

EXTRACTION OF BORIC ACID FROM ULEXITE MINERAL BY SUPERCRITICAL CO₂

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ABSTRACT

Supercritical CO₂ is an important solvent which was used in the extraction of boric acid from ulexite mineral. Heterogeneous reaction between ulexite and CO₂ was studied in the presence of water at various CO₂ pressures (50-90 bar). Supercritical conditions enhanced the extraction efficiency of boric acid from ulexite mineral. A 88.7% boric acid extraction efficiency was obtained at 70 °C, 90 bar and for 2 h of reaction time. FTIR, XRD, TGA and SEM were used in the characterization of products. A powder crystallized from filtrate of reaction was determined as H₃BO₃ and filter cake formed at the end of reaction was determined as CaCO₃ according to the XRD analysis. CO₂ was utilized as a raw material in the extraction of boric acid from ulexite mineral and it was successfully converted into a stable form that may help to decrease the amount of CO₂ released to atmosphere. CO₂ binding capacity of ulexite mineral was determined as 123 g CO₂/kg ulexite mineral.

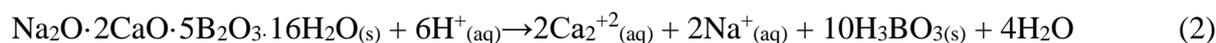
INTRODUCTION

Boron is an element possessing the ability to form a large number of complex chemical compounds. The utilization of boron compounds has substantially increased recently, in the nuclear technology, rocket engines, the production of heat-resistant materials such as refractories and ceramics, high quality steel, heat-resistant polymers, catalysts due to increasing demand for these compounds [1]. Boron compounds present in nature in the form of metal borates, generally salt of sodium, calcium, sodium-calcium and magnesium borates [2]. Although there are more than 200 boron minerals known in the world, only calcium borates and sodium borates have commercial importance and they consist of about 90% of the existing boron reserves in the world [3].

Turkey has the 72% of boron reserves in the world. Ulexite, Na₂O·2CaO·5B₂O₃·16H₂O, is one of the most common boron minerals and it is abundant in Turkey. It has a triclinic crystal system, usually in rounded masses of fine, transparent, white fibrous crystals (cotton balls) and parallel fibrous aggregates. Boric acid is commercially important boron compound which is produced from boron minerals like colemanite, borax and ulexite. Boric acid is used as a raw material in the preparation of different boron compounds, including synthetic borate salts, boron phosphates, fluoroborates, boron tri-halides and borate esters [4, 5]. The commercial production of boric acid is performed by the reaction of boron mineral and inorganic acid. Sulfuric acid, nitric acid and hydrochloric acid are mainly studied acids in this production [6]. In Europe, boric acid is industrially produced from the reaction of colemanite with sulfuric acid at ~90 °C (Eq. 1) [7].



Supercritical fluid extraction, precipitation, crystallization, washing, filtration, and drying operations are generally used for boric acid production [7 8, 9]. In equation 1, gypsum is formed as a by-product and precipitates in the reactor, while boric acid, which is highly soluble in water, remains in the liquid phase throughout the reaction. Gypsum is removed by filtration, and boric acid remained in the gypsum, is washed and filtered. Boric acid dissolved in aqueous phase is crystallized by cooling at about 40 °C [10, 11]. In the northwest part of Argentina, boric acid is produced by leaching low-grade ulexite with sulfuric or hydrochloric acid as shown in Eqn. 2 [12].



Boric acid is produced by solid-liquid reaction of ulexite and sulfuric acid in which mineral structure is digested by proton and liberated B₂O₃ forms boric acid in aqueous phase. The process consists of filtration, crystallization steps. Gypsum is also formed as a by-product and precipitates in the reactor. Anhydrous sodium sulfate is obtained as a by-product using a fractional crystallization process: vacuum crystallization for boric acid and evaporative crystallization for sodium sulfate.

There are many studies performed on ulexite leaching. Dissolution kinetics of ulexite was determined in acetic acid medium using a batch reactor. The dissolution rate increases with rising the solution temperature and acid concentration, and with decreasing solid/liquid ratio and particle size. The dissolution kinetics is compatible with a shrinking core model with the surface chemical reaction as a rate-controlling step. It was reported that the activation energy of the dissolution reaction was as 55.8 kJ/mol [5]. Optimum conditions for the dissolution of ulexite in citric acid solutions were determined as 80 °C for the leaching temperature, 5% (w/v) for the solid/liquid ratio, 0.4 M for the citric acid concentration, 15 min. for leaching time. Under these conditions, the dissolution of B₂O₃ was found to be as 97.28% [13]. It is difficult to separate the boric acid from other by-products in the mother solution obtained at the end of ulexite dissolution reaction. Since solubility of boric acid and other by-products are close to each other, they cannot be separated based on solubility difference. Boric acid separation may be possible by solvent extraction with methanol [14].

The aim of this study is to investigate the extraction of boric acid from ulexite mineral using carbon dioxide at different conditions such as temperature, pressure and reaction time. The solid by-products formed at the end of reaction and powder that crystallized from filtrate solution were characterized by FTIR, XRD, TGA and SEM analyses. B₂O₃% contents of solid phase remained/formed at the end of reaction and filtrate were determined by volumetric analyses.

MATERIAL AND METHODS

Ulexite mineral obtained from Eti Maden Inc. was used in all experiments. First of all, B₂O₃% and moisture content %(wt) of this mineral were determined analytically. About 10 kg of mineral was prepared as feedstock by grinding and sieving. CO₂ obtained from HABAŞ (99.8% vol.) was used to extract boric acid from ulexite. Autoclave reactor having 0.2 dm³ volume was used in all runs where it was placed into water bath heated and stirred by magnetic mixer (Wise Stir MSH-20D). Vacuum pump (Rocker 300) and filtration system was utilized to filtrate a mother liquor solution at the end of reaction. Amount of boric acid formed at the end of reaction was determined by volumetric titration. NaOH (weight %99 Merck), glycerin (C₃H₈O₃, weight %99,9 Merck), phenolphthalein (C₂₀H₁₄O₄) and potassium hydrogen phthalate (C₈H₄KO₄, weight %99,5 Merck) were used in all volumetric titrations.

Firstly, 10 g of ulexite mineral (-45 µm), corresponding amounts of H₂O according to solid liquid ratio of 0.1, calculated amount of solid CO₂ for desired pressure were added into

autoclave reactor. After that, autoclave reactor was put on water bath. The experimental setup is shown in Figure 1. The expected reaction is given in Eqn. 3.

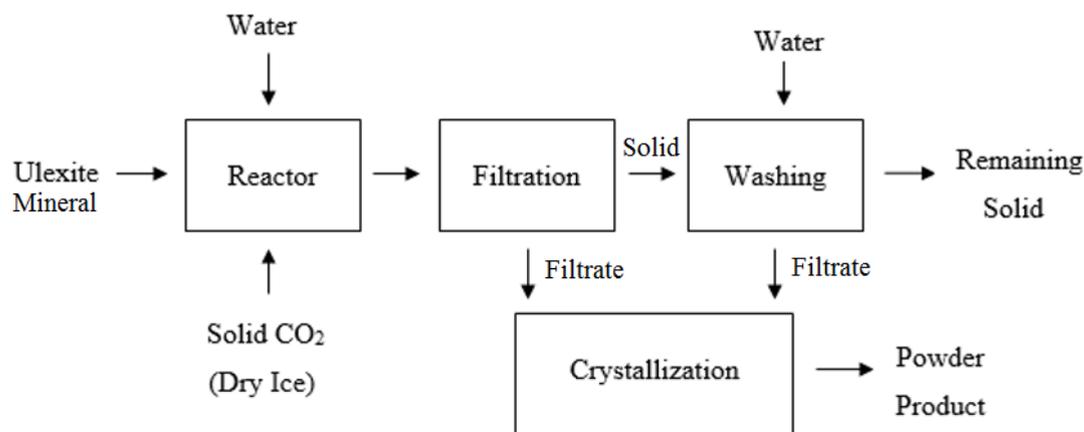


Figure 1. Flowsheet of experimental setup

CO₂ pressure in autoclave, reaction temperature and reaction time were investigated in this study. 0.1 of solid/liquid ratio, 45 μm of particle size and 300 rpm of mixing rate were kept constant in order to determine effects of other parameters. After the reaction completed, reaction medium was filtered to separate liquid and solid phases. Then, filtrate cake was washed by distilled water several times to remove boric acid in solid phase. Filter cake was put in drying oven which was at 105 °C to remove moisture. A mother liquor solution was titrated by 0.5 M NaOH solution to determine amount of boric acid in the solution. Then, mother liquor solution was evaporated to obtain crystallized powder. Characterization of ulexite mineral, filter cake and crystallized powder from a mother liquor solution were done using FTIR, XRD, TGA and SEM.

RESULTS AND DISCUSSIONS

Experimental parameters conducted for extraction of boric acid from ulexite mineral is shown in Table 1. The effects of pressure, temperature and reaction time on boric acid extraction were investigated. The highest extraction yield was found to be 88.7% at the temperature of 70 °C, 90 bar pressure and for 2h of reaction time (run 14 in Table 1). Supercritical CO₂ condition has significantly affected extraction yield as understood from the comparison of yields at different CO₂ pressures. The reason behind this is the removal of mass transfer limitations between CO₂–ulexite [16]. According to runs 6, 15 and 9, 13 in Table 1, when the reaction time is increased from 1h to 3h, the extraction yield is increased from 73.7% to 83.3% (at 70 bar, 70 °C). Moreover, when the reaction time is increased from 1h to 3h, the extraction yield increases from 39.4% to 59.1% (at 70 bar, 30 °C). According to runs 6, 13 and 9, 15 in Table 1, when the temperature is decreased from 70 to 30, the extraction yield is decreased from 73.7% to 39.4% (at 70 bar, 1 hour). In addition, when temperature is decreased from 70 °C to 30 °C, the extraction yield is decreased from 83.3% to 59.1% (at 70 bar, 3 hour). According to runs 10, 12 and 2, 3 in Table 1, when the pressure is increased from 50 to 90 bar, the extraction yield is increased from 45.0% to 71.3% (at 50 °C, 1 hour). When the pressure is increased from 50 to 90 bar, the extraction yield is increased from 71.7% to 81.6% (at 50 °C, 3 hour). Therefore, it can be said that increasing CO₂ pressure in the reactor, temperature and reaction time

significantly risen the extraction efficiency because of higher interactions of the molecules in the reaction medium.

Table 1. Experimental conditions for ulexite-CO₂ reaction

Runs	Temperature (°C)	Pressure (bar)	Time (hour)	Yield (%)
1	50	70	2	67.5
2	50	50	3	71.7
3	50	90	3	81.6
4	50	70	2	68.8
5	30	90	2	65.5
6	70	70	1	73.7
7	50	70	2	68.2
8	70	50	2	72.3
9	30	70	3	59.1
10	50	50	1	45.0
11	30	50	2	40.2
12	50	90	1	71.3
13	30	70	1	39.4
14	70	90	2	88.7
15	70	70	3	83.3

FTIR Analysis: The FTIR spectra of powder crystallized from filtrate and of solid phase remained at the end of reaction as filter-cake were shown in Fig. 2a and Fig. 2b, respectively. As it can be seen in Fig 2a., the peaks at between 3363-3196 cm⁻¹, 1430-1355 cm⁻¹, 779-669 cm⁻¹ represent O–H, B–O, O–H vibrations, respectively. The characteristic stretching vibration of O–H were between 3500 and 3200 cm⁻¹, characteristic peaks of B–O bond were between 1430 and 1355 cm⁻¹, and surface curvature of O–H was between 769 and 659 cm⁻¹ as depicted by the FTIR spectrum of boric acid in the literature and the peaks of pure boric acid coincide with its peaks in powder crystallized from filtrate (Fig. 2a and 2b) [15]. It can be said that the powder crystallized from filtrate was boric acid as peaks on its IR spectrum are consistent with the literature. However, the other peaks observed on Fig. 2a represent the presence of sodium borate that formed in the reaction medium [16]. Separation of boric acid from this mixture requires advanced methods as by-products either sodium borate or sodium carbonate are soluble in water, as well.

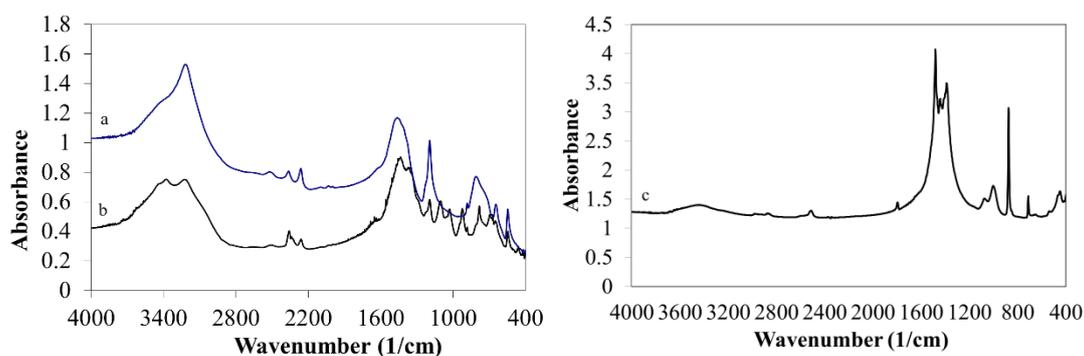


Figure 2. The FTIR spectra of a)- pure boric acid, b)- powder crystallized from filtrate and c)- of filter-cake.

FTIR spectrum of filter-cake obtained at the end of reaction between ulexite and CO_2 is shown in Fig. 2c. Main peaks at 710 , 874 and 1480 cm^{-1} were related to the in-plane bending vibrations of carbonate anion. The peak at 1790 cm^{-1} was attributed to $\text{C}=\text{O}$ stretching vibration. Peaks located at 713 , 875 and 1444 cm^{-1} were attributed to in-plane bending vibration, out of plane bending vibration, symmetric and the asymmetric stretching vibrations of CO_3^{2-} , respectively. The band located at 1787 cm^{-1} was assigned to the combination vibrations of $\text{C}=\text{O}$ stretching [17]. It can be seen that filter cake obtained in this study is consistent with the FTIR spectrum of calcite and the extra bands at 1372 - 1498 cm^{-1} may be resulted from impurities like MgCO_3 in ulexite mineral.

XRD Analysis: XRD patterns of the solid sample crystallized from mother liquor and filter cake remained at the end of reaction are given in Fig. 3a and Fig. 3b, respectively. Both XRD patterns were recorded at 2θ range of 5° - 80° . The peaks at 2θ value of 14.55° and 27.96° on Fig. 3a correspond to characteristics peaks of boric acid reported by JCPDS, 30-0199. The main peak at 2θ value of 29.52° on Fig. 3b corresponds to characteristics peak of calcium carbonate reported by JCPDS 5-0586.

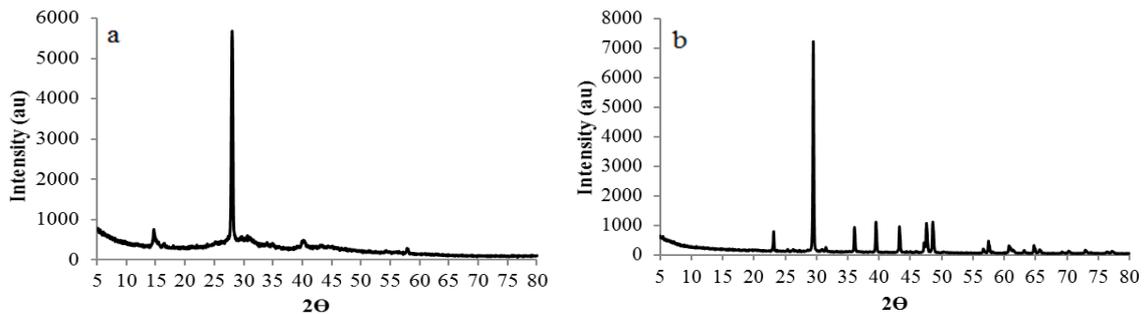


Figure 3. X-ray diffraction diagram of a)- powder crystallized from filtrate and b)- filter-cake.

Boric acid was extracted from ulexite mineral by supercritical carbon dioxide. Main peaks of the solid powder crystallized from mother liquor and the filter cake are similar to those peaks found in the literature [18].

SEM Analysis: The morphological structures of the solid powder and filter cake were determined by SEM and their SEM microphotographs are shown in Fig. 4a and Fig. 4b, respectively. As it can be seen in Fig. 4a, solid powder crystallized display a smooth surface. According to SEM image, it can be said that solid particles formed from the reaction of ulexite and carbon dioxide has spherical morphology and they are uniformly dispersed. The particle size changes between 2 and 5 micron. Those smaller particles tend to agglomerate due to their surface energies (Fig. 4b).

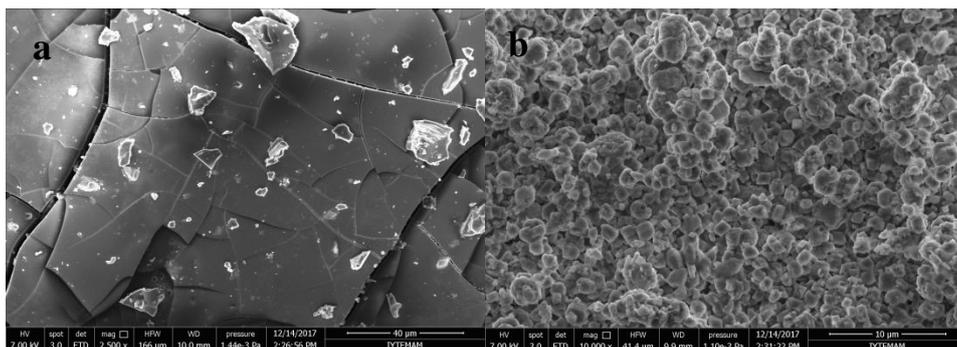


Figure 4. SEM images of a)- powder crystallized from filtrate and b)- of filter-cake.

TGA Analysis: Figure 5a and 5b show TG curves of solid powder crystallized from a mother liquor solution and filter cake, respectively. Thermograms were recorded in the temperature range of 30-1000 °C. The powder crystallized from filtrate is subjected to degradation at 100-650 °C and the mass loss is approximately 26%. The mass loss of boric acid was determined as 43.68% at a range of 20-600 °C [19]. The loss of mass in the TG curve on Fig. 5a is lower than the theoretical mass loss of boric acid, indicating that some of the boric acid reacted with sodium cations to produce sodium borate that is present in the solid powder.

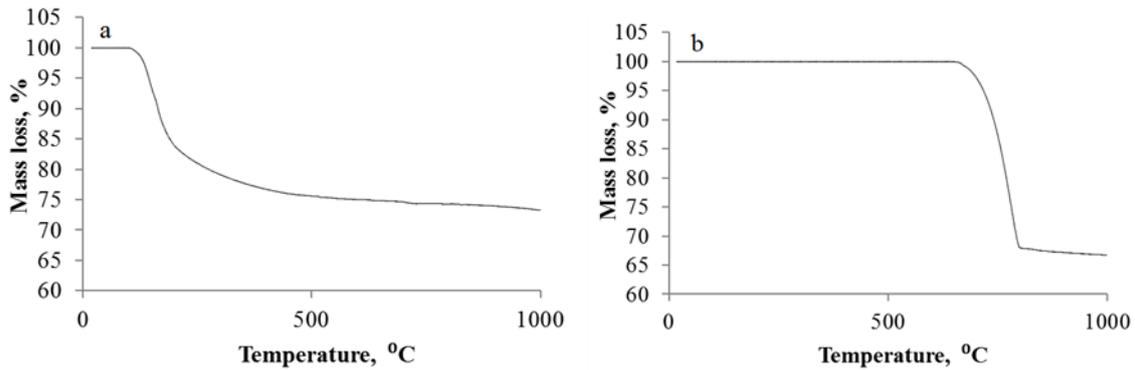


Figure 5. TGA curves of a)- powder crystallized from filtrate and b)- of filter-cake.

The filter cake is subjected to degradation at 550-800 °C and the mass loss is approximately 35%. The mass loss of pure calcium carbonate was determined as 43.8% at a range of 600-850 °C [20]. The mass loss of filter cake is less than the theoretical mass loss of pure calcium carbonate. The reason for this fact is that mineral includes some impurities like quartz and silicates. According to XRF results of ulexite mineral provided by Eti Maden Inc., ulexite mineral includes impurities which include $MgCO_3$, $CaCO_3$ and SiO_2 [21]. The mass loss calculated from the TGA curve includes the $CaCO_3$ formed from the CO_2 -sequestration of CaO in ulexite structure and the decomposition of initial carbonates of $CaCO_3$ and $MgCO_3$. The CO_2 binding capacity of ulexite was calculated as 123 g CO_2 /kg ulexite mineral.

CONCLUSION

The extraction of boric acid from the ulexite mineral by supercritical CO_2 has been successfully performed. Filter cake and the powder crystallized from the filtrate were characterized as calcium carbonate and boric acid, respectively, according to the XRD, FTIR and TEM analyses. Due to the water-insolubility of calcium carbonate, boric acid is easily separated from the formed calcium carbonate by filtration. It was determined that boric acid is present in the composition of solid powder obtained from a mother liquor solution according to XRD and FTIR analysis. The extraction yield was found to be 88.7% at the optimum conditions of at 70 °C, 90 bar and 2 extraction time. The CO_2 binding capacity of ulexite was determined as 123 g CO_2 /kg ulexite mineral. At the same time, the use of CO_2 in this process makes it environmentally friendly as it is converted into a stable carbonate form. Formation of soluble carbonate salts might be a problem in separation of boric acid. Further studies are necessary for the solution of this problem.

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