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Usage of acetic acid for boric acid production from boron wastes

Bor atıklarından borik asit üretiminde asetik asidin kullanımı

Emine Yoğurtcuoğlu[1,*],

[1] Niğde Ömer Halisdemir University, Mining Engineering Department, 51240, Niğde, Turkey

Abstract

Turkey's boric acid production has the highest production share among refined boron products. This production is takes place at the Bandırma (Balıkesir) and Emet (Kütahya) Boric Acid Plants of ETI Maden Operations. Concentrated ore (by physical processes) and high-grade wastes accumulated in waste ponds/dams are obtained from boron production plants. In this study, slime size (d_{80}=52.70µm) wastes belonging to the Bigadiç field with 9-12% B_2O_3 (ulexite-colemanite) content have been evaluated. Due to the small size of feeding without the need for grinding, the sample was subjected to leaching of acetic acid at 60°C for 1 hour, at a mixing speed of 1500 rpm, at 7% solids. In addition to the recovery of 90% H_3BO_3 (at 4% acid concentration) after the leaching process, different compounds such as Na_2O, and CaO were also obtained. Similar peaks were found in the FT-IR analyzes of boric acid and the product obtained. This study is an important output in terms of evaluating the % B_2O_3 content in the wastes of both this plant and other boron plants.

Keywords: Boron waste, Boric acid, Ulexite, colemanite, Acetic acid

1 Introduction

Turkey's boron reserves are in the first place, as it has 73.6% of the world's reserves [1, 2]. The most abundant minerals are tincal, colemanite, and ulexite [3]. The densest minerals in terms of B_2O_3 content are tincal, colemanite, and ulexite, and they also have the same trade names (Table 1) [4-7]. Among these minerals, ulexite is mostly found and processed in the Balıkesir-Bigadiç field. In addition to this field, it is also obtained as a by-product in Bursa-Kestelek [8-10, 24]. Although the colemanite mineral is found in most areas (Kütahya–Emet, Balıkesir–Bigadiç, Bursa–Kestelek), it is extensively obtained from Hisarcık and Espey fields within the Emet Operation Plant [11-13]. The tincal mineral is mostly found in the Eskişehir-Kırka plant [2, 14-16]. The products obtained after physical processes are called concentrated/run-out boron products. The products obtained after chemical processes are called refined boron products. Boron products refined within Eti Maden include boric acid, borax pentahydrate, borax decahydrate, boron oxide, ground colemanite, ground ulexite, and agricultural boron, anhydrous borax, zinc borate, and calcined tincal [2, 5, 17].

Öz

Türkiye'nin borik asit üretimi rafine bor ürünleri arasında en yüksek üretim payına sahiptir. Söz konusu bu üretim ETİ Maden İşletmelerinin Bandırma (Balıkesir) ve Emet (Kütahya) Borik Asit Tesislerinden üretilmektedir. Bor üretim tesislerinden konsantre cevher (fiziksel işlemlerle) ve atık havuzlarında/barajlarda biriktirilen yüksek tenörlü atıklar elde edilmektedir. Bu çalışmada, Bigadiç sahasına ait %9-12 B_2O_3 (üleksit-kolemanit) içeriğine sahip şlam boyutundaki (d_{90}=81.94µm) atıklar değerlendirilmiştir. Numune, öğütülmeye ihtiyaç duyulmadan küçük besleme boyutundan dolayı 60°C'de 1 saat, 1500 rpm karıştırma hızında, %7 katı oranında asetik asit liç işlemine tabi tutulmuştur. Liç işlemi sonrasında %90 H_3BO_3 (%4 asit konsantrasyonunda) veriminin yanı sıra Na_2O ve CaO gibi farklı bileşikler de elde edilmiştir. Borik asit ve elde edilen ürünün FT-IR analizlerinde benzer pikler bulunmuştur. Bu çalışma, hem bu tesisin hem de diğer bor tesislerinin atıklarındaki % B_2O_3 içeriğinin değerlendirilmesi açısından önemli bir çıktıdır.

Anahtar kelimeler: Bor atığı, Borik asit, Üleksit, kolemanit, Asetik asit

Table 1. Commercial boron minerals [2, 6, 7]

Minerals	Formula	B_2O_3 Content (% wt)
Colemanite	$Ca_2B_6O_{11}.5H_2O$	50.8
Borax/Tincal	$Na_2B_4O_7.10H_2O$	43.0
Ulexite	$NaCaB_5O_9.8H_2O$	35.5
Kernite	$Na_2B_{14}O_7.4H_2O$	51.0
Probertite	$NaCaB_5O_9.5H_2O$	50.5
Pandermite	$Ca_4B_{10}O_9.7H_2O$	49.8
Hydroboracite	$CaMgB_6O_{11}.6H_2O$	50.5

In general, the usage areas of boron products are glass and glass fiber production, cleaning and whitening, ceramic and enamel industry, textile, metallurgy-material, agriculture, wood protection, insulation, health, and energy industries. Boron, which can be used in concentrated as well as refined form, can be consumed in the military and armored vehicles, glass, electronics - computers, energy, photography and vision systems, pharmaceuticals, cosmetics, communications, construction, agriculture, plastics, chemistry, paper, metallurgy, textiles, automobiles. It finds

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[*] Sorumlu yazar / Corresponding author, e-posta / e-mail: eyogurtcuoglu@ohu.edu.tr (E. Yoğurtcuoğlu)

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use in many different sectors such as space, aviation, and energy [2, 3, 5, 18, and 19].

Boric acid is a strategically and industrially important boron compound used in many different fields such as glass, ceramics, the pharmaceutical industry, and nuclear energy [18]. In the Bigadic (Balıkesir) Operation Plant, the production of boron has been carried out with ulexite and colemanite minerals since 1950. The B_2O_3 densities and contents of these minerals are 1.98 g/cm^3 for 43% B_2O_3-and 2.4 g/cm^3 for 50.8% B_2O_3, respectively [1, 3, 13, 20-23]. Besides these minerals, the side rocks are composed of carbonate and silicate minerals and their densities are generally 2.6-2.7 g/cm^3 [22].

While concentrated boron products (raw boron products) are produced from the concentrator plants, wastes with high B_2O_3 content (9-22% B_2O_3 at varying rates) accumulate in waste ponds/dams every year [9, 10, 25, 26]. Besides being an economic loss, these wastes attract attention in terms of many environmental factors such as waste dam/pond area insufficiency, and wastewater problems [27, 28]. Boron wastes have been examined from three different aspects: proper storage of waste, recovery of valuable contents, and evaluation of clay minerals [29]. The production of boric acid has been conducted with a dissolution efficiency of approximately 97% in a study that investigating the application of bioleaching (aspergillus niger pure culture) to colemanite wastes of the Kütahya Emet Plant. This dissolution efficiency has obtained at a 3% (wt) solid ratio, -75 µm grain size, 3.98 pH, 25±2 °C, and 15 days [12, 30].

In the heap leaching studies of Bigadiç Plant's colemanite and ulexite wastes, boric acid has been obtained at a concentration of 4.7% H_2SO_4 (95%) at room temperature with 80% efficiency in 6 hours [9]. In the tank leaching process containing sulfuric acid applied to a similar sample, the production of boric acid has been performed at 85-90% recovery efficiency at 60-65°C, 7% solid ratio, and 1-6% acid concentration [26]. In a different study on the leaching of citric acid, 58-71% recovery efficiencies were achieved in the experiments performed under similar conditions with sulfuric acid at 2-9% acid concentration [10]. Reverse flotation tests on Bigadiç Plant wastes (+75 µm) were carried out with Sulfanate type Cyanamid R801 and R825 under natural pH (9-9.5) conditions. The best result was a product with 60% efficiency and 17% B_2O_3 grade [8].

In the study of Ediz and Özdağ, the physical enrichment process of tincal ore and its wastes were investigated using a helical transporter. As a result of the tests, it was obtained as 88.66% B_2O_3 from the ore sample. The test conditions of this sample are 70°C temperature, 15° slope, 7 r/min rotation speed and 1/8 solid/liquid ratio. The recovery efficiency of the waste sample is 87.83% B_2O_3. The test conditions of the waste sample are 50°C temperature, 10° slope, 12 rpm rotation speed and 1/12 solid/liquid ratio [31].

Another study shows that, in dissolving ulexite with acetic acid, the dissolution rate was positively affected by solution concentration and temperature, while solid-liquid ratio and particle size were negatively affected [32]. Similar dissolution results were also found in the acetic acid solution of colemanite [11]. A similar situation was observed by Bayca in the production of boric acid by sulfuric acid leaching of Balıkesir Bigadiç's colemanite waste [33]. The boric acid has also been obtained from colemanite using propionic acid and sulfuric acid. This solution produced has been more pure and efficient because it prevents sodium and potassium transfer [34-36]. The decomposition of acetic acid into its ions in an aqueous medium is as follows (1) [37, 38]:

$$8CH_3COOH_{(l)} + 8H_2O_{(l)} \leftrightarrow 8CH_3COO^-_{(aq)} + 8H_3O^+_{(aq)} \qquad (1)$$

The general dissolution reactions of ulexite mineral (2) [32] and colemanite mineral (3) [11, 39] in acidic medium are as follows:

$$Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 16H_2O_{(s)}+6CH_3COOH_{(aq)}\rightarrow 2Na_{(aq)}^{+}+ 2Ca_{(aq)}^{2+}+6CH_3COO_{(aq)}^{-}+10H_3BO_{3(aq)} +4H_2O_{(l)} \qquad (2)$$

$$2[2CaO.3B_2O_3.5H_2O_{(s)}] + 8CH_3COOH_{(l)} + 4H_2O_{(l)} \leftrightarrow 8CH_3COO^-_{(aq)} + 4Ca^{2+}_{(aq)} + 12H_3BO_{3(aq)} \qquad (3)$$

Dissolution studies have been carried out on the reactions of colemanite and ulexite with many organic such as sulfuric acid [6, 9, 26, 33] and inorganic acids such as oxalic [6, 9, 26, 33], citric [10, 30], acetic [11, 32, 37-38], propionic acid [34, 36].

In this study, recovery efficiencies of the process that dissolving sludge waste taken from the waste ponds of Bigadiç Plant Concentrator Plant with acetic acid as an organic acid were evaluated.

2 Material and methods

The sample used in the experiments is the slime wastes of the waste ponds of Bigadiç Boron Operations (Eti Maden). Approximately 55-60 kg of samples were dried, blended, divided, and packaged.

The chemical (Rigaku ZSX Primus X-Ray Fluorescence) and particle size (Malvern Mastersizer 3000) analyses of the test sample were performed in Bigadiç Plant Laboratories. % B_2O_3 content analyses on all samples were carried out by titration method. XRD analysis was performed to determine mineral structures with a Panalytical-Empyrean model device. In order to understand the mineral structure changes by examining the bond structures, FT-IR analyses (wavelength range of 4000-400 cm^{-1}) was performed with Bruker Vertex 70 spectrometer in NOHU Central Research Laboratory.

According to the particle size distributions given in Table 2, it has been determined that 80% of the sample is below 52.7 µm, while 10 % of it is below 2.19 µm.

Table 2. The particle size distribution [9, 10, 26]

size	µm
d_{90}	81.94
d_{80}	52.70
d_{50}	16.49
d_{30}	6.36
d_{10}	2.19

The experiment samples were weighed in at approximately 130 g and prepared at a 7% solid ratio. The water used in all stages of the experiments (such as filter washing water) is distilled water. The acid used is Tekkim brand acetic acid with 99% purity. The experiments were carried out in a fume hood and using stirrers with magnetic heaters. Experimental parameters are the temperature of 60 °C, leaching time of 1 hour, stirring speed of 1500 rpm, at 7% solids, and acid concentration of 2-22%. After the experiment, solid-liquid separation was done by the filtering process. Each filter cake was washed and dried. XRF analyses were made from the leaching wastes obtained. Recovery efficiencies were calculated according to the dissolved solids.

The chemical analysis of the sample used in the experiments is given in Table 3. The B_2O_3 content is also between 8-12%. According to the table, the contents of some compounds in the waste are 1.16% Na_2O, 16.61% CaO, and 0.26% Fe_2O_3 [9, 10, 26].

Table 3. Chemical analysis of test material

Compound	% Content
SiO_2	32.11
CaO	16.61
Na_2O	1.16
MgO	25.23
SO_3	0.27
SrO	0.55
Fe_2O_3	0.26

In the XRD analysis of the test sample (Figure 1), colemanite, ulexite, montmorillonite ($Al_2H_2O_{12}Si_4$), illite-smectite ($(K, H_3O)(Al, Mg, Fe)_2(Si, Al)_4O_{10}[(OH)_2\cdot(H_2O)]$), quartz ($SiO_2$), and gypsum ($CaSO_4.2H_2O$) minerals were detected.

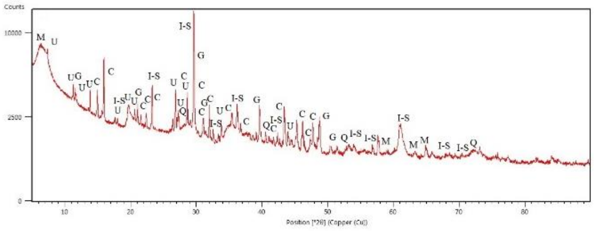

Figure 1. XRD Analysis of the raw material [M: Montmorillonite; C: Colemanite; U: Ulexite; I-S: Illite-Smectite; G: Gypsum; Q: Quartz]

3 Result and discussion

In order to investigate the mineral bond structure, FT-IR analyzes were performed on raw material (RM), waste (WS), product (PS), and boric acid (BA) samples (Figure 2). In the test sample, 3674, 3597, 3404 cm^{-1} peaks indicate O-H bonds of clay structures such as illite minerals [40-44]. The 1626 cm^{-1} peak of this sample indicates the existence of an H_2O structure [41] and C=O bonds [44]. Apart from these, $CaCO_3$ (1393-872-711 cm^{-1}), and Si-O or other carbon bonds (1225-579 cm^{-1}) were also observed in this sample [42, 44, 45].

The peaks of 3185, 1415, 670, and 643 cm^{-1} determined in the product sample are similar to the peaks of boric acid. In addition, the presence of B_3-O, and B_4-O bond peaks belonging to ulexite and colemanite minerals are also observed in the test and product samples. These boron-containing peaks are 1360, 1349, 1321, 1005, 967, 761, 748, 728, and 711 cm^{-1} [45, 46].

When the peaks of the waste sample were examined, carbon bonds such as C-H (1550-1416 cm^{-1}) and the presence of boric acid leaks were observed [18, 47-49].

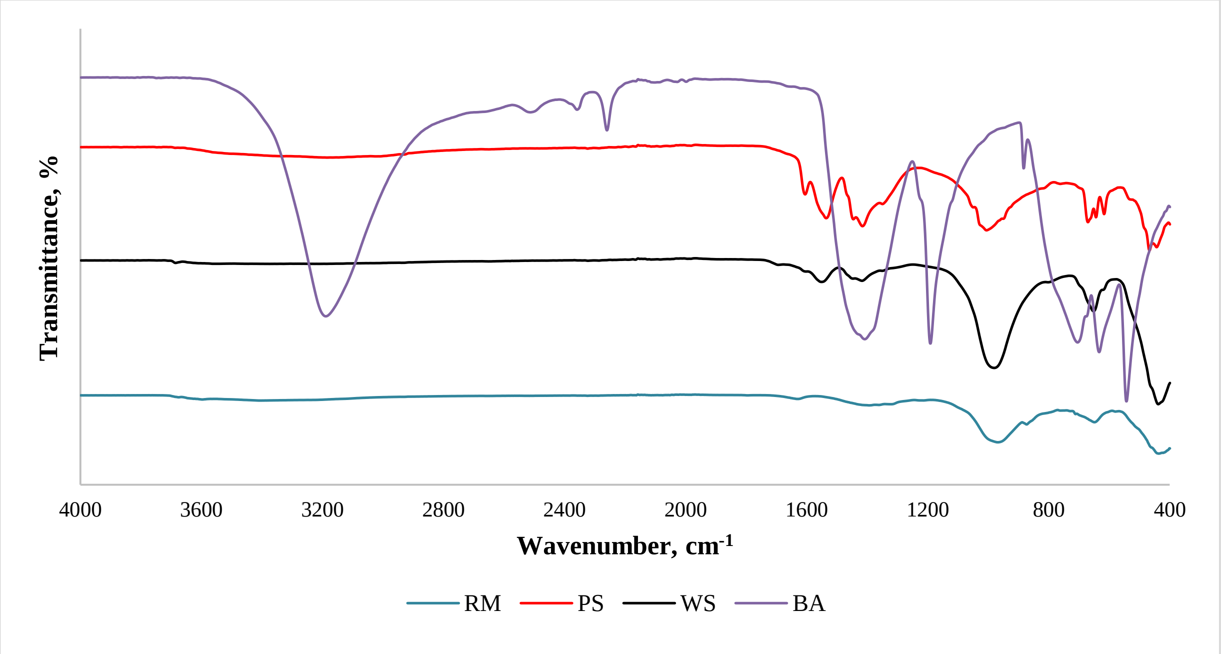

Figure 2. FT-IR Analyses of samples [RM: The raw material, PS: The product sample, WS: The waste sample, and BA: The boric acid sample]

As a result of the acetic acid leaching process, different compounds, especially boric acid, were also recovered. According to Figure 3, the recovery yield values of boric acid were between 68.2-90.2%, and the highest recovery was obtained from the 4% acetic acid leaching process similarly to other dissolutions.

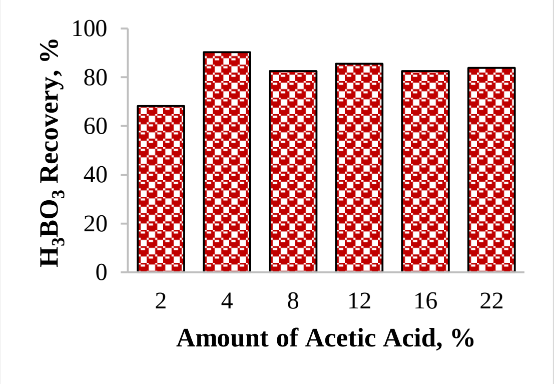

Figure 3. Boric acid % recovery after acetic acid leaching

Dense clay-containing minerals determined by chemical and XRD analyses of the sample were important in determining the solid amount percentage of the experiments. Because these minerals generally swell by gaining volume in the aquatic environment. Therefore, the mixing speed of the experiments was kept high (1500 rpm). Thus, in the experiments after the 4% acid concentration ratio, the acid could not affect the mineral structure anymore. Therefore, these test results are in the range of 83-85%. Although acetic acid is a weak acid, the amount of solid dissolved after the experiment is also high. In order to determine the % B_2O_3 (remaining dissolution) amount in the XRF analysis of the waste samples obtained as a result of the experiments, it could not be carried out at solid rates lower than 7%.

In addition, the % amounts of other compounds (except for B_2O_3) obtained after dissolution are also shown in Figures 4 and 5. Among these compounds, CaO was dissolved in the range of 52-80%, and almost all of MgO (95-97%) was. SO_3 and SrO dissolution were also found to be 28-73% and 34-73%, respectively.

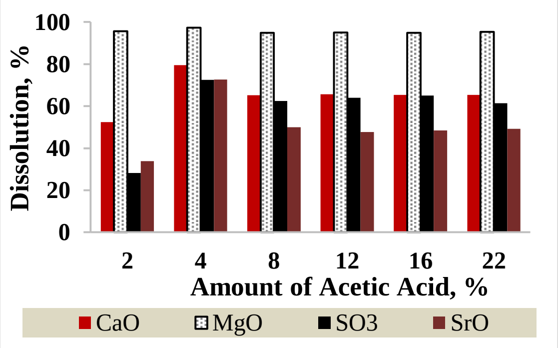

Figure 4. The dissolution of the compounds of CaO, MgO, SO_3, and SrO after acetic acid leaching

The lowest percentage of dissolution of these compounds was seen at a 2% acid concentration. In particular, the dissolved CaO compound shows that the content of ulexite and colemanite minerals can be degraded. On the other hand, dissolution of other compounds showed that gangue mineral structures such as clay and calcite were also affected. In addition, as in B_2O_3, the highest resolutions of these compounds have been performed at a 4% acid concentration.

Similarly, the highest solubility of Na_2O, SiO_2, and Fe_2O_3 compounds at 4% acid concentration was determined as 58.6%, 64.5%, and 65.3%, respectively. The lowest dissolution percentages of these compounds were found at different acid concentrations. However, the highest acid concentration has resulted as in the other two graphs above (4%). Na_2O dissolution demonstrates that the ulexite mineral structure is decomposed, as in CaO. Compared to inorganic solvents such as HCl and H_2SO_4, acetic acid is more advantageous, especially since impurities such as iron dissolve to a lesser extent [50]. As a result of this study, the solubility percentage/rate of Fe_2O_3 has been obtained at low values.

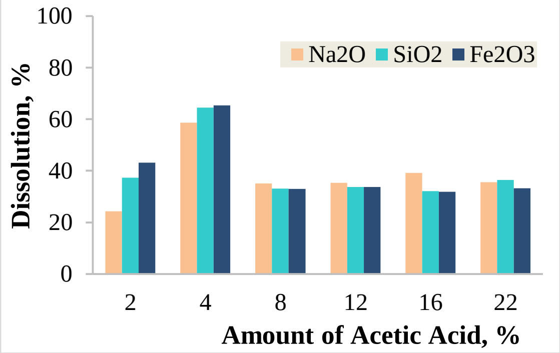

Figure 5. The Dissolution of the compounds of Na_2O, SiO_2, and Fe_2O_3 after acetic acid leaching

It has been stated that the solubility or crystallization of silica occurs either in high pH, high ionic strength, or acidic solution pH<9 and at high temperature. Therefore, when Ca and Si in calcium-rich blast furnace slag are dissolved with acetic acid, 5% acid is completely dissolved in 30 minutes at room temperature. In addition to these elements, Al and Mg elements were also extracted [51-52]. As a result of this research, similar outcomes have been obtained in an acetic acid environment.

As a general principle, H_3BO_3 obtained by dissolving sulfuric acid in boric acid plants is filtered by filtration processes and crystallized at 85-90 °C. Then, the moisture of crystallized boric acid with 5% moisture content at 46 °C is dried in fluid bed dryers. The remaining weak solution is fed back to the plant [19]. In the case of evaluation of this research, crystalline boric acid can be obtained by similar processes.

4 Conclusions

The amount of boron waste with high B_2O_3 content is increasing every year, especially in the Bigadiç Plant's, and this situation seriously affects the waste stock capacity. This research makes it possible to evaluate the boron wastes of this plant with acetic acid, an organic acid. There are ulexite-colemanite minerals containing highly B_2O_3 in this plant's wastes. As seen in this study, it is possible to obtain these contents in the form of boric acid. This result also provides the undermentioned advantages.

1. The experiments have been performed at low temperatures (60°C), acid concentrations (2-22 %), and time (1 hour). Consequently, the recoveries have reached around 90%.
2. This research issue is important in terms of obtaining wastes with less impurity by dissolving them with low-cost acetic acid.
3. It is a remarkable output that the valuable % B_2O_3 content in the waste of this concentrator plant is recoverable. This result is also important in terms of its application in other boron concentrator plant wastes.
4. After the valuable boron content is recovered, the remaining clay-containing wastes will be more suitable for use in many areas (such as ceramics, bricks, cement, glass, silica, refractory).
5. After the B_2O_3 content is obtained, the wastes can also be used in mining, apart from the sectors mentioned above. In this sector, it has applicability as a filling material in open pit and underground mining.
6. Besides all these contributions, the evaluation of valuable %B_2O_3 wastes will also help with new stock problems and the search for pools/dams.

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Conflict of interest

The authors declare that there is no conflict of interest.

Similarity rate (iThenticate): %10

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