

## The effect of Stirring Rate on Dissolution of Colemanite and Particle Size of Gypsum Crystals during the Boric Acid Production in a Batch Reactor

A. Erdoğan, G. Ö. Çakal, I. Eroğlu

Middle East Technical University, Faculty of Engineering, Department of Chemical Engineering, Ankara

S. Özkar

Middle East Technical University, Faculty of Art and Science, Department of Chemistry, Ankara

**ABSTRACT:** One of the most commonly used boron compounds, boric acid, is produced by dissolving colemanite ( $2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$ ) in aqueous sulfuric acid whereby gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ) is formed as a byproduct. In this study it was aimed to investigate the effect of stirring rate on the dissolution of colemanite and particle size of gypsum formed during the boric acid production. The experiments were performed at  $\text{CaO}/\text{SO}_4^{2-}$  molar ratio of 1.00 and reaction temperature was kept constant at  $85^\circ\text{C}$ . The colemanite minerals having particle size between 250 and 1000  $\mu\text{m}$  were dissolved in aqueous sulfuric acid. The effect of stirring rate on dissolution of colemanite and particle size distribution of gypsum crystals obtained in the production of boric acid was analyzed at 350, 400 and 500 rpm stirring rates. The increase in stirring rate increases the mass transfer rate from the liquid to solid surface. So, it increases the dissolution rate of colemanite. However, volume weighted mean diameter of the gypsum crystals decreased with increasing stirring rate.

**ÖZET:** En önemli bor bileşiklerinden biri olan borik asit, kolemanitin ( $2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$ ) sülfürik asitte çözünmesinden oluşmaktadır. Bu tepkime sonucunda yan ürün olarak da jips ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ) oluşmaktadır. Bu çalışmada karıştırma hızının kolemanit çözünmesine ve jips kristallerinin parça boyutuna etkisinin incelenmesi amaçlanmıştır. Deneyle  $\text{CaO}/\text{SO}_4^{2-}$  mol oranı 1.0 ve reaksiyon sıcaklığı  $85^\circ\text{C}$ 'de sabit tutularak yapılmıştır. Tane büyüklüğü 250 ile 1000  $\mu\text{m}$  arasında değişen kolemanit minerali seyreltik sülfürik asitte çözünmüştür. Karıştırma hızının kolemanit çözünme ve borik asit üretiminde oluşan jip kristallerinin parça boyutuna etkisi 350, 400 ve 500 dev/dak karıştırma hızlarında incelenmiştir. Karıştırma hızının artması ile sıvıdan katıya kütle transfer hızı artırmaktadır. Böylece, kolemanitin çözünme hızını artırıcı bir etki yaratmaktadır. Ayrıca, jips kristallerinin hacimce ortalama parça boyutu karıştırma hızı artıkça azalmaktadır.

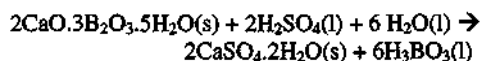
### 1. INTRODUCTION

Boron does not occur in nature in its elemental form. It is available in nature in its compounds, mostly in sodium and calcium compounds. Elemental boron is used mainly in the metal industry. Certain compounds of boron, such as borax and boric acid, have been known and used for a long time in glass, ceramic and mining industries (Uumann, 2002). Boron minerals occur in a few locations in the world, but the largest boron deposits are placed in Turkey. It was estimated that Turkey has about 63.9% ( $\text{B}_2\text{O}_3$ ) of the known reserves of the world, whereas USA has the 16.6%

of the share (Roskill, 2002). Colemanite ( $2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$ ), which is a kind of hydrated calcium borate, is one of the most important boron minerals. It is used as a raw material in the production of boric acid.

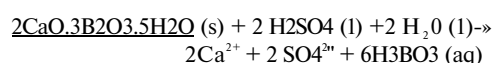
Boric acid is used to prepare a variety of glasses including fiber glass, heat resistant borosilicate glass and sealing glasses. It also is used to make porcelain. A major application of boric acid is to prepare a number of boron compounds including inorganic borate salts, boron halides, borate esters, fluoroborates and many boron alloys (Patnaik, 2002).

Boric acid is produced in Turkey and Europe mainly from the reaction of colemanite with sulfuric acid (Roskill, 2002). The overall reaction is as follows

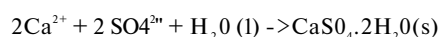


This overall reaction consists of two consecutive reactions, dissolution of colemanite and formation of gypsum. In the first reaction boric acid is produced and this is a very fast reaction.

#### Boric Acid Production Reaction:



#### Gypsum Crystallization Reaction:



In the latter step, gypsum crystals are formed and stay in the reaction mixture to grow up to a size large enough to be filtered out of the solution.

Bilal and coworkers (2003) studied the dissolution of colemanite in sulfuric acid in a batch reactor at different temperatures, initial concentration of sulfuric acid and the amounts of boric acid initially added to the system. It was found that the reaction of colemanite with sulfuric acid was very fast and complete conversion was obtained in nearly 15 minutes. The saturation concentration of gypsum decreased with the increasing temperature. Initial boric acid concentration had insignificant effect on dissolution rate of colemanite.

The factors which affect the formation of gypsum during the dissolution of colemanite and the crystallization kinetics of gypsum were studied by Balkan and Tolun (1985). It was found that the growth rate of gypsum crystals increased as the temperature increased up to 80 °C and then decreased.

The crystallization kinetics of calcium sulfate dihydrate was studied during the dissolution of colemanite in aqueous sulfuric acid (Çetin et al., 2001). It was found that the crystal growth of

gypsum on seed crystals follows a second order kinetics from the solution supersaturated in calcium and sulfate ions. The rate law for the crystallization was given as in Equation 1.

$$-\frac{d[\text{Ca}^{2+}]}{dt} = k([\text{Ca}^{2+}] - [\text{Ca}^{2+}]_{\text{sat}})^2 \quad (1)$$

where the crystal growth rate is given in mol L<sup>-1</sup> s<sup>-1</sup>, k is the rate constant in L mol<sup>-1</sup> s<sup>-1</sup> and [Ca<sup>2+</sup>]<sub>sat</sub> is the saturation concentration of calcium ion in solution.

The effect of particle size of colemanite on gypsum crystallization in batch reactor was investigated in the previous study (Erdoğan et al., 2003). Also, the dissolution of colemanite and formation of gypsum during boric acid production in a batch reactor was investigated by varying temperatures, stirring rates and particle sizes of colemanite by Erdoğan (2004).

In this study, the effect of stirring rate on dissolution of colemanite and gypsum particle size distribution was analyzed at different stirring rates.

## 2. EXPERIMENTAL

### 2.1 Materials

In this study; colemanite, sulfuric acid and distilled water were used as reactants for the boric acid production reaction.

The colemanite mineral was provided from a region of Emet, Kütahya, Turkey. The colemanite mineral having particle sizes of 250-1000 µm was used in this study. The B<sub>2</sub>O<sub>3</sub> and CaO content of the colemanite was 43.87% and 28.61%, respectively. The sulfuric acid was supplied by Eti Holding A.S. Its grade was 93% by weight. The third reactant, the distilled water, was obtained by a water distillation apparatus (Nüve NS 108). All the other chemicals used in the analysis were purchased in reagent grade from Merck and J.T Baker.

### 2.2 Set-up and Procedure

Experimental set-up consists of a reactor, a mechanical stirrer, a heating jacket, a pH meter, a thermocouple, a temperature control unit and a vacuum pump. The reactor having volume of 1.5 L is made up of borosilicate glass (İldam Kimya,

Ankara, Turkey). Firstly, a given amount of distilled water was put into the reactor. Then sulfuric acid was added slowly into the reactor. The temperature control unit was adjusted to reaction temperature. Certain amount of colemanite was fed into the reactor at once. This time was considered as the starting time of the reaction. The samples were withdrawn by syringe. Then, samples were filtered immediately by using vacuum pump. Solid particles and liquid were collected on filter paper and flask, respectively. The liquid portion was analyzed for boric acid and calcium ion concentration. The filtrates were analyzed for investigating the growth and determining the volume weighted mean diameter of gypsum crystals.

### 2.3 Analysis

#### 2.3.1 Calcium Ion and Boric Acid Concentration Determination

The calcium ion concentration of the solution was determined by Atomic Absorption Spectrophotometer (Philips PU 9200 X). The boric acid concentration of the liquid phase was determined as follows: 5 ml of sample was taken from the solution, which was filtered by using blue band filter. Methyl red indicator was put on it and 1-2 drops of 1:3 (by vol.) H<sub>2</sub>SO<sub>4</sub> was added to the solution. Then, 6 N NaOH was put until the color changes from pink to yellow. After this step, H<sub>2</sub>SO<sub>4</sub> was again added to the solution until the color turns back to pink. This solution is titrated with 0.5 N NaOH until a pH of 4.5 is obtained. Then, phenolphthalein indicator and mannitol was added to the solution. The solution was again titrated with 0.5 N NaOH until the pH of the solution becomes 8.5. The volume of the NaOH used in this step was recorded and used to calculate the boric acid concentration from the following formula:

$$[H_3BO_3] \text{ (mol/l)} = V_{NaOH} F_{NaOH} N_{NaOH} / V_{sample}$$

where V<sub>NaOH</sub>, F<sub>NaOH</sub>, N<sub>NaOH</sub> and V<sub>sample</sub> are the volume of the NaOH used, factor of the NaOH, normality of NaOH, and the volume of the sample, respectively.

#### 2.3.2 Laser diffraction particle size analysis

The particle size distributions of the solid samples were determined by a particle size analyzer

(Malvern Instruments, Mastersizer 2000) utilizing the principle of laser ensemble light scattering. This instrument can detect the particle range of 0.02-2000 μm. The analysis was done by using wet dispersion method with a repeatability of +/- 0.5%. Tap water was used as dispersant in the analysis.

#### 2.3.3 Light Microscope Images

Morphology of gypsum crystals was obtained by a light microscope connecting to online to a computer by a Pro Series, high performance CCD Camera. Images were seen live in monitor by Image Pro Plus 3.0 software.

## 3. RESULTS

Three experiments were performed at the initial CaO/SO<sub>4</sub><sup>2-</sup> molar ratio of 1.00 and at 85 °C. The effect of stirring rate the dissolution of colemanite and particle size of gypsum formed during the boric acid production was analyzed at 350, 400 and 500 rpm stirring rates.

The tip speed of agitator was calculated from Equation 2.

$$U = \pi d \frac{n}{60} \quad (2)$$

where U is the tip speed in m s<sup>-1</sup>, d is the diameter of the agitator in m and n is the stirring rate in rpm.

The diameter of the agitator was 0.06 m. The diameter of the reactor was 0.12 m. The agitator tip speeds were calculated for 350, 400 and 500 rpm stirring rates and found as 1.1, 1.26 and 1.57 m s<sup>-1</sup>, respectively.

#### 3.1 Dissolution of Colemanite

During the experiments, variation of the boric acid concentration was determined. As the colemanite dissolves, the boric acid concentration in the liquid phase increases. The change in boric acid concentration in the liquid phase in dependency of the time at different stirring rate is shown in Figure 1. As seen from the figure, the dissolution of colemanite was instantaneous. However, after 10 minutes the dissolution rate slowed down and a

plateau was seen. That region might indicate the importance of mass transfer on dissolution rate. The increase in stirring rate increases the mass transfer rate from the liquid to solid surface. Therefore, higher boric acid concentrations were obtained at stirring rates above 400 rpm.

### 3.2 Gypsum Formation and Growth

The crystallization of gypsum from the solution can be followed by the calcium ion concentration in the solution as it decreases by the formation of gypsum precipitate. Figure 1 illustrates the effect of stirring

rate on calcium ion concentration in the liquid phase. As it was observed in figure, calcium ion concentration in the liquid phase undergoes a rapid exponential decay and then approaches an asymptotic value of saturation concentration. The calcium ion concentration decreased faster at 400-500 rpm compared with 350 rpm. By increasing stirring rate, the mass transfer of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions from the bulk to crystal surface is increased. Therefore most probably the rate of crystal growth rate at stirring rates higher than 400 rpm are controlled by the surface reaction.

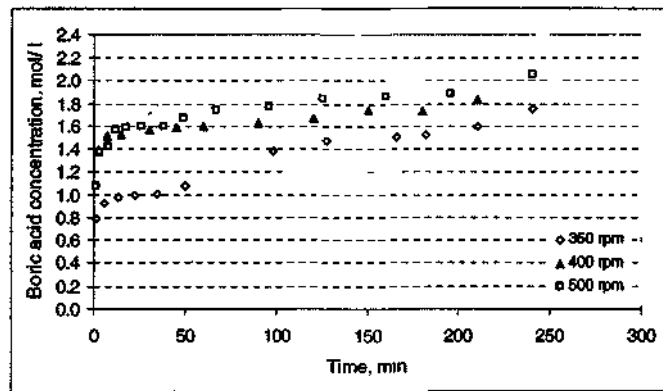


Figure 1. Variation of boric acid concentration in solution with respect to time at different stirring rates (Colemanite minerals having particle size between 250-1000  $\mu\text{m}$ ,  $\text{CaO}/\text{SO}_4^{2-} = 1.0$ ,  $T = 85^\circ\text{C}$ )

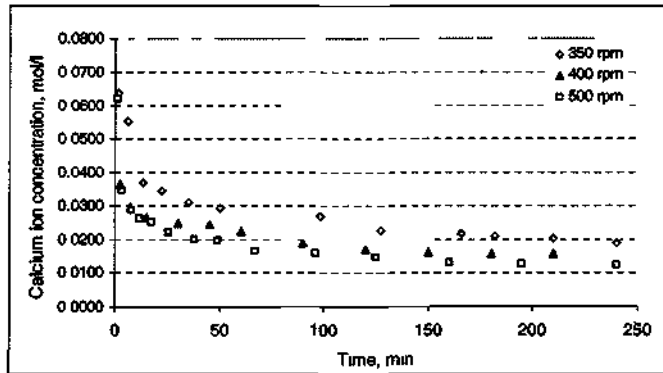


Figure 2. Variation of calcium ion concentration in liquid with respect to time at different stirring rates (Colemanite minerals having particle size between 250-1000  $\mu\text{m}$ ,  $\text{CaO}/\text{SO}_4^{2-} = 1.0$ ,  $T = 85^\circ\text{C}$ )

### 3.3 Partide Size Distribution of Gypsum Crystals

Figure 3 illustrates size distribution of the gypsum crystals obtained at 210 minutes at different stirring rates. As, the shape of the particles is not recognized by the laser diffraction instrument, the particle size distribution is based on volume of spherical particles. While comparing the distributions taken from the particle size analyzer, it should be kept in mind that the gypsum crystals are rod-like (Çetin et al., 2001). The volume weighted mean diameters are reported by the analyzer.

The maximum volume percent in Figure 3 was detected at 500 urn at all stirring rates. The maximum volume percents were 10%, 7% and 6% at 350 rpm, 400 rpm and 500 rpm, respectively. It was seen that the biggest particles were obtained at slower stirring rates.

The volume percents, for particles smaller than 200 urn, at the stirring rates of 350 rpm, 400 rpm and 500 rpm were smaller than 0.5%, 1.5% and 2%, respectively. On the other hand, for particles smaller than 20 urn, the volume percent at 350 rpm was negligible, and the volume percent smaller than 1.5% was detected for 400 rpm and 500 rpm. This

indicated that at higher stirring rates, the number of smaller crystals increased.

The volume weighted mean diameters of the crystals were reported as 563 urn, 427 urn and 377 urn at 350 rpm, 400 rpm and 500 rpm, respectively. At higher stirring speeds, the gypsum crystals may break.

### 3.4 Images of Gypsum Crystals

The time dependent growth of gypsum crystals can be seen from the Figures 4. In the first minutes, the crystals were small and thin. On the prolong crystallization, the gypsum crystals became longer and wider. Figure 4 illustrates gypsum crystals images obtained during the experiment performed at 350 rpm. The scale used in the views a-b were 20 jim and c-d were 50 urn. Average dimensions of crystals in first few minutes were 1-70 urn length and 1-10 width. The clump formation of gypsum crystals was observed during the prolong crystallization.

In a continuous flow production process of boric acid, on the other hand, the gypsum crystals grew bigger in either dimension (Çakal et al., 2004). There existed no clump formation of the crystals.

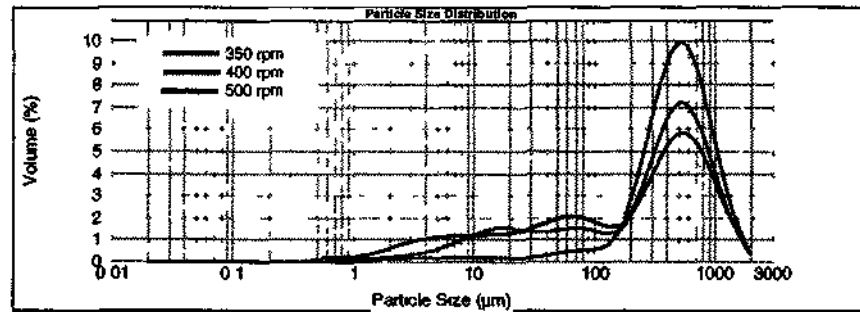


Figure 3. Particle size distribution of the gypsum crystals obtained at 210 minutes at different stirring rates (Colemanite minerals having particle size between 250-1000 urn,  $\text{CaO}/\text{SO}_4^{2-} = 1.0$ ,  $T = 85^\circ\text{C}$ )

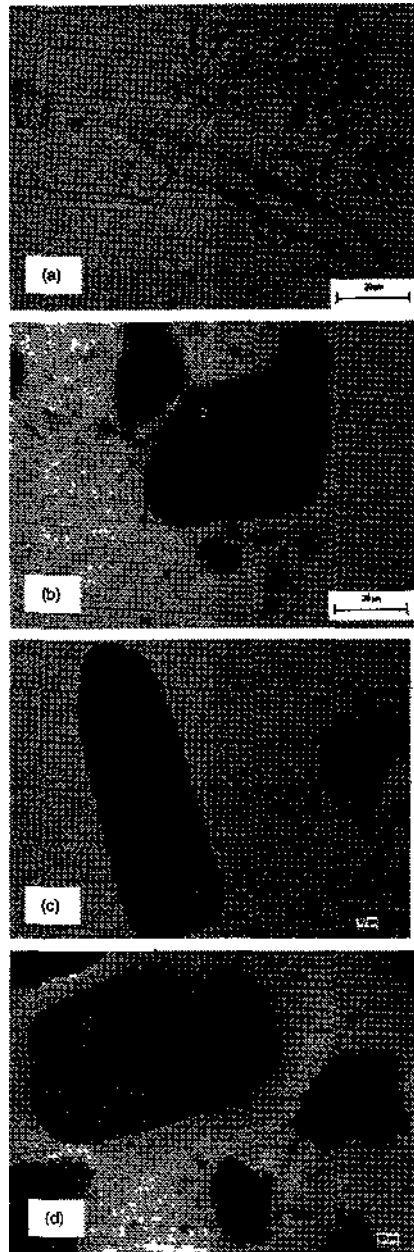


Figure 4. light microscope images of gypsum (Colemanite minerals having particle size between 250-1000  $\mu\text{m}$ ,  $\text{CaO}/\text{SO}_4^{2-} = 1.0$ ,  $T = 85^\circ\text{C}$ ),  $\text{CaO}/\text{SO}_4^{2-} = 1.0$ , Stirring Rate = 350 rpm,  $T = 85^\circ\text{C}$  (a) 6.5 min, (b) 60 min, (c) 98 min, (d) 180 min.

#### 4. CONCLUSIONS

It was concluded that, the colemanite dissolution rate increased with increasing stirring rate due to increasing mass transfer. Volume weighted mean diameter of the gypsum crystals at 350 rpm, 400 rpm and 500 rpm were 563  $\mu\text{m}$ , 427  $\mu\text{m}$  and 377  $\mu\text{m}$ , respectively. It showed that gypsum crystals were broken at higher stirring rates producing smaller crystals. During the filtration process, when small crystals were present in the slurry, the chance of the gypsum crystals passing through the boric acid solution increases. Therefore, this brings impurity to the boric acid solution.

The clump formation of gypsum crystals was observed during the prolong crystallization of gypsum when the colemanite particles larger than 250  $\mu\text{m}$  were used during the production of boric acid. Since, clumps hindered valuable boric acid solution inside of them; it decreased the yield of the process. Therefore, colemanite particles smaller than 250  $\mu\text{m}$  should be used during the boric acid production.

#### ACKNOWLEDGEMENT

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