

Extraction of boric acid from tincal mineral by supercritical ethanol



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ABSTRACT

In this study, extraction of boric acid from tincal mineral and borax by ethanol was investigated at supercritical and subcritical ethanol conditions. Experiments were carried out in a high pressure stainless steel reactor having volume of 0.1 dm³ under a mixing rate of 800 rpm. Solid/liquid ratio of 0.05 and 0.075; three different particle sizes were used between 20–63 microns. Tincal mineral decomposed at high temperature and the liberated boric acid reacted with ethanol to form volatile tri-ethylborate. Characterization of the powder crystallized from the ethanol phase and the remaining powder in the reactor was carried out by FTIR, XRD and TGA and have revealed that boric acid was extracted from tincal mineral by an esterification reaction. The maximum boric acid extraction efficiency was determined as 32.6 wt% at 250 °C and particle size of –20 μm for the solid/liquid ratio of 0.05 g/cm³ from tincal mineral.

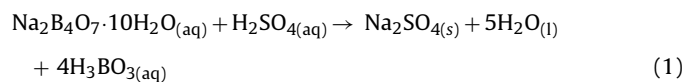
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1. Introduction

Boron exists in the form of borate salts in nature. Most of the boron reserves in the world are located in the western part of Turkey. Boric acid (H₃BO₃) is an important boron based chemical which can be produced from different boron minerals such as colemanite, tincal, kernite, ulexite or from the brines having dissolved boron salts. Although there are more than 200 boron compounds explored in the world, only calcium borates and sodium borates have commercial importance and together they form 90% of the existing boron reserves [1]. The state owned Eti Maden Inc. from Turkey is the second largest producer of boron minerals in the world. Boric acid is mainly produced from the colemanite mineral as it composes 70% of the boron reserves in Turkey. There are also studies for utilizing other minerals, such as ulexite and tincal for boric acid production. Boric acid has been widely used in the production of different boron compounds namely, zinc borate, borate esters, boron carbide, boron nitrite etc. Boric acid is also found naturally as sassolite mineral. The melting point of boric acid is 170 °C, however when heated slowly it is converted into metaboric acid (HBO₂) due the loss of a water molecule between 100 and 130 °C. The water is formed by condensation of hydroxyl groups in the structure. Diboron trioxide (B₂O₃) is obtained as a result of heating to temperatures exceeding 160 °C [2]. However, it was reported that boric acid may sublime from its solid state [3] or vaporize

from its aqueous solutions [4]. Sublimation of solid boric acid in the range of 20–100 °C was studied by Attina and her co-workers. Its vapor pressure was measured at 20 °C and 80 °C as 1 × 10⁻⁷ and 3 × 10⁻⁵ Torr, respectively. It was found that the remaining product after evaporation was mainly undecomposed H₃BO₃, since its surface was coated by HBO₂ preventing further decomposition [5]. The sublimation and volatilization of boric acid from its solid state or its aqueous solutions must be taken into account during its production, especially during the crystallization and drying of boric acid which involves the thermal treatment of the product, and thus can result in the loss of boric acid.

Although boric acid is mainly produced from colemanite mineral using sulfuric acid, there are also some studies for the production of boric acid from other abundant boron minerals, e.g., tincal and ulexite [6,7]. Since tincal mineral contains soluble borax and insoluble impurities, it is firstly treated to separate those impurities by dissolving it in hot water. After this separation step, it reacts with sulfuric acid to produce boric acid as main product and sodium sulfate as by-product. The reaction is carried out at 90 °C for ½ h as pointed out in Eq. (1) [8].



In those methods, there were problems reported regarding environmental regulations such as increasing amounts of solid by-product, sodium sulfate; large amounts of discharge water having boron content above the acceptable limits, and corrosion problem

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inside the reactor. In order to solve these aforementioned problems, different organic and inorganic acids were investigated for the dissolution of boron minerals in the literature. For instance, leaching kinetics of tincal mineral using oxalic acid [9]; dissolution kinetics of ulexite in acetic acid solution [7] were studied. None of them were able to replace sulfuric acid in a commercial application since there are difficulties in separating by-products from the mother liquor. Most acids suggested are not practical from an economic standpoint. In industry, H_2SO_4 is the most widely used acid for producing boric acid from boron minerals.

During the production of borax from tincal in Turkey, 400,000 tons of solid waste are generated each year [10]. The composition of that waste was reported as 19.44% B_2O_3 ; 16.85% CaO ; 13.01% MgO ; 9.82% SiO_2 ; 10.3% Na_2O ; 1.30% Al_2O_3 ; 1.49% Fe_2O_3 and the rest was ignition loss by weight. Since the boron level in both water and solid is critically important for plants and other living species, boron content of side streams from production plants must be monitored and controlled. While the European Union (EU) has decided that the maximum boron level is set as 1 mg/dm^3 ; World Health Organization (WHO) has determined that the critical level of boron in drinking water is set as 0.5 mg/dm^3 [11]. Instead of treating solid and liquid waste streams from the production facility, novel techniques must be investigated to find a solution to problems at their source.

Supercritical fluids (SCF) have been used for producing novel materials or to provide alternatives to conventional processes. The use of SCF processes have been increasing as environmental regulations have become more important for the well-being of human life. The most important feature of supercritical fluid is that its properties can be adjusted from a gas to a liquid state by varying pressure and temperature [12,13]. Design of inorganic materials using supercritical fluids is accomplished through two main approaches. In the first one, the driving force for particle formation is a physical transformation of matter by a rapid depressurization and/or anti-solvent effect. The detailed information about these techniques can be found in the literature [14,15]. In the latter, supercritical fluids are used as a reaction media to synthesize a number of different materials, such as oxides, metals, semiconductors etc.[13].

Supercritical ethanol was used for drying of borate salts to obtain nano sized products [16]. It was reported that zinc borate with particle size of 20–50 nm was obtained by supercritical ethanol (SCE) drying and the final product has decreased the friction coefficient of base oil. Zinc borates of $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ and $\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ were dried by supercritical ethanol drying process to investigate the interaction between zinc borates and ethanol at the supercritical conditions of ethanol [17]. While zinc borate of $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ was partially decomposed and lost its water, zinc borate of $\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ has decomposed completely into zinc oxide (ZnO) and boric acid with SCE drying. It was anticipated that critical temperature and pressure of ethanol play an important role in the decomposition of zinc borates. Two major decomposition products were obtained in SCE drying: a powder product, mainly consisted of ZnO remaining in the reactor, and the ethanol solution rich in boric acid. Since it was demonstrated that boric acid can be extracted from zinc borates using supercritical ethanol, it was hypothesized that supercritical ethanol may also be a suitable solvent for the extraction of boric acid from sodium borates, such as tincal.

Therefore, the major objective of this study is to use ethanol for extracting boric acid from tincal mineral at supercritical and sub-critical conditions and to investigate the interactions between boric acid and ethanol during the extraction process. For this purpose, tincal mineral was used in the extraction; the powder remained in the extractor and the materials dissolved in the ethanol phase were characterized by advanced analytical techniques.

2. Experimental

2.1. Materials

Tincal mineral and borax used in this study were obtained from Eti Maden Works Inc. in Turkey. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) with purity of 99.8% (v/v) (Sigma-Aldrich) was used in the extraction experiments. Sodium hydroxide, NaOH, 99.0% (w/w) (Merck), glycerol 99.5%, (v/v), Dalan Chemical Inc. and phenolphthalein ($\text{C}_{20}\text{H}_{14}\text{O}_4$, Merck) as indicator were used in the volumetric determination of boric acid. Potassium bromide, KBr, 99.99%, (w/w) (Merck), was used to prepare pellets in IR analysis. NaOH solution (0.5 M) was adjusted by using potassium hydrogen phthalate, $\text{C}_8\text{H}_4\text{KO}_4$ 99.5%, (w/w) (Merck). The water content in the ethanol phase after supercritical ethanol extraction of borax was determined using $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ 98.0% (w/w) (Sigma-Aldrich) in UV spectrometer.

2.2. Methods

Tincal mineral was milled and sieved by using sieves with 20, 40, 63 μm sizes. The extraction system consists of a high temperature and pressure reactor (PARR 5513), an expansion vessel, a temperature controller (PARR 4848), a nitrogen cylinder and a circulating cooling bath (PolyScience 9606). The experimental setup is shown in Fig. 1.

Experiments were carried out in the high temperature and high pressure reactor having 0.1 dm^3 volume. Different solid/liquid (S/L) ratios of 0.05 and 0.075 g/cm^3 at atmospheric pressure and at ambient temperature were used in the experiments as shown in Table 1. Before heating the reactor, nitrogen gas was passed through the system to remove any remaining oxygen in the reactor and pipelines. In the experiments, tincal-ethanol mixture was heated to the predetermined temperatures and to the corresponding pressures under a mixing rate of 800 rpm for different extraction times. When the reactor achieved the desired pressure, it was kept under these conditions for the predetermined extraction time, and then mixing was stopped and the mixture was transferred into the expansion vessel at the intervals of 10 atm. by opening the valve between them and keeping the reactor temperature constant during the transfer. When the pressure in the reactor decreased to the atmospheric pressure, the system was again purged with N_2 gas. A 0.010 dm^3 of the ethanol phase in the expansion vessel was transferred to a petri-dish and dried at room temperature in a fume hood. To see the effects of impurities in the tincal mineral, borax was used in the ethanol extraction, as well. H_2O content of the ethanol phase after extraction was determined by using UV analysis.

2.3. Characterization

Chemical analysis of tincal mineral (except B_2O_3) was performed by using a X-ray fluorescence (XRF) spectrometer (Spectro

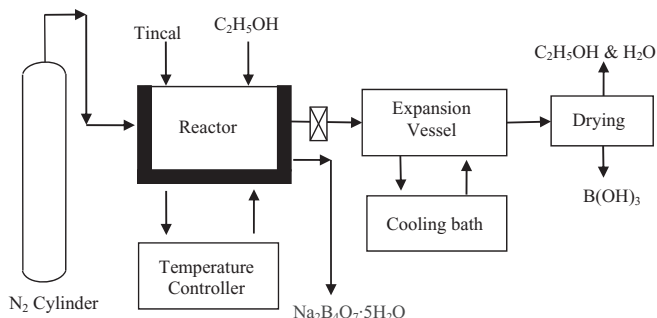


Fig. 1. Experimental setup.

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