

Comparison of the Partide Sizes of Gypsum Crystals Obtained in the Production of Boric Acid by Batch and Continuous Flow Systems

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ABSTRACT: Colemanite, one of the important boron minerals, is dissolved in aqueous sulfuric acid to produce boric acid. In this reaction gypsum is obtained as a by-product. Gypsum crystals are in the shape of thin needles. These crystals should be grown to an easily filterable size in order to increase the production yield and purity of boric acid. In this paper, the particle size distributions and the volume weighted mean diameters of the gypsum crystals obtained in batch and continuous flow systems were compared. During the experiments, the temperature of the reactors were 85°C, stirring rates were 400 rpm and the inlet CaO / SO₄²⁻ ratio was 1.00. In these experiments, colemanite mineral having particle size smaller than 150 (µm) was used. The average diameter of the gypsum crystals obtained at 3.5 hours from the batch reactor was found as 37 (µm). This value for the continuous system at steady state was observed to change between 44-163 µm. The particle size of the gypsum was found to increase with the residence time of the solid in the continuous system.

ÖZET: Önemli bor minerallerinden biri olan kolemanit seyrettik sülfürik asitte çözünmekte, borik asit ve yan ürün olarak jips oluşmaktadır. Jips ince iğneler şeklinde kristaller oluşturmaktadır. Elde edilen bu kristaller, üretim verimim ve borik asit saflığını arttırabilmek için, kolayca filtre edilebilecek uygun bir boyuta büyütülmelidir. Bu bildiride, kesikli ve sürekli akış sistemlerinde elde edilen jips kristallerinin parça boyut dağıtımları ve hacimce ortalama çapları karşılaştırılmaktadır. Kesikli reaktör koşulları ile sürekli reaktör koşulları çalışma sırasında aynı alınmıştır. Deneyler esnasında reaktörlerin sıcaklığı 85°C, karıştırma hızı 400 dev/dakika ve giriş CaO/ SO₄²⁻ oranı 1.00 olarak sabit tutulmuştur. Bu deneylerde, 150 µm'dan küçük parça boyutuna sahip kolemanit minerali kullanılmıştır. Kesikli reaktörde 3.5 saat sonunda jipsin ortalama çapının 37 (µm) olduğu ve sürekli sistemde, yatışkın durumda, ise bu değer 44-163 µm arası değiştiği gözlenmiştir. Sürekli sistemde, katının reaktörde kalış süresi arttığı zaman jipsin parça boyutunun da arttığı bulunmuştur.

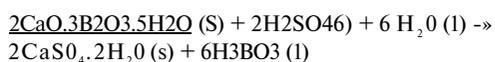
1. INTRODUCTION

Boron is one of the most important elements in the world, whose compounds are used in all the manufacturing applications, except food, in highly industrialized countries. More than one half of the boron compounds are consumed in the manufacture of various kinds of glasses such as pyrex, frits and insulation-grade and textile grade fibers. The other important uses include soaps, detergents and bleaches (Roskill, 2002). Boron does not occur in nature as a free element, but it always combined

with oxygen to form borates. There are more than 230 borate minerals in the world. Borax (tincal) and colemanite (2CaO·3B₂O₃·5H₂O) are the most important ones (Kirk Othmer, 1992). The largest reserves of boron minerals in the world are in the western part of Turkey (Özbayoğlu and Poslu, 1992).

Boric acid is produced in Turkey and Europe mainly from the reaction of colemanite with sulfuric acid. The overall reaction is as follows:

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Gypsum (Calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) crystallizes in the reactor. Filtration of gypsum crystals after the reaction is a crucial process in the production of boric acid in high purity and with high efficiency, as the subsequent crystallization of boric acid from the supernatant solution is affected by contaminations.

Gypsum crystallization kinetics was studied by Çetin et.al (2001). The growth of the gypsum crystals was studied by Erdoğan (2004) and Çakal (2004) in a batch reactor and continuous flow system, respectively. This study compares the particle sizes of gypsum crystals obtained in the production of boric acid by batch and continuous flow systems.

2. EXPERIMENTAL

2.1 Materials

Colemanite mineral (25-100 mm, Hisarcık, Turkey), sulfuric acid (93 wt%) and boric acid (99.9% b.w.) were supplied by Eti Holding A.Ş. (Ankara, Turkey). The colemanite mineral having particle sizes of 0-150 urn was used in this study. The B_2O_3 and CaO content of the colemanite was 34.61% and 28.41%, respectively.

2.2 Experimental Set-ups

The batch reactor experimental setup consists of a reactor, a mechanical stirrer, a heating jacket, a thermocouple and a temperature control unit. The reactor having volume of 1.5 L is made up of borosilicate glass (İdam Kimya, Ankara, Turkey) (Erdogdu et.al, 2004).

The continuous flow experimental set-up consists of a solid feeding unit, an acid feeding unit, and four continuously stirred reactors in series unit, followed by a filtration unit. Each reactor was heated and continuously stirred by means of mechanical stirrers (Heidolph RZR 2041). First reactor had a silicone heating tape connected to a temperature controller (Isopad TD2000) and a thermocouple. The other three reactors were

jacketed and hot water was circulated around each of them by means by a circulating water bath (Heto HWT 100, OBN 28) (Çakal, 2004).

2.3 Experimental Procedure

2.3.1. Batch Reactor Experiments:

The sulfuric acid was added to distilled water in the reactor and the reactor was heated to the reaction temperature. The colemanite was fed to the reactor at one lot and this time was taken as the start of the reaction. Solid samples were collected at 3.5 hours and washed with hot water.

2.3.2. Continuous Flow Experiments:

The colemanite and acid feed rates were calibrated before the experiments. The controller of the heating tape was adjusted to 85°C in the first reactor and hot water was circulated through die jackets of the last three reactors. At the beginning of the experiment, the colemanite and acid feeders were operated at the same time and this time was accepted as the zero time, which describes the starting moment of the reaction. Solid samples were collected from each of the reactors at steady state and washed.

2.4 Analysis of Solid Samples

2.4.1. 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 urn. The analysis was done by using wet dispersion method with a repeatability of +/- 0.5%. The dispersant used in the analysis was tap water.

In the analysis, some amount of solid was put into beaker filled with water. This beaker was put on its place in the analyzer. Then the analyzer was ready to give the crystal size distribution of the sample.

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.

2.4.2. Light microscope images:

The solid samples were also examined under the light microscope. In the analysis, Prior Laboratory Microscope Model B 3000 was used. Microscope was connected online to a computer by Pro Series, high performance CCD camera. Images were seen live in monitor by «r-analytical imaging software called Image Pro Plus 3.0 for Windows.

3. RESULTS

3.1. Particle Size Distribution of Gypsum Crystals

The solid analysis showed that after the dissolution of colemanite in sulfuric acid, there were no

unreacted colemanite in the solid phase, i.e. no B₂O₃ was detected, both in batch and continuous operations.

Figure 1 illustrates the particle size distribution of the gypsum crystals collected at 3.5 hours from the batch reactor. As it was seen from this figure, there existed only one peak in the particle size distribution of gypsum in a batch reactor.

The distribution in Figure 1 was an even distribution. A maximum volume percent of 4.3% was detected at 15 µm. Particles smaller than 1 µm had a maximum volume percent of 0.75%, whereas particles in the range of 200-700 µm had a maximum volume percent of 0.5%. The volume weighted mean diameter of the gypsum crystals reported by the analyzer was 37 µm.

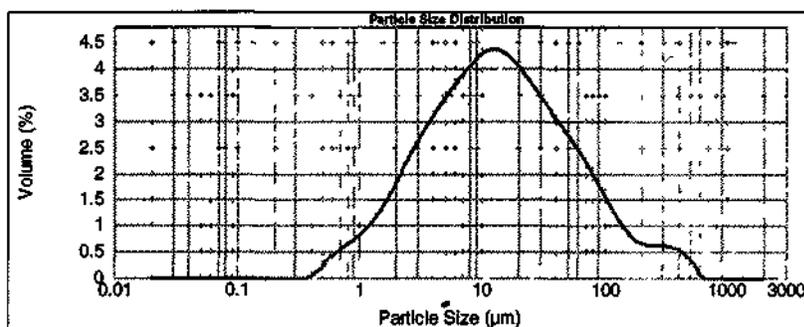


Figure 1. The particle size distribution of gypsum crystals during the dissolution of 0-150 µm colemanite in aqueous sulfuric acid at initial CaO/SO₄²⁻ molar ratio of 1.0 at 85°C and a stirring rate of 400 rpm

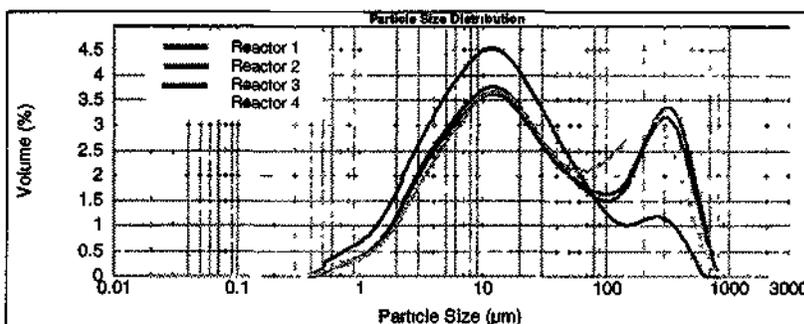


Figure 2. The particle size distribution of gypsum crystals at each of the reactors in continuous flow experiment performed by using 0-150 µm colemanite at the initial CaO/SO₄²⁻ molar ratio of 1.00, and colemanite feed rate of 10 g/min

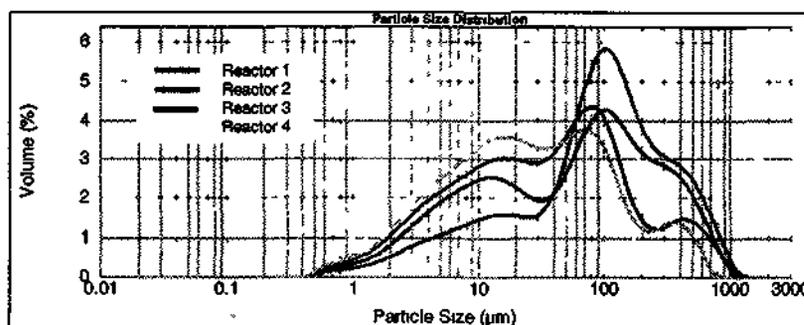


Figure 3. The particle size distribution of gypsum crystals at each of the reactors in continuous flow experiment performed by using 0-150 µm colemanite at the initial CaO/SO²⁺ molar ratio of 1.00, and colemanite feed rate of 3.5 g/min

Table 1. Comparison of the volume weighted mean diameter of gypsum crystals obtained by dissolving 0-150 µm colemanite in sulfuric acid at initial CaO/SO²⁺ molar ratio of 1.00, stirring rate =400 rpm, temperature = 85 °C and by batch and continuous flow reactors

		Residence Time of Solid, min	Mean Diameter of Gypsum, µm
Batch Reactor		210	37
Continuous Flow Reactor Expl	Reactor 1	20	106
	Reactor 2	20	99
	Reactor 3	20	44
	Reactor 4	20	91
Continuous Flow Reactor Exp 2	Reactor 1	60	131
	Reactor 2	60	163
	Reactor 3	60	96
	Reactor 4	60	69

The particle size distributions of the gypsum crystals in continuous flow stirred slurry reactors are given in Figures 2 and 3. The colemanite feed rate in Figure 2 was 10 g/min. The residence time of the solid in each of the reactors was 20 min. In this figure there existed two peaks, which denoted that the small and big gypsum particles had their own distributions. The maximum volume percents were detected at 15 µm for the particles smaller than 100 µm. The maximum volume percent at the third reactor was 4.5%, whereas the maximum volume

percent for the other three reactors were 3.75%. This means that there existed more small particles in the third reactor (Table 1).

The maximum volume percents for particles in the range of 100-800 µm, on the other hand, were detected at 300 µm and 250 µm in reactors 1-2 and 3-4, respectively. The maximum volume percents for reactors 1, 2, 3 and 4 were 3.4%, 3.25%, 1.2% and 3.2%, respectively. This indicated that there

existed more big crystals in the first reactor (Table 1).

The volume weighted mean diameters of the crystals recorded for Figure 2 were in the range of 44-106 μm , the highest particle size belonging to the first reactor (Table 1).

Figure 3 illustrates the particle size distributions of the gypsum crystals in continuous flow stirred slurry reactors having a colemanite feed rate of 3.5 g/min. The residence time of the solid in each of the reactors was 60 min. In this figure there existed three peaks. The maximum volume percents were detected at 15 μm for the gypsum particles smaller than 30 μm . The maximum volume percents were 2.5%, 1.5%, 3% and 3.5% at reactors 1,2,3 and 4, respectively for the small particles. This means that there existed more small particles in the fourth reactor (Table 1).

The maximum volume percents for particles in the range of 30-250 μm , on the other hand, were detected at 100 μm and 80 μm in reactors 1-2 and 3-4, respectively. The maximum volume percents for reactors 1, 2, 3 and 4 were 4.25%, 5.75%, 4.25% and 3.75%, respectively. This indicated that there existed more big crystals in the second reactor (Table 1).

The crystal particles in the range of 250-1000 μm were detected to have their maximum volume percents at 400 μm . The maximum volume percents were 2.75%, 2.9%, 1.5% and 1.4% at reactors 1, 2, 3 and 4, respectively for the biggest particles.

The volume weighted mean diameters of the crystals were in the range of 69-163 μm , the highest particle size belonging to the second reactor (Table 1).

The comparison of volume weighted mean diameters of the gypsum crystals obtained in batch and continuous flow systems are given in Table 1.

The diameters of the gypsum crystals obtained in the continuous flow reactor experiments were bigger, as seen in Table 1, compared to the batch reactor experiments.

It was also observed that with the increase of residence time of solid in the reactors in continuous flow experiments, the gypsum crystals grew bigger. The crystals were seen to break in the after first or second reactor due to high stirring rates, 400 rpm. The stirring rate in the latter reactors can be decreased for the increase of volume weighted mean diameters of gypsum crystals.

3.2. Images of Gypsum Crystals

The dimensions of the gypsum crystals were also examined under the light microscope. The views of the crystals for batch reactor experiments are given in Figure 4. The scale used in the views were 20 μm . It was seen in the images that the crystals had a width of 1-10 μm and length of 10-80 μm .

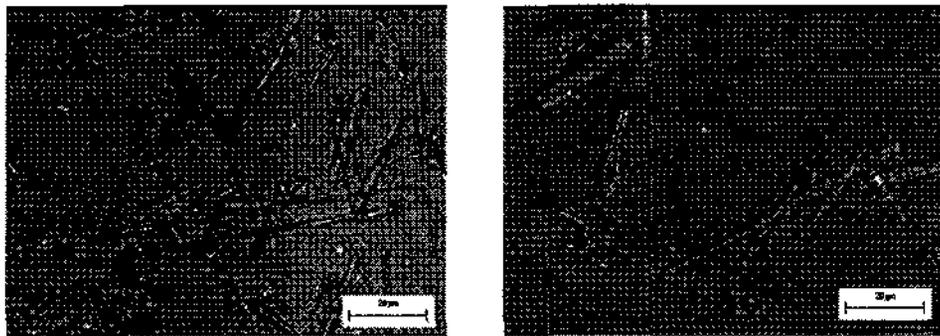


Figure 4. Light microscope images of gypsum crystals obtained by the batch reactor experiment. The residence time of the crystals was 210 min

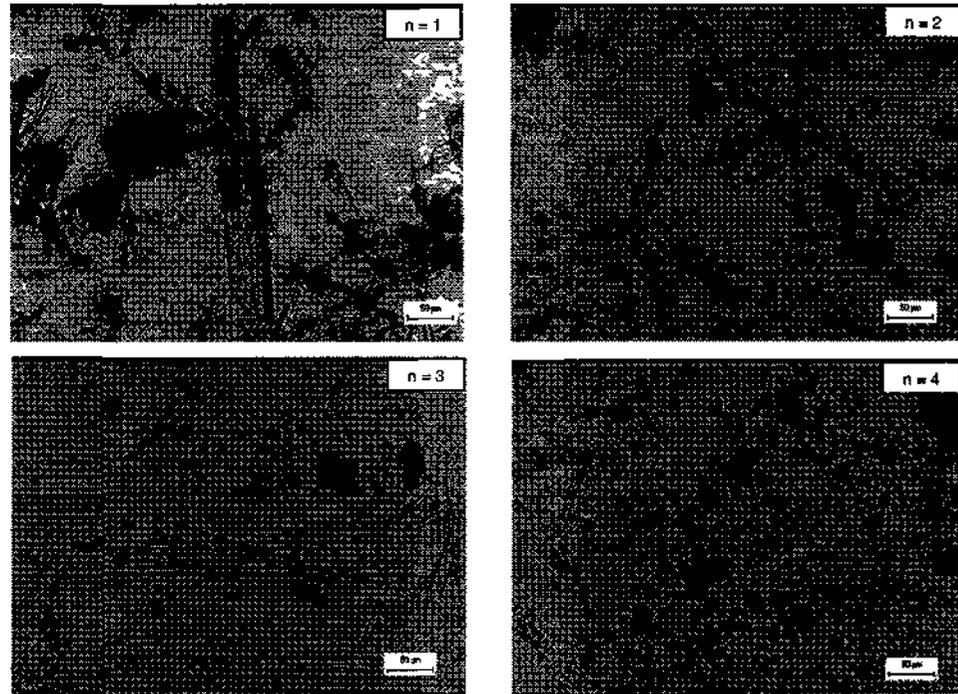


Figure 5. Light microscope images of gypsum crystals obtained by the continuous reactor experiment. The residence time of the crystals in each reactor is 20 min. The reactor number, n , is shown on top of each figure

The views of the gypsum crystals for continuous flow reactor experiments were given in Figures 5 and 6, for the solid residence times of 20 and 60 min in each of the reactors, respectively. The scale of the views for these cases were 50 μm .

Tall and wide crystals were seen in Figure 5 compared to the images in Figure 4. The biggest dimensions of crystals were observed in the first reactor. The width of the crystals in the first image was 5-40 μm and the length was 25-300 μm . The crystals were seen to break in the other reactors as seen in Figure 5.

The gypsum crystals grew wider and taller in Figure 6. The crystals had dimensions even bigger than 250 μm as seen in the images. The width of some of the crystals was even 100 μm . The crystals width seemed to be higher in this figure, compared to Figure 5, due to the high residence time of the solid in the reactor, 60 min. The crystals in Figure 5 did not have enough time to grow up in the reactor when the solid residence time was 20 min.

The images in Figures 5 and 6 showed the significance of working with continuous reactors when compared with the images of the batch reactor byproduct gypsum, Figure 4.

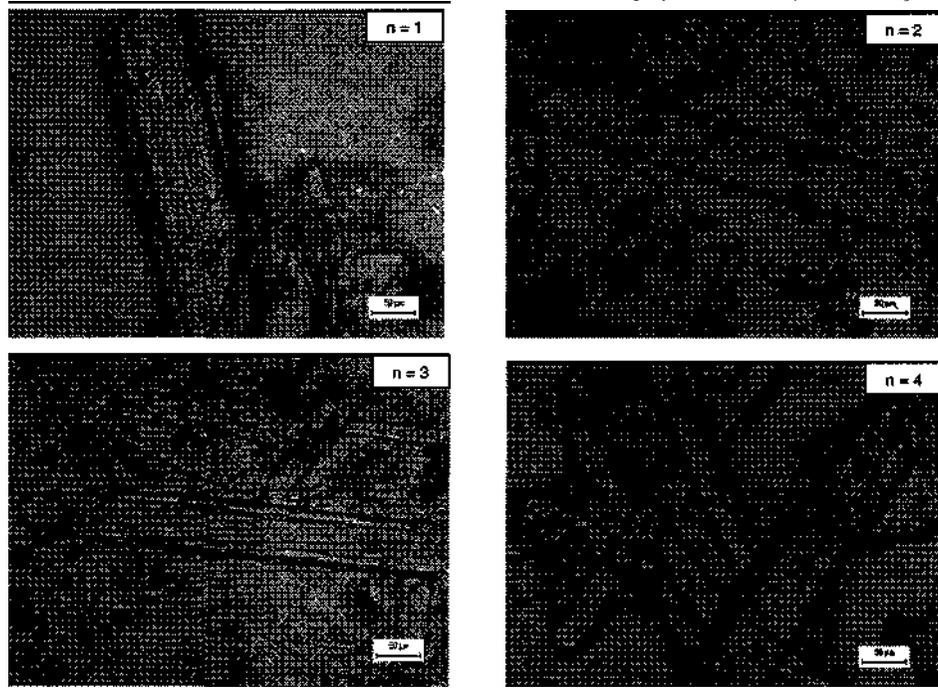


Figure 6. Light microscope images of gypsum crystals obtained by the continuous reactor experiment. The residence time of the crystals in each reactor is 60 min. The reactor number, n, is shown on top of each figure.

4. CONCLUSION

Examining the particle size distributions of the gypsum crystals that were produced in a batch and continuous flow system, it was seen that the width and length of the crystals were small in the batch process compared to the crystals obtained in a continuous flow system. The crystals grew bigger in the continuous process, especially when the residence time of the solid in the reactor was higher. In this case, the crystals had enough time to grow up in the reactor. So, it was better to have a high residence of solid in the reactors.

In the continuous process, it was seen that after the second reactor the particle size of the crystals decreased. Therefore, it was better to decrease the stirring rate after that reactor.

Wider and taller gypsum crystals were obtained in the continuous flow production of boric acid. This

brings advantage to the filtration process because the gypsum crystals obtained in the continuous operation had an easily filterable size. Therefore, using continuous flow stirred slurry reactors for boric acid production was more appropriate compared to the batch production process.

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