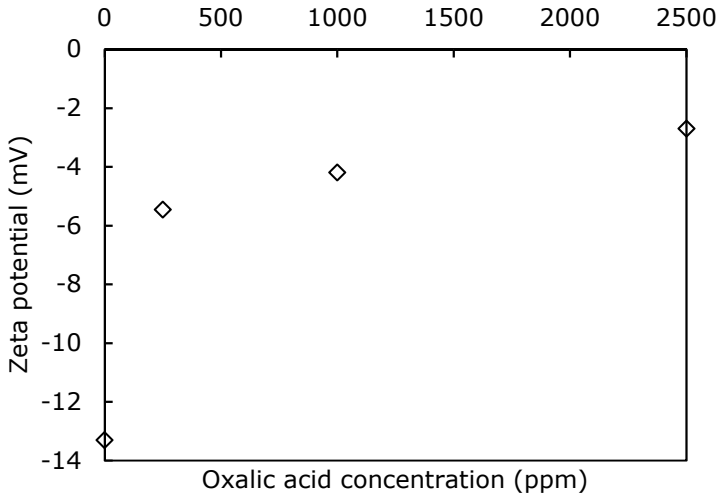

Figure 3. Influence of oxalic acid concentration on zeta potential of calcium sulfate dihydrate.

Oxalic acid had a significant effect on the surface charge of crystals. As the oxalic acid concentration increased from 0 to 2500 ppm, the zeta potentials of crystals varied from -13.3 mV to -2.7 mV. This change that occurred in the zeta potential values indicated that oxalic acid could adsorb on the crystal surface.

CONCLUSIONS

The crystallization kinetic models of calcium sulfate dihydrate in pure media and in the presence of oxalic acid were studied. It was detected that the growth rates of calcium sulfate dihydrate crystals depend on crystal size. Evaluations were carried out in accordance with the Bransom,

MJ2, and MJ3 size-dependent growth models. By comparison of experimental population density data obtaining from these models, it was determined that the MJ3 model was the most appropriate model among the other used models. It was also found that oxalic acid in the media affected both crystal shape and crystal growth rate.

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Türkçe Öz ve Anahtar Kelimeler

Oksalik Asit Varlığında Kalsiyum Sülfat Dihidratın Büyüme Kinetiği

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Öz: Bu çalışma, kalsiyum sülfat dihidratın kristalizasyon kinetiği üzerine odaklanmaktadır. Kalsiyum sülfat dihidrat kristalizasyonu, sürekli beslemeli ve sürekli ürün çekişli (MSMPR) bir kristalizörde saf ortamda ve 250, 1000 ve 2500 ppm oksalik asit konsantrasyonlarında gerçekleştirilmiştir. Kalsiyum sülfat dihidrat kristallerinin büyüme kinetiği tane boyutundan bağımsız ve tane boyutuna bağlı büyüme modellerine göre analiz edilmiştir. Kalsiyum sülfat dihidrat kristal büyüme hızının tane boyutuna bağlı olduğu bulunmuş ve kinetik parametreler Bransom, MJ2 ve MJ3 modellerine göre değerlendirilmiştir. Ayrıca korelasyon katsayı, ortalama hata karesi ve varyans değerleri her model için hesaplanmış; MJ3 modelinin sistemi en iyi karakterize eden model olduğu bulunmuştur.

Anahtar kelimeler: Kalsiyum sülfat dihidrat; kristalizasyon kinetik modelleri; oksalik asit.

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