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Yazar Mücahit Uğur

Gönderim Tarihi: 31-Tem-2022 09:24PM (UTC+0300)

Gönderim Numarası: 1877254811

Dosya adı: turniitn.docx (290.63K)

Kelime sayısı: 1474

Karakter sayısı: 7769



Investigation of Mg⁺² Ion Behavior in Colemanite Propionic Acid Solutions

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Abstract

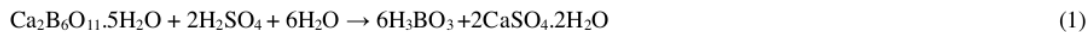
Colemanite ore, one of the most commercially important boron minerals, is used in industry to produce various boron compounds due to its rich B₂O₃ content. Turkey's most important commercially extracted boron ores are colemanite, tincal and ulexite as the second ore. In our country, various boraxes are produced by dissolving boric acid from colemanite by the sulfuric acid process and tincalin is dissolved in hot water, and ulexite is concentrated and exported. The main problem in the production of boric acid by the sulfuric acid process is impurities. One of the impurities is Mg⁺² ions that pass into the solution and it is important to examine the kinetics of this ion in the solution. In this study, the dissolution of colemanite ore in propionic acid solution in an aqueous medium in a batch reactor under atmospheric pressure was investigated. As dissolution parameters; colemanite particle size (D) 100 150, 150-250, 250-400*, 400-600 µm and solid/liquid ratio (K/S) 20 40*-60-80 g/L. As a result of the experiments, the time-dependent variation of the Mg⁺² concentration in the solution was observed.

Keywords: Colemanite, Propionic acid, Mg⁺² impurity, Dissolution

1. Introduction

Boron and boron minerals are one of the most important mines in the world in terms of industry [1]. Boron and boron derivatives are mostly found in the form of natural compounds containing different proportions of boroxide in their structures [2]. It is known that there are about 230 free boron minerals in nature. However, colemanite (Ca₂B₆O₁₁.5H₂O), tincal (Na₂B₄O₇.10H₂O) and ulexite (NaCaB₅O₉.8H₂O) are the leading ones that have commercial importance in the world [3, 4, 5]. Turkey alone has a share of 73% of the world's boron reserves and has colemanite, tincal and ulexite ore reserves, respectively [6, 7, 8]. Boron and boron derivatives are used in nearly 500 sectors from fiberglass and glass industry [9], rubber and paint industry [6], wood protection and agriculture industry, high-quality steel and heat resistant polymers [10], nuclear technology products [1] to rocket engine fuels [11] disinfectants and detergent sector [12].

Boric acid is industrially produced according to the reaction in Equation 1 with colemanite and sulfuric acid solution at 92°C. For 1 mole of colemanite ore, 6 moles of boric acid (H₃BO₃) are produced.



There are scientific studies in the literature on the dissolution of colemanite ore in solutions saturated with organic and inorganic acids or different acidic gases in the production of boron compounds. In the literature, leaching solutions and rate control steps of these dissolution processes are given [6]. Industrially, there are several problems in the production of boric acid from colemanite by the sulfuric acid process. Most of these problems are mainly due to the presence of calcium and magnesium-containing minerals in the colemanite ore. Ca²⁺ and Mg²⁺, which go into solution in acidic environment, form impurities in boric acid and reduce product quality. For this reason, in our study, the effect of grain size and solid/liquid ratio on the dissolution of Mg⁺² ions passing from the colemanite ore to the solution in the presence of propionic acid was investigated.

2. Materials and Methods

The colemanite used in the study was obtained from boron deposits of Eti Mine Works. After the impurities on the ore were cleaned by mechanical means, they were ground with the help of a crusher-grinder, and a chemical

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analysis was carried out. It is divided into 4 sizes with ASTM standard sieves 100-150, 150-250, 250-400, and 400-600 μm . The chemicals used in the study were obtained from various companies with high purity. The chemical analysis of the ore used in the study is given in Table 1.

Table 1. Chemical analyses of the colemanite ore used in the studies

Component	B ₂ O ₃	CaO	H ₂ O	MgO	Humidity
%	35.22	20.25	15.76	2.72	0.73

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X-Ray diffraction (XRD) to determine the phase composition of the raw colemanite ore is given in Figure 1.

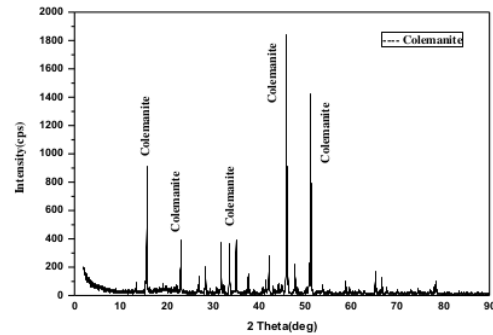


Figure 1. XRD analysis of colemanite

Parameter levels for dissolution were determined as a result of preliminary testing and are given in Table 1. The grain size is in two size ranges. The experimental design plan prepared accordingly is given in Appendix 1. The amount of Mg^{+2} in the solutions taken at certain intervals during the experiment was analyzed with the help of an AAS (Atomic Absorption Spectrophotometer). Table 1. Chemical analyses of the colemanite ore used in the studies.

Table 2. Parameters and levels selected in the investigation of the behavior of Mg^{+2} released into solution in the reaction of colemanite ore with propionic acid in an aqueous solution

	PARAMETERS	LEVELS
A	Grain size, (μm)	100-150, 150-250, 250-400* , 400-600
B	Solid/liquid ratio, (g/L)	20, 40* , 60, 80

*Fixed parameters

The dissolution process is carried out in a batch reactor and the experimental system for the dissolution process is given in Figure 2. Experimental studies were carried out in a 500 mL jacketed glass reactor. The solution is left in the reactor with the solid/liquid ratio determined under the experimental conditions, and it is heated to the desired temperature. Then, a certain amount of colemanite was added and mixed through a mechanical mixer. During the reaction, solutions are taken at certain times and after the volume is completed to a certain amount, the amount of Mg^{+2} is determined.

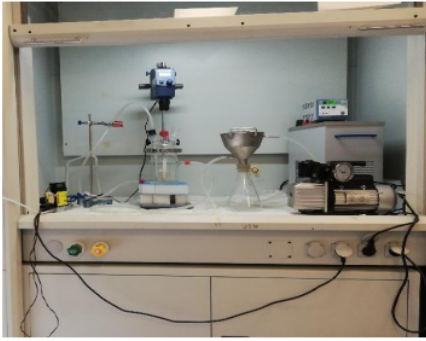
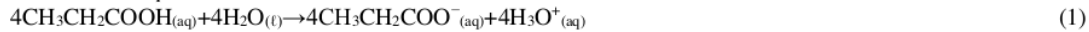


Figure 2. The experimental setup used in our experimental studies

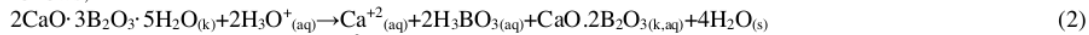
3. Results and Discussion

3.1 Reactions to solutions

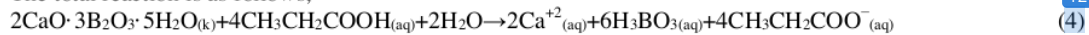
The reaction related to the dissolution of colemanite in the presence of propionic acid in aqueous solution can be written as in Equation 1-4:



The reactions that occur in the environment when colemanite is added to the propionic acid solution are as follows;



The total reaction is as follows;



3.2 Effect of parameters

The behavior of solid-liquid ratio and particle size, Mg^{+2} into solution upon dissolution of colemanite ore in propionic acid solutions in a batch reactor under atmospheric pressure were investigated. Experimental results are plotted as percent dissolution of Mg^{+2} ion behavior versus time.

Effect of particle size

The effect of particle size on the solution penetration rate of Mg^{+2} was investigated at grain sizes of 100-150 μm , 150-250 μm , 250-400 μm and 400-600 μm . During the study, the reaction temperature was 303°K, the acid concentration was 6.75 M, the solid-liquid ratio was 40 g/L, and the stirring speed was kept constant at 400 rpm. The percentages of the dissolution fraction of Mg^{+2} that passed into the solution as a result of the experiment are given in Figure 3. As seen in the time versus percent dissolution graph in Figure 7., there is an inverse relationship between the increase in grain size and the penetration of Mg^{+2} into solution. It is seen that the dissolution rate decreases with increasing grain size.

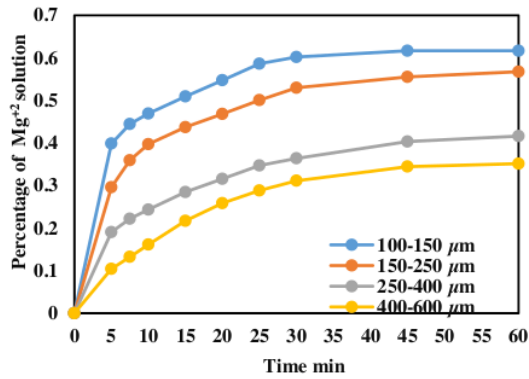


Figure 3. The effect of grain size on the passage of Mg^{+2} into solution in the dissolution of colemanite

Effect of solid-liquid ratio

The effect of solid/liquid ratio on the rate of Mg^{+2} passing into solution was investigated in solid-liquid ratios of 20 g.L-1, 40 g.L-1, 60 g.L-1 and 80 g.L-1. During the study, the reaction temperature was 303°K, the acid concentration was 6.75 M, the particle size was 250-400 μm , and the stirring speed was kept constant at 400 rpm. The percentages of the dissolution fraction of Mg^{+2} , which passed into the solution as a result of the experiment, are given in Figure 2. As seen in the time versus percent dissolution graph in Figure 4., there is an inverse relationship between the increase in the solid/liquid ratio and the passage of Mg^{+2} into solution. It is seen that the dissolution rate decreases with the increase in the solid-liquid ratio.

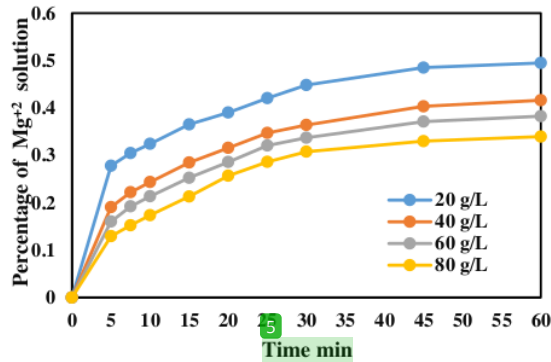


Figure 4. The effect of solid-liquid ratio on the transition of Mg^{+2} to solution in the dissolution of colemanite.

4. Results

This study aims to investigate the Mg^{+2} ion behavior of colemanite in propionic acid solution in a batch reactor at atmospheric pressure and to determine an alternative reactant for boric acid production.

- ✓ It is seen that there is an inverse relationship between the increase in solid-liquid ratio and the particle size of the colemanite ore, and the rate of Mg^{+2} ion passing into the solution.
- ✓ It was determined that propionic acid, which has weak acidic properties, can dissolve colemanite ore for boric acid production.

Appendix

Table 1 Experimental plan

Experiment No	Sabit Parametreler	Particle size (μm)	Solid/fluid ratio (g/L)
1	303 K	100-150	40
2	6,75 M	150-250	40
3	400 rpm	250-400	40
4	40 g/L	400-600	40
5	303 K	250-400	20
6	6,75 M	250-400	60
7	400 rpm 250-400 μm	250-400	80

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