

Recovery of Boric Acid From Colemanite Waste by Sulfuric Acid Leaching and Crystallization

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Abstract: The Balıkesir -Bigadic mine is worked by open pit operations to produce colemanite ore. Colemanite ores are processed by mineral processing techniques to prepare colemanite concentrates in the Bigadic plant. Colemanite process waste from this concentrator is pumped to the four tailing dams of the plant. Each passing day increases the amount of this waste stored since it is not using in the industry. In this study, recovery of boric acid from colemanite waste by sulfuric acid leaching and crystallization process was investigated. Colemanite waste was leached using sulfuric acid solutions. The experiments of leaching parameters were solid/liquid ratio, stirring speed, acid concentration, and reaction temperature. The most significant parameters were found in the leaching. The optimum leaching conditions were determined by these parameters. The filtered leach solutions were studied by using crystallization to obtain high purity boric acid. For this purpose, the influence of crystallization time was affected on purity of boric acid. The effects of reaction time on the particle size of gypsum were investigated. The results showed that high purity boric acid crystals were obtained using colemanite waste.

Keywords: Boric acid; Colemanite waste; Leaching; Crystallization; Sulphuric acid.

Introduction

Boric acid is used as a product in the industry. It is also used as a raw material to produce boron compounds. Boric acid has triclinic crystal structure and its chemical composition is H_3BO_3 containing 56.3% B_2O_3 (Jansen, 1999). Turkey uses colemanite concentrate to produce boric acid in sulfuric acid solutions at Bandırma (capacity 85,000 t/yr) and at Emet (capacity 100,000 t/yr).

Boron minerals colemanite, ulexite, and tincal are commercially produced in large amounts with colemanite ore produced in open mines in Bigadic, Balıkesir province (Turkey). Colemanite is a calcium borate mineral (theoretically, 50.8% B_2O_3) with monoclinic crystal structure and a chemical composition of $Ca_2B_6O_{11} \cdot 5H_2O$. The colemanite process is carried out in ore preparation facilities near the ore mines in Bigadic. Colemanite is enriched via processes such as crushing, wetting in water, washing in a thumbling, sieving, triage and classification, produced for sale as concentrated colemanite in different grain sizes and chemical compositions. A major portion of the produced concentrated colemanite is exported (Bayca, 2009).

Recently, experimental studies on the colemanite leaching have been investigated by researchers. Alkan and Dogan (2004 CEP) were investigated dissolution kinetics of colemanite in oxalic acid solutions they found that the dissolution rate increased with decreasing particle size and increasing temperature, but it was not affected by stirring speed. Cavus and Kuslu (2005) studied dissolution of colemanite in citric acid solutions. They reported that the dissolution rate increases with increasing temperature, and decreases with decreasing particle size and solid/liquid ratio. Kurtbas et al. (2006) investigated dissolution of Colemanite in Aqueous Solutions Saturated with Both Sulfur Dioxide (SO_2) Gas and Boric Acid. They found that the conversion rate increased as the particle size and solid-to-liquid ratio each decreased and the temperature increased; however, the effect of stirring speed was very minimal. Taylan et al. (2007) investigated effects of ultrasound on the reaction step of boric acid production process from colemanite. They found that the dissolution rate increases, as expected, with decreasing particle size in both absence and presence of ultrasound. It was found that ultrasound enhances the dissolution of colemanite in aqueous solutions containing boric acid and sulfuric acid after 1 h. Ultrasound decreases the particle size of gypsum probably due to the increasing of primary and secondary nucleation rates as well as the breakage of the crystals by ultrasonic effect. Ekinici et al. (2007) studied that optimization and modeling of boric acid extraction from colemanite in water saturated with carbon dioxide and sulphur dioxide

gases. They reported that the optimum conditions were found to be as follows: reaction temperature, 41 °C; solid-to-liquid ratio, 0.0685 g/mL; mean particle size, 0.2835 mm; stirring speed, 266 rpm; reaction time, 7 min. The calculated boric acid extraction efficiency from colemanite ore was approximately 99.9% under the optimum conditions. Gur (2007) investigated Dissolution mechanism of colemanite in sulphuric acid solutions. He found that the analysis of the experimental data shows that increasing H_3O^+ acid concentration increased the dissolution rate, but increasing SO_4^{-2} concentration reduced dissolution rate because of the precipitation of a solid film of CaSO_4 and $\text{CaSO}_4 \cdot \text{H}_2\text{O}$. Tunc et al (2007) studied dissolution of colemanite in $(\text{NH}_4)_2\text{SO}_4$ solutions. they found that the conversion rate was increased by decreasing particle size and solid to liquid ratio, by increasing ammonium sulfate concentration and temperature. Bulutcu et al. (2008) investigated Impurity control in the production of boric acid from colemanite in the presence of propionic acid. They determined that increasing the ratio of propionic acid in the acid mixtures leads to increase the reaction time, but to decrease the soluble impurity level in strong boric acid solution. Gur and Alkan (2008) studied leaching kinetics of colemanite in perchloric acid solutions. they reported that the dissolution rate of colemanite was found to increase with decreasing particle size and solid to liquid ratio, with increasing reaction temperature and acid concentration, while it was not affected by stirring speed.

The colemanite waste contains high amounts of boron. Therefore, colemanite waste can not be discharged into any river. In the Bigadic Process Plant, colemanite waste is pumped to waste dams. Although the supernatant water is used as water in the process, all dams are almost full. New tailing dams must be constructed for waste. However, these regions are agricultural areas. Therefore, a solution should be found this waste problem.

The aim of present study is to investigate the leaching of colemanite waste in sulphuric acid solutions, to find the optimum conditions of the leaching process, to find the most effect parameters of leaching rate, to find the optimum conditions of completely separation of gypsum by crystallization from leach solution, to obtain high purity boric acid crystals from the waste, to reduce environmental damage of the waste and to increase economic value of colemanite waste.

Materials and methods

Materials

The waste sample used in the experiments in this study was obtained from Eti Mine Bigadic Boron Works (Balıkesir, Turkey). The Bigadic mine is worked by open pit operations. Colemanite ores are processed by mineral processing techniques to produce colemanite concentrates in the Bigadic plant. Colemanite process waste from this concentrator is pumped to the four tailing dams of the plant. Samples were taken from the first waste dam. This waste contains between 5 – 15 % solid. The sample is mainly comprised of colemanite and small amounts of quartz and calcite. This waste was dried at atmospheric conditions. The dried samples were sieved to determine particle size, and the results are given in Figure 1. This original particle size in the waste was used in the leaching experiments. Sulfuric acid, d-mannitol, sodium hydroxide, methyl red and phenolphthalein reagents were of analytical grade. X-ray diffraction (XRD) analysis of the sample was carried out on a Shimadzu with $\text{Cu K}\alpha$ radiation, and the results are given in Figure 2. The chemical analysis results from XRF of the colemanite process waste (except B_2O_3) are given in Table 1.

Methods

Leaching

Figure 3 is a flow chart of the processes used for recovery of boric acid crystals from colemanite waste. The leaching experiments were carried out in a 500-mL three-necked glass reactor at atmospheric pressure. A mechanical stirrer with a digital display was used to agitate the solution. The heating or cooling of the reactor was carried out with a bath. A programmable refrigerated bath/circulator was used to keep the reaction medium at a constant temperature. The initial leaching conditions was selected as 0.25 mol/L H_2SO_4 , solid to liquid ratio of 3 %, stirring speed of 300 rpm, at 30°C. In the dissolution process, 100 mL of sulfuric acid solution was placed into the reactor, and the stirring was started. After the desired reaction temperature was reached, a given amount of dried waste was added to the solution.

Crystallization

The leach solution was filtered by filter paper without any change in temperature. Two phases, which were solid residue and leach liquor, were obtained by filtration. The leach liquor was crystallized by a programmable refrigerated circulator with cooling process at 35 °C. The crystals were centrifuging for separating of solids and the supernatant was discarded. The solids, crystals, were drying at 40 °C for obtaining of boric acid crystals. The dried crystals of liquid phase were analyzed by XRD (Rigaku D/Max-2200/PC). The image of dried crystal boric acid was analyzed by an SEM (JSM-6060 JEOL). Each experiment was repeated at least twice. The amount of B₂O₃ in the filtrate leach liquid was determined by a volumetric method (Scott, 1963), and the experimental parameters used in the dissolution processes are given in Table.2.

Results and discussion

Effects of parameters on leaching

The tests were carried out at 3 – 10 % range with a stirring speed of 300 rpm and acid concentration of 0.25 mol/L at 30°C. Figure 4 shows that the slowest leaching rate was obtained at 10% solid/liquid ratio. The leaching rate decreases with increasing solid/liquid ratio. This may be attributed to the fact that an increase in the amount of solids in the suspension corresponds to declining the amounts of reagents. The experiments were performed at 300 – 700 rpm stirring speed range with a solid/liquid ratio of 5% and acid concentration of 0.25 mol/L at 30°C. As seen in Figure 5, the leaching rate was not affected by stirring speed. This may be attributed to the fact that the dissolution of colemanite waste was a chemical reaction controlled rather than diffusion controlled mass transfer. Similar results were found for colemanite in oxalic acid solutions (Alkan and Dogan, 2004) and for colemanite in SO₂-saturated water (Ozmetin et al., 1996). All subsequent tests were performed at stirring speeds of 500 rpm that was used only to homogenize the solution for heat transfer. The influence of acid concentration on dissolution rate of colemanite waste is investigated at 30°C, stirring speed of 500 rpm and with a solid/liquid ratio of 6%. As seen in Figure 5, the maximum leaching rate was observed at 1.0 mol/L acid concentration. The extraction yield slowly increases as acid concentration increases from 0.25 to 1.0 mol/L and then decreases as acid concentration increases from 1.0 to 2.0 mol/L. This may be attributed to the fact that the more boric acid forms with increasing acid concentration. This occurred boric acid film on the particle inhibits diffusion rate of sulphuric acid into particle surface. Several studies showed similar results using colemanite dissolved in acetic acid solutions (Alkan and Dogan, 2004), oxalic acid solutions (Ozmetin et al., 1996) and using tincal in oxalic acid solutions (Abali et al., 2006). The experiments were carried out at different temperatures between 30 and 70°C. The influence of temperature on the dissolution rate of waste was investigated at a sulfuric acid concentration of 1.0 mol/L with a solid-to-liquid ratio of 5%, and stirring speed of 500 rpm. It was shown that the leaching rate increases with increasing temperature, which is expected from the exponential dependence of the rate constant in the Arrhenius equation. As seen in Figure 7, the maximum leaching rate was obtained at 70°C.

Characterization of the leaching solid residuals

In this study, the optimum conditions of waste leaching in sulfuric acid solutions were found to be: solid-to-liquid ratio of 5%, stirring speed of 500 rpm, acid concentration of 1.0 mol/L and temperature of 70 °C. The waste was leached with sulfuric acid solutions at the optimum conditions. The leaching solid residue was dried at ambient temperature. The solid-phase XRD patterns are shown in Figure 8. The XRD patterns indicate diffraction peaks of gypsum (CaSO₄.2H₂O). This result is in agreement with equations (6) and (7).



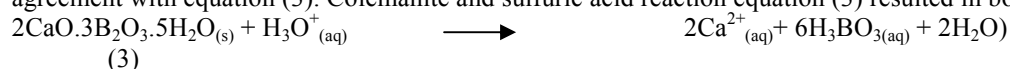
Colemanite and sulfuric acid reaction equation (6) resulted in calcium sulfate dihydrate (CaSO₄.2H₂O) products. Furthermore, equation (7), calcite (CaCO₃) and sulfuric acid reaction resulted in calcium sulfate dihydrate.

Crystallization

The liquid phase was crystallized in water bath medium at a temperature of 35°C to obtain boric acid crystals. The liquid phase was not dried at ambient temperature due to hygroscopic gypsum. Instead, the liquid phase was dried in an oven at 110°C for XRD analysis. As seen in Figure 9, anhydride (gypsum) and boric acid were observed in the XRD analysis. As the solid phase was dried at 110°C, the crystal water evaporated from gypsum which became anhydrous because of its low dehydration temperature.

A leaching solution containing gypsum and boron oxide was obtained from the leaching of waste. Gypsum must be completely separated from the leaching solution to obtain pure boric acid crystals. Leaching time is the dissolution time for the boron oxide. However, this time also serves as the crystallization time for gypsum. Boron oxide in the waste water can be completely dissolved in a leaching time of 30 minutes. A crystallization time of 30 minutes for gypsum was insufficient as gypsum remained in the solution after filtering. Gypsum crystals did not pass through the filter after crystallization of 120 minutes. Hence, the solution passing through the filter was sufficiently pure. Pure boric acid crystals were obtained by crystallization out of this solution. Taylan et al., (2007) reported that the size of gypsum crystals increases with time due to crystal growth.

The waste was leached using sulfuric acid solutions at the aforementioned the optimum conditions for 120 minutes. The leachant solutions were filtered, and the liquid phase was crystallized at 35°C. The obtained crystals were dried at ambient temperature due to the low dehydration temperature of boric acid, and the crystallized liquid phase was analyzed by XRD (Rigaku D/Max-2200/PC). Figure 10 shows the XRD patterns of the crystals. Only boric acid (H₃BO₃) peaks were observed with XRD analysis. The result of XRD is in agreement with equation (3). Colemanite and sulfuric acid reaction equation (3) resulted in boric acid.



An SEM (JSM-6060 JEOL) image of crystal boric acid is given in Figure 11. The boric acid crystals, which have a triclinic structure, can be observed in the SEM images. The XRD and SEM analyses show that pure boric acid crystals can be produced using colemanite waste.

Conclusions

The leaching of colemanite waste in sulfuric acid solutions was studied in a batch reactor. The results showed that the leaching rate increases with increasing reaction temperature and decreasing solid-to-liquid ratio. The most important parameter on the leaching rate was found to be the reaction temperature while the least important parameter on the leaching rate was found to be the stirring speed. The optimum conditions were found to be a solid-to-liquid ratio of 5%, a stirring speed of 500 rpm, acid concentration of 1 mol/L and temperature of 70°C. Maximum boron oxide extraction efficiency is 99.99%. The leaching solution containing gypsum and boron oxide was obtained from the leaching of waste. Gypsum must be completely separated from the leaching solution to obtain pure boric acid crystals. Leaching time is the dissolution time for the boron oxide. However, this time also serves as the crystallization time for gypsum. Therefore, leaching time should be at least 2 hours. The XRD and SEM analyses show that pure boric acid crystals can be produced using colemanite waste. Boric acid has a great deal of utility as a raw material in various industries. Moreover, boric acid has been sold commercially as an expensive product with a price of \$800/t. The highest boric acid purity crystals were obtained from colemanite waste. These results suggest that commercial boric acid can be produced by using colemanite waste. Thus, environmental problems from tailing dams will be reduced and waste will gain an economic value.

Acknowledgments

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References

- A. Gur, Korean Journal of Chemical Engineering, 24 (2007) 588 – 591.
- A.N. Bulutcu C.O. Ertekin, M.B. Kuskay Celikoyan, Chemical Engineering and Processing 47 (2008) 2270–2274.

- Abali, Y., Bayca, S.U., Mistincik, E., 2006, *Chemical Engineering Journal*, 123, 25–30.
- Abdusselam Kurtbas, M. Muhtar Kocakerim, Özkan Küçük, and Ahmet Yartaşı, *Ind. Eng. Chem. Res.*, 45 (2006) 1857–1862.
- Alkan, M., Dogan, M., 2004b, *Chemical Engineering and Processing*, 43: 867–872.
- Bayca, Salih Ugur, 2009, *Journal of Ceramic Processing Research*, No. 2, 10: 162–166.
- Cavus, F., Kuslu, S., 2005, *Ind. Eng. Chem. Res.*, 44, 8164–8170.
- Gur A, Alkan M. E. **journal of chemical engineering of japan 41 (2008) 354-360.**
- Jansen, L. H., 1999, *Boron Compounds*, Kirk-Othmer Encyclopedia of Chemical Technology, Vol.4, John Wiley & Sons, p. 377.
- Mehmet Tunc, Mehmet Muhtar Kocakerim, Ozkan Kucuk, and Mehmet Aluz, *Korean Journal of Chemical Engineering*, 24 (2007) 55 – 59.
- Ozmetin, C., Kocakerim, M.M., Yapici, S., Yartasi, A., 1996, *Ind. Eng. Chem Res.*, 35: 2355–2359.
- Scott, W. W., 1963, *Standard Methods of Chemical Analysis*, D. Van Nostrand, New York.
- Taylan, N., Gurbuz, H., Bulutcu, A. N., 2007, *Ultrasonics Sonochemistry* 14: 633 – 638.
- Zafer Ekinci, Enes Sayan, Ayse Vildan Bese, Osman Nuri Ata, *Int. J. Miner. Process.* 82 (2007) 187–194.

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	B ₂ O ₃	CaO	MgO	Na ₂ O	SrO	LOI
Waste, %	7.27	0.28	0.11	40.72	23.03	3.14	0.05	1.18	23.80

Table 1. Chemical analysis of the studied tailings

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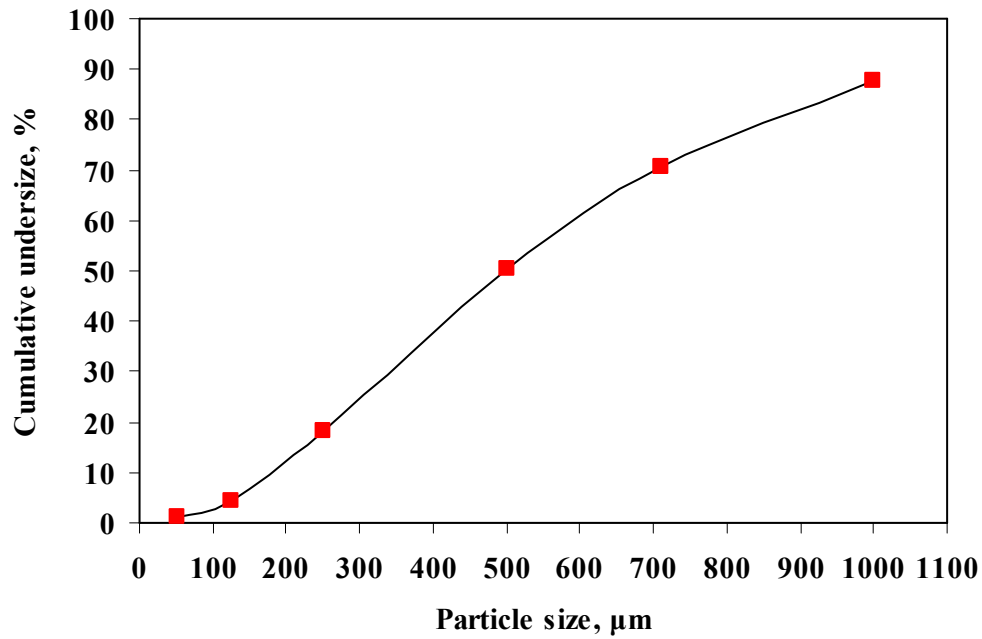


Figure 1. Cumulative undersize of colemanite waste

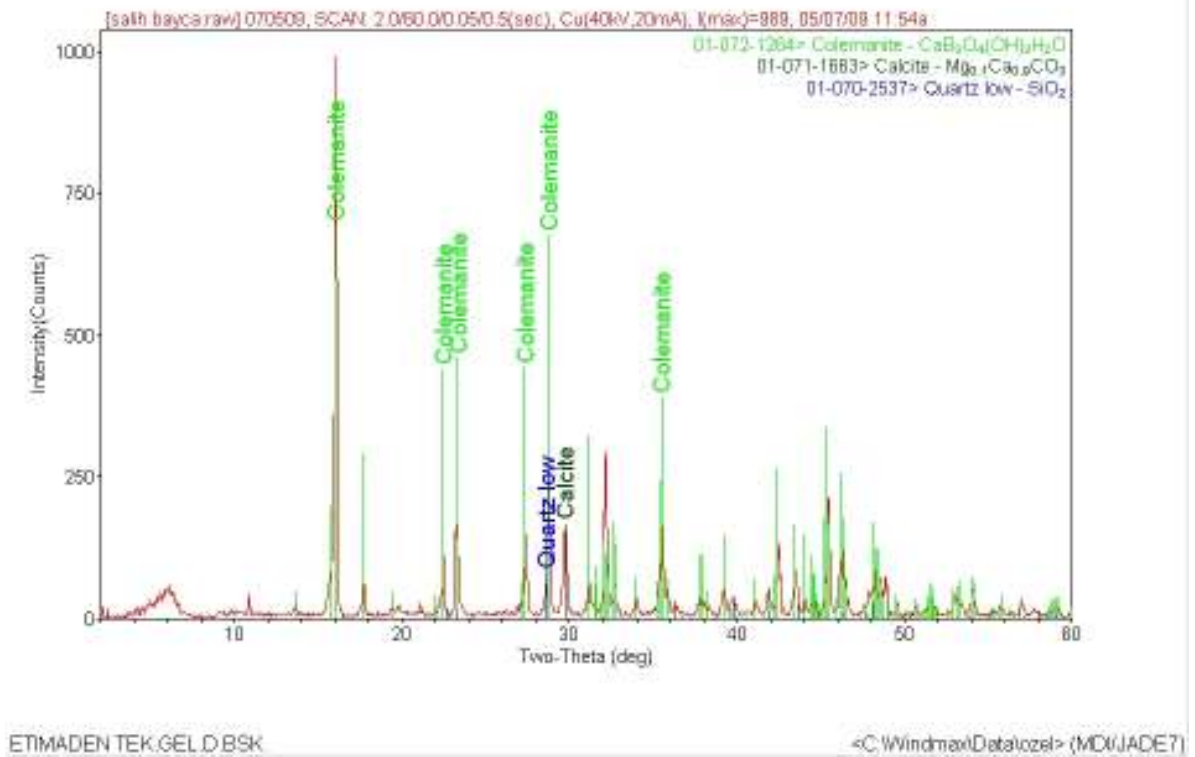


Figure 2. X-ray diffraction analysis of waste.

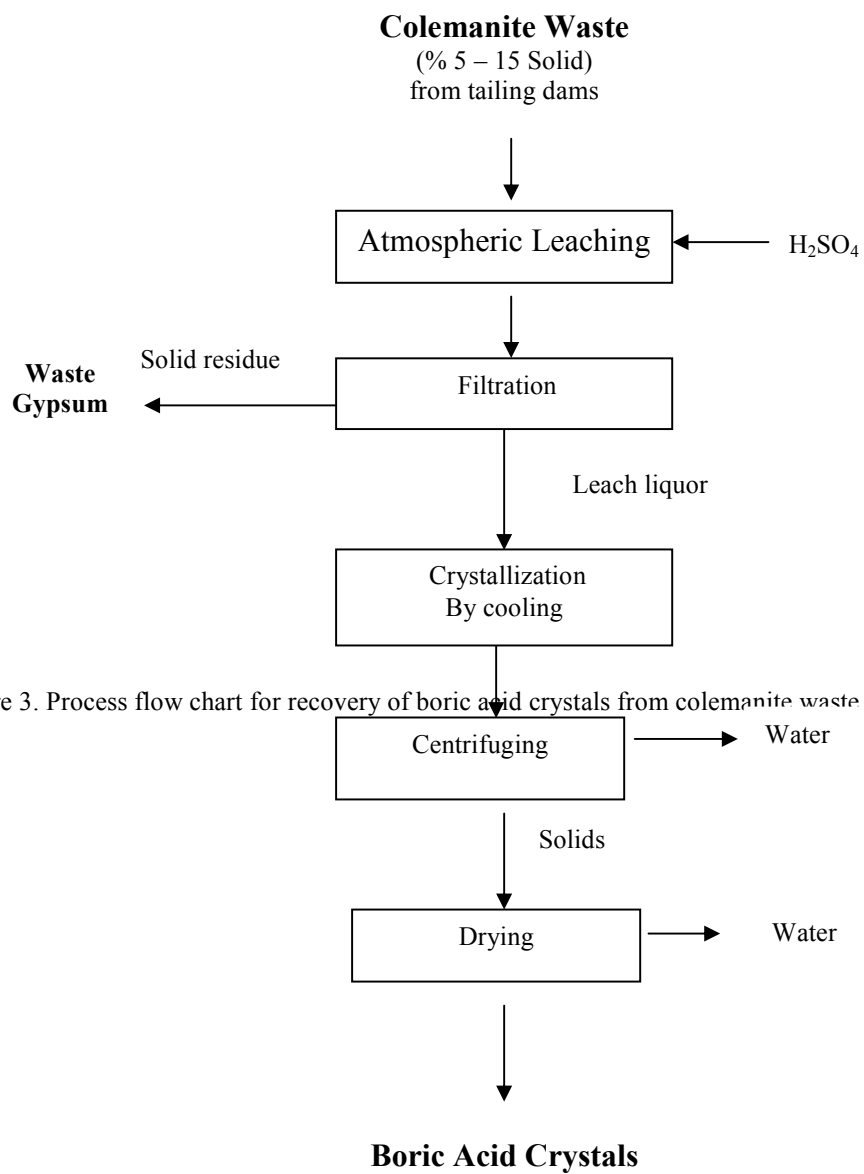


Figure 3. Process flow chart for recovery of boric acid crystals from colemanite waste

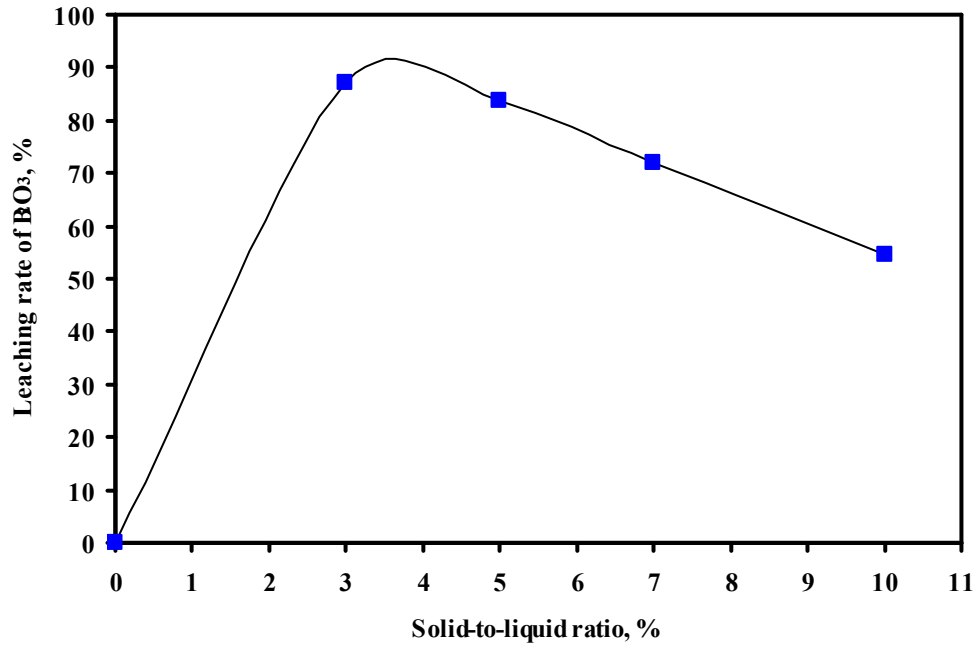


Figure 2. Effect of solid-to-liquid on leaching of waste.

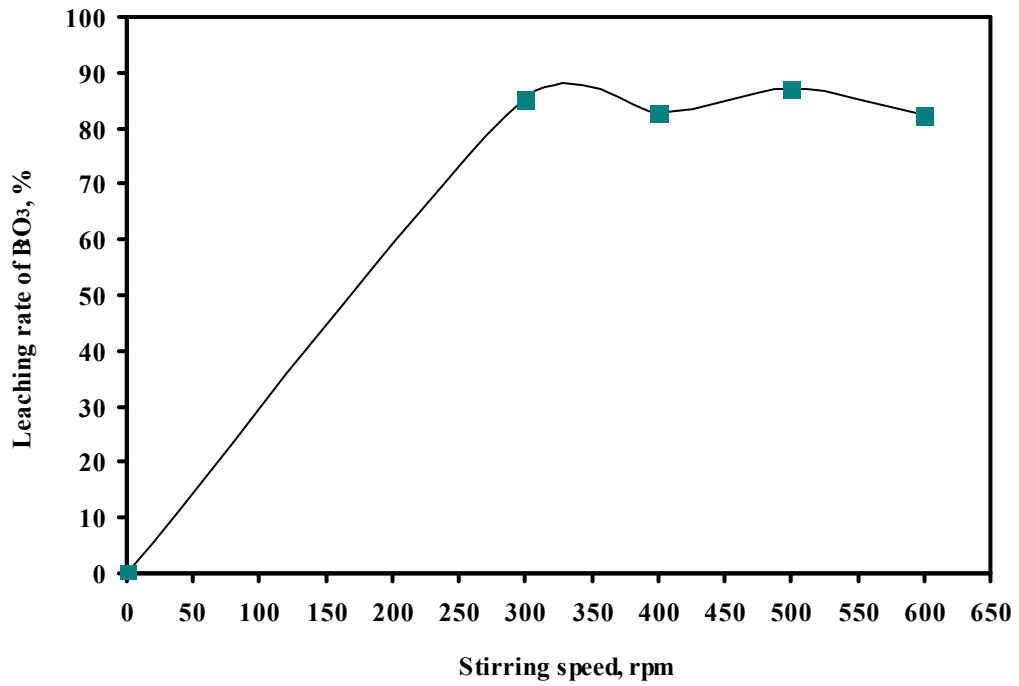


Figure 3. Effect of stirring speed on leaching of waste.

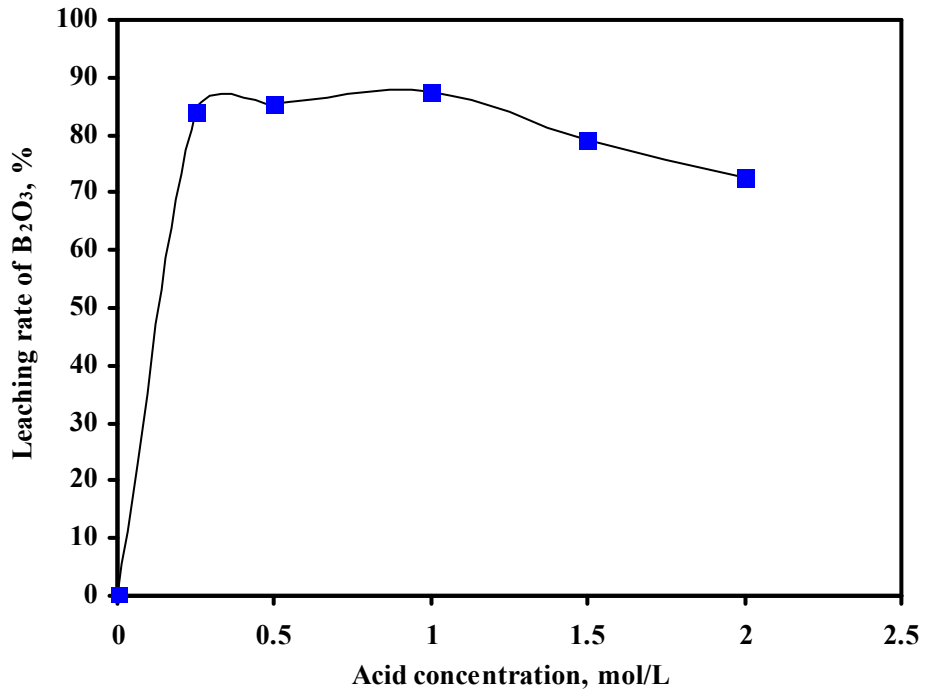


Figure 4. Effect of acid concentration on leaching of waste.

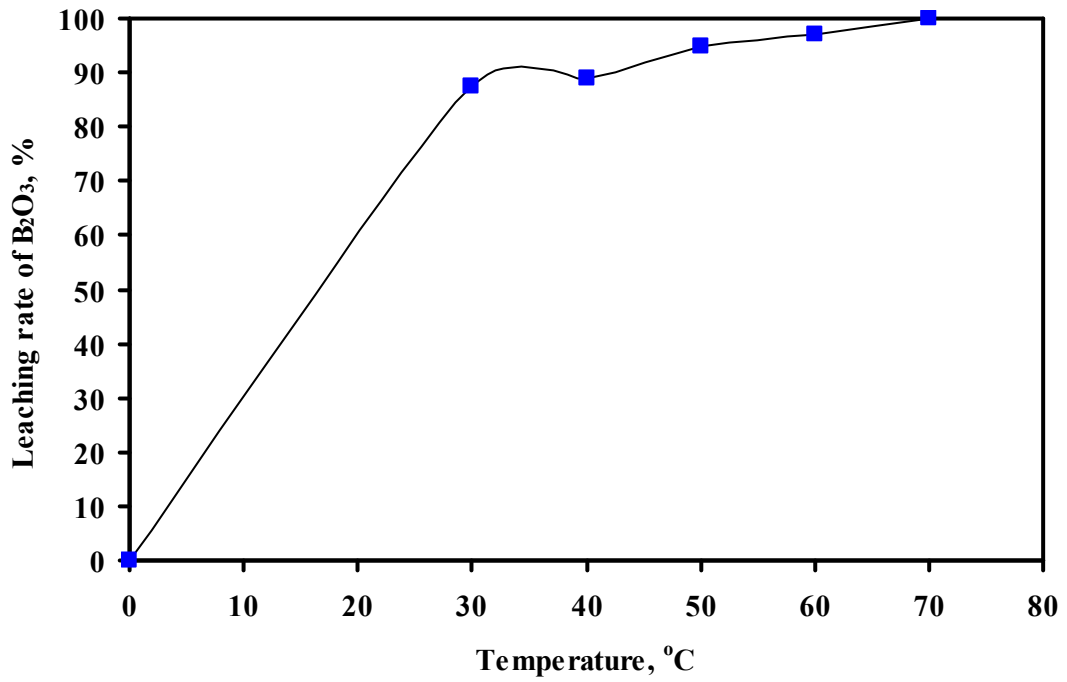
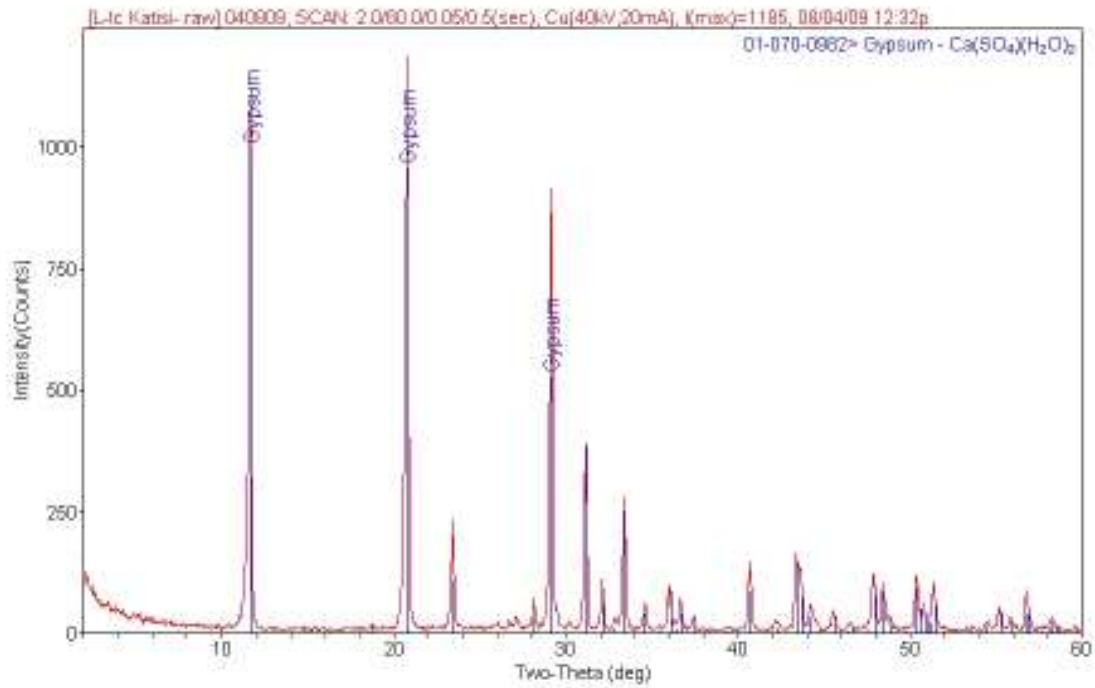


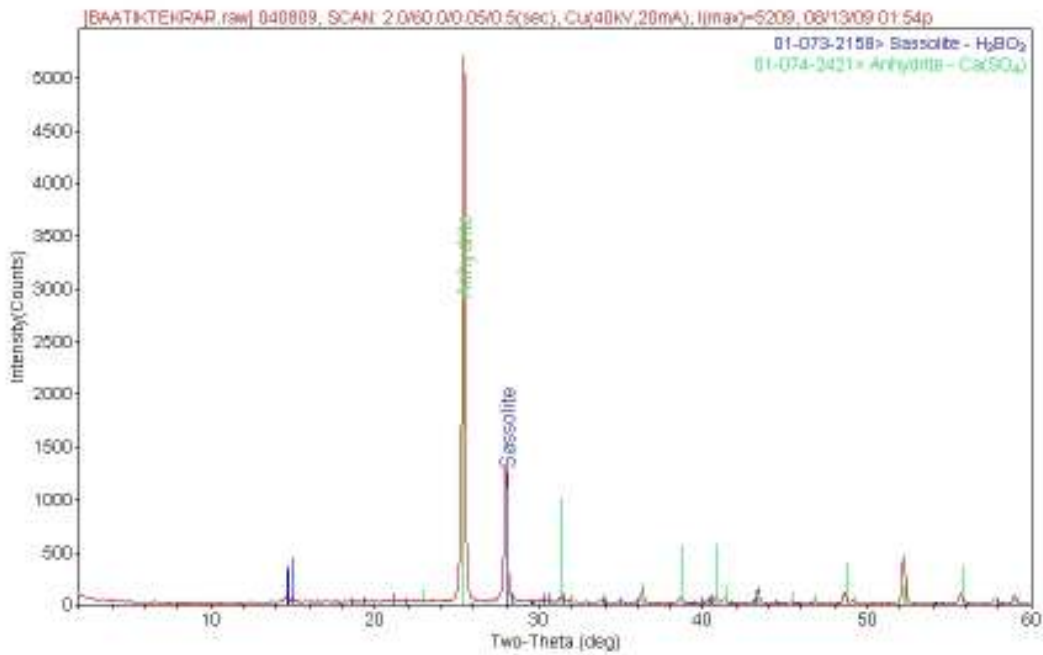
Figure 5. Effect of reaction temperature on leaching of waste.



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Figure 8. X-ray diffraction analysis of leaching solid residue (acid concentration of 1.0 mol/L, solid to liquid ratio of 5 %, speed of 500 rpm, for 30 minutes).



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Figure 9. X-ray diffraction analysis of crystallized liquid phase.

(acid concentration of 1.0 mol/L, solid to liquid ratio of 5 %, speed of 500 rpm, for 30 minutes).

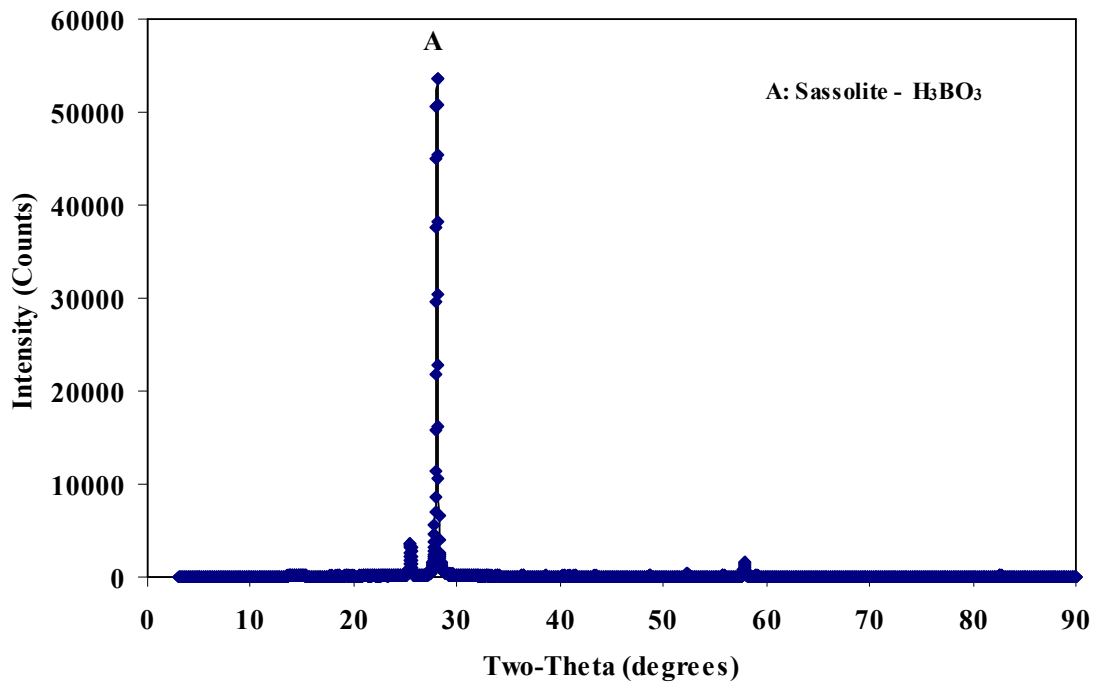
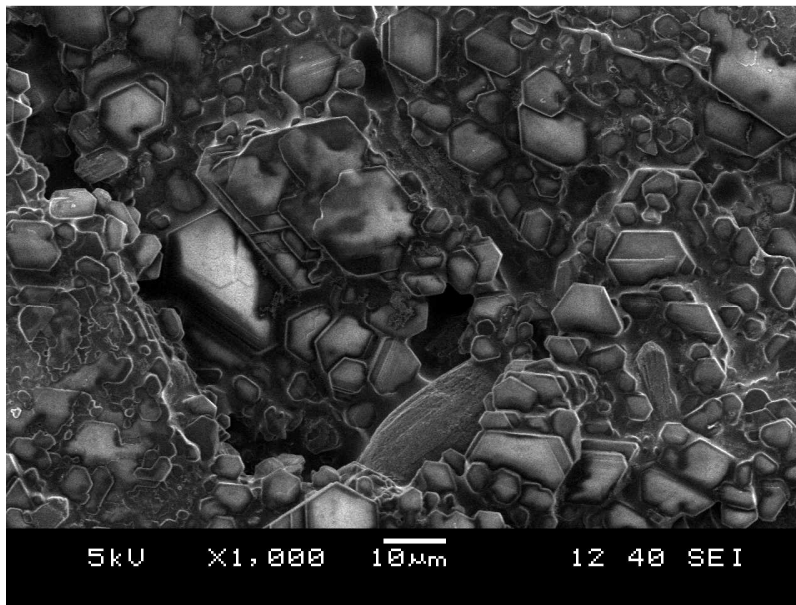
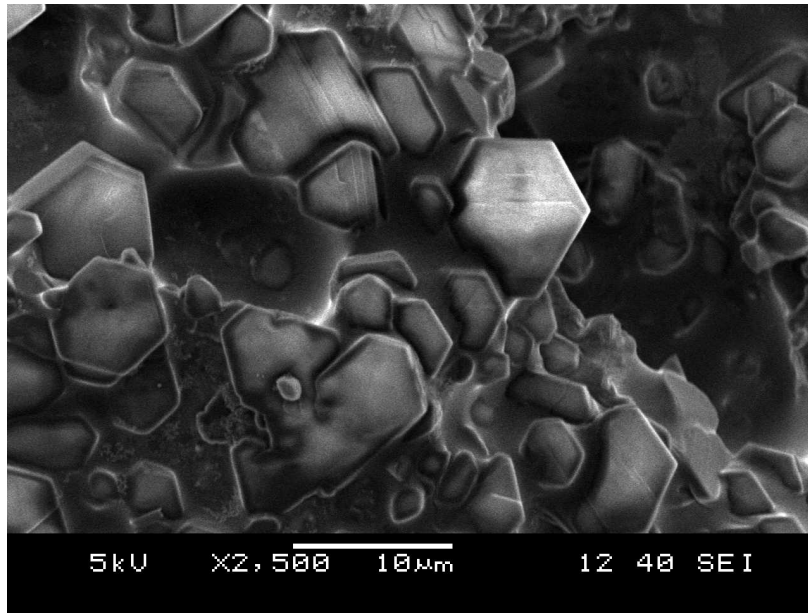


Figure 10. X-ray diffraction analysis of crystallized liquid phase for 120 min. (acid concentration of 1.0 mol/L, solid to liquid ratio of 5 %, speed of 500 rpm, for 120 minutes).



a)



b)

Figure 11. SEM images of crystal boric acid a) x1000 and b) x2500 (acid concentration of 1.0 mol/L, solid to liquid ratio of 5 %, speed of 500 rpm, for 120 minutes).