



Extraction of boric acid from colemanite mineral by supercritical carbon dioxide



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ABSTRACT

The use of H₂SO₄ in boric acid production from colemanite mineral has several problems, related to product impurities, corrosion and environmental discharge limits. To overcome these problems and to increase extraction efficiency of boric acid, heterogeneous reaction between colemanite and CO₂ dissolved in H₂O was studied at and above supercritical CO₂ conditions. Supercritical conditions enhanced the extraction efficiency of boric acid from colemanite mineral, with 96.9% boric acid extraction efficiency being obtained from CO₂-colemanite reaction at 60 °C, for 2 h of reaction time for particles in the range of +20–40 μm. A powder crystallized from filtrate of reaction was determined as H₃BO₃ and the solid formed at the end of reaction was characterized mostly as CaCO₃ according to FTIR, XRD, TGA and SEM analyses. The use of supercritical CO₂ as a leaching agent in colemanite does not only produce boric acid but also helps to reduce the amount of CO₂ in the atmosphere. Based on these facts, supercritical CO₂ as extractant makes this process green and sustainable for recovering boric acid from boron minerals.

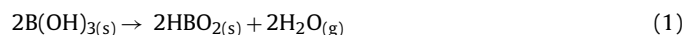
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1. Introduction

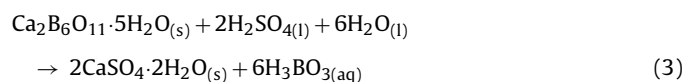
Boric acid (H₃BO₃) is an important boron chemical which can be produced from different boron minerals, such as colemanite (calcium borate), tincal, kernite (sodium borates), ulexite (sodium and calcium borate) and ascharite (magnesium borate). Although there are more than 200 boron compounds defined in the world, only calcium borates and sodium borates are commercially important and they form 90% of existing reserves [1]. Eti Maden Works (Turkey), which is the second largest producer in the world, produces boric acid from either tincal or colemanite feed stocks. Since the colemanite reserves are greater than the other boron minerals in Turkey, boric acid is mostly produced from colemanite mineral.

Boric acid has been widely used in the production of different boron compounds namely, zinc borate, borate esters, boron carbide, and boron nitride. Boric acid is also found in a small percent as a sassolite mineral in nature. Its normal melting point is 170 °C, however when heated slowly it is converted into metaboric acid (HBO₂) by losing water in the range of 100–130 °C. It turns into diboron trioxide as a result of heating to temperatures higher than

in 160 °C [2]. Decomposition reactions of boric acid are shown in Eqs. (1) and (2):



Conventional boric acid production from colemanite ore consists of the following steps: crushing and milling of colemanite ore, dissolution of boric acid in aqueous phase by reaction of colemanite with sulfuric acid, crystallization and filtration of by-product, calcium sulfate (CaSO₄·2H₂O), and crystallization and filtration of boric acid [3]. The reaction between colemanite and sulfuric acid is given in Eq. (3). It is carried out at 90–98 °C, for period of 3–3.5 h under atmospheric pressure.

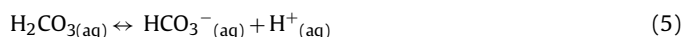


In the production of boric acid from boron mineral, there are many issues related with the environment, these are an increasing amount of solid by-products with higher boron content, consumption of large quantities of water, and presence of impurities like MgSO₄ in the product. On the other hand, since concentrated sulfuric acid is used in the process, corrosion problems occur, especially for equipment used in the reactor. To find a solution to the above problems, different organic and inorganic acids were studied for the

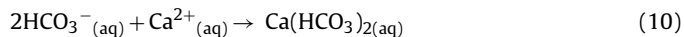
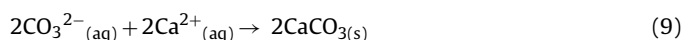
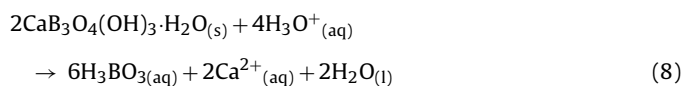
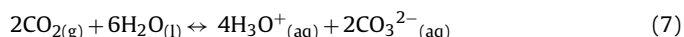
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dissolution of boron minerals. For instance, leaching kinetics of tinal using oxalic acid [4]; dissolution kinetics of colemanite in oxalic acid [5]; extraction of boric acid from colemanite ore by nitric acid solution [6]; dissolution kinetics of ulexite in acetic acid solution [7] were investigated. However none of these methods have been able to replace the sulfuric acid commercially since there are difficulties in the separation of by-products from the mother solution when those acids were used and most of them were not cheap enough to be used in large quantities and they have a very low dissolution rate. On the other hand, the use ultrasound in solid–liquid heterogeneous reaction of colemanite and sulfuric acid was also studied [8]. Although ultrasonic treatment enhances the dissolution of colemanite, commercialization of this method on a large scale seems to be difficult. At present H_2SO_4 is the most widely used mineral acid industrially for producing boric acid from boron ores which forms a significant amount of boron-containing solid and liquid wastes.

The presence of arsenic in colemanite mineral creates another problem in boric acid production [9,10]. Sodium sulfide, hydrogen sulfide and ammonia have been used to precipitate arsenic, iron and aluminum impurities in the solution. Since boron level in both water and soil is critically important for plants and living organisms, boron content of the side streams from production facility must be monitored and controlled [11]. Instead of treating solid and liquid waste streams from production side, novel techniques must be investigated to find a solution to the problems at their source. For this purpose, the use CO_2 and SO_2 gases dissolved in aqueous solution at atmospheric pressure has been studied for extracting boric acid from colemanite mineral to find alternative ways [12]. Carbon dioxide dissolves in water by forming carbonic acid according to Eq. (4). The formed carbonic acid produces proton (Eq. (5)) that is used in acid leaching of the mineral. The formed bicarbonate anion further dissociates into carbonate ion and H^+ as shown in Eq. (6).



The solubility of CO_2 in water can be raised by increasing pressure and decreasing the temperature. But temperature should not be below the critical temperature of CO_2 (31.1 °C). At 10 MPa and 35 °C, the solubility value of CO_2 in water was reported as 29.13 cm^3 at standard temperature and pressure (STP)/g H_2O [13]. The pH of the aqueous solution is also related to the amount of CO_2 dissolved in aqueous phase. The hydronium ion (H_3O^+) formed when CO_2 dissolved in water (Eq. (7)) attacks to the colemanite structure according to the reaction in Eq. (8), and Ca^{2+} cation is formed. The Ca^{2+} cations and carbonate anions react to produce calcium carbonate in Eq. (9). Apart from those reactions, calcium bicarbonate may be produced from reaction of calcium and bicarbonate ions as shown in Eq. (10).



At this point, supercritical fluids or supercritical conditions may provide alternative solutions. Supercritical fluids (SCF) have been widely used for the last few decades in the synthesis of novel

Table 1

Chemical composition of colemanite mineral, product and by-product.

Oxide formula	Theoretical composition, %	Colemanite by XRF, % (w/w)
B_2O_3	50.8	43.4 ^a
CaO	27.3	19.3
SiO_2	–	5.9
MgO	–	3.0
Al_2O_3	–	1.4
SrO	–	0.9
Na_2O	–	0.7
K_2O	–	0.6
As_2O_3	–	0.5
Fe_2O_3	–	0.5
Others	–	0.4

^a Determined by analytical titration.

materials. The use of SCF processes has been increasing as the environmental and food regulations become more and more important for human being. The most important feature of supercritical fluid is that its properties can be adjusted from gas to liquid with small variations in pressure and temperature [14,15]. Design of inorganic materials using supercritical fluid methods is accomplished through two distinctive processes. In the first one, the driving force for particle formation is a physical transformation of matter by a rapid depressurization or antisolvent effect. The detailed information about these processes can be found in literature. In the second group of processes, supercritical fluids are used as a reaction media to synthesize a number of different materials, such as oxides, metals, or semiconductors [14]. It is expected that the reaction between CO_2 and colemanite in the aqueous phase would be enhanced at supercritical conditions of CO_2 .

The aim of this study is to use environmentally friendly solvent, supercritical CO_2 , for extracting boric acid from colemanite mineral and to determine the optimum parameters for boric acid production at supercritical CO_2 conditions. The solid by-product formed at the end of reaction and powder crystallized from filtrate of reaction were characterized by FTIR, XRD, TGA and SEM analyses. B_2O_3 contents of solid phase remained/formed at the end of reaction and filtrate were determined by volumetric analyses.

2. Experimental

2.1. Materials

Colemanite used in this study was obtained from the Bigadiç-Balıkesir plant of Eti Maden Works in Turkey. Carbon dioxide, CO_2 (99.9% v/v, Habaş) was used for the experiments at supercritical conditions. Sodium hydroxide, NaOH (99.0% w/w Merck), glycerol, $C_3H_8O_3$ (99.0% w/w, Dalan Chemical Industry) and phenolphthalein ($C_{20}H_{14}O_4$, Merck) and methyl red ($C_{15}H_{15}N_3O_2$, Merck) indicators, sulfuric acid, H_2SO_4 (96% w/w, Merck), sodium carbonate, Na_2CO_3 (99%, w/w, Merck) were used in the analytical determination of B_2O_3 content of aqueous phase and initial raw colemanite mineral. The factor value of NaOH solution was determined by using a potassium hydrogen phthalate (KHP) $C_8H_4KO_4$ (99.5% w/w, Merck), which is not affected by the humidity in air during weighing. So a solution prepared by KHP can be used to determine the precision of the NaOH solution in the titration procedure. Potassium bromide, KBr (99.9% w/w, Merck) was used in the preparation of pellets in IR analyses. $CaCO_3$ (99.0% w/w, Merck) was used as reference material in IR analyses.

2.2. Raw material characterization and analysis of B_2O_3

Chemical analysis of colemanite mineral (Table 1) was performed by using X-ray fluorescence (XRF) spectrometer (Spectro

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