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LEACHING OF BORON FROM A COLEMANITE ORE IN SOME ORGANIC AND MIXED ORGANIC-AQUEOUS SOLVENT SYSTEMS

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ABSTRACT

In order to leach boron from colemanite ore (from Hisarcık (Kütahya)-Turkey), various organic and mixed organic–aqueous solvent systems have been considered, which are aqueous solutions of glycerol, ethylene glycol, ethanolamine and diethylene glycol in different concentrations. The highest percentage of boron leached has been achieved by water-glycerol system with 1:1 by volume. While 50.5 % of the B₂O₃ in colemanite has been extracted in acidic medium, it is found that the use of very strongly acidic medium is not necessary. Moreover, heating the leaching solution does not increase the percentage of boron leached, either.

Keywords: Leaching of Boron, Azomethine H Method, organic–aqueous solvent systems, glycerol, Colemanite.

1. INTRODUCTION

Colemanite is one of the hydrated boron minerals having the composition of Ca₂B₆O₁₁·5H₂O (Hydrated Calcium Borate Hydroxide). Others to be mentioned are borax Na₂B₄O₇·10H₂O, Boronatrocalcite (NaCaB₅O₉·8H₂O), hydroborocalcite (MgCaB₆O₁₁·6H₂O)

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and pandermite ($\text{Ca}_4\text{B}_{10}\text{O}_{19}\cdot 7\text{H}_2\text{O}$) [1]. Colemanite like other borates, is a complex mineral, that is found in playa lakes and other evaporite deposits. The basic structure of colemanite contains endless chains of interlocking $\text{BO}_2(\text{OH})$ triangles and $\text{BO}_3(\text{OH})$ tetrahedrons with the calciums, water molecules and extra hydroxides interspersed between the chains.

Turkey has 60 % of the world boron deposits in which its minerals are in the form of hydrated borates containing Ca, Mg, and Na. Colemanite is also found in California and Nevada in USA. In Chile colemanite ores are deposited near Bacos del Toro. Boron ores are used in glass, ceramics, soap, and detergent industries, in metallurgical and nuclear processes, and in the production of various boron compounds used in different industrial areas. Boric acid, borax, boric oxide, and refined hydrated sodium borates and perborates are important boron compounds economically.

Various studies have been carried out to produce boron compounds, especially boric acid and borax from boron ores. The dissolution kinetics of pure and clay-containing colemanite were studied in SO_2 -saturated water, and it was found that dissolution processes were chemically controlled for both cases. However, the former had a larger apparent activation energy than the latter [2,3]. In another study (Boncuğuoğlu et al.[4]), the evaluation of the reactor waste in borax production was investigated to recover B_2O_3 and therefore to reduce the toxic effect of the waste. Also, some of these studies include the production borax from colemanite by using NaCl and seawater,[5] boric acid from sulfuric acid and borax [6]. In addition, the dissolution of colemanite and other boron ores has been carried out in various acid solutions [7- 15].

Several complexing agents are commonly used for the spectrophotometric determination of boron in water including curcumin, carmine, and dianthrimide. However, their adaptation to automated procedures is not feasible because either evaporation to dryness or a strong acid medium is required prior to color development.

The condensation product of H acid (8-amino-1-naphthol-3,6-disulfonic acid) and salicylaldehyde, azomethine H, was used by Shanina et al.[16] for the determination of boron in complex boranes and boranes. Basson et al.[17] successfully adapted azomethine H into an automated procedure for the determination of boron in aqueous plant tissue extracts. Basson et al.[18] later incorporated an in situ preparation of azomethine H into the manifold to circumvent the time required for outside preparation of the complexing agent.

The purpose of this study was to adapt the azomethine H procedure for the routine determination of boron, leached from colemanite by a variety of organic solvents (glycerol, ethylene glycol, ethanolamine and diethylene glycol). The azomethine H method worked in a buffered system, is a good alternative to most attractive detection systems, such as, inductively coupled plasma (ICP-OES) spectrometry, with high sensitivity [19].

2. EXPERIMENTAL METHOD

Colemanite ore obtained from Hisarcık (Kütahya)-Turkey has a particle size of $150\ \mu$ and it is known to contain 39.4 % B_2O_3 . Table 1 displays the composition of the ore.

18.4 ppm boron stock solution has been prepared by dissolving 0.114 g of analytical reagent grade H_3BO_3 in water and diluting to 1 L. A series of standards in the concentration range from 1.84 to 9.22 ppm boron have been prepared by appropriate dilution of the stock with water. The boron stock and standard solutions can also be prepared from $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$.

The azomethine H solution has been prepared by dissolving 0.45 g of azomethine H and 1.0 g of ascorbic acid in water with gentle heating (50 °C) and stirring and diluting to 100 mL. This temperature is not critical and is used only to hasten dissolution of the reagents.

The buffer solution has been prepared by dissolving 250 g of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) and 15 g EDTA in a solution containing 400 mL water and 125 mL acetic acid. Ca, Mg and Fe which are present in the ore may interfere when boron is determined directly in samples. It is found that ascorbic acid and EDTA addition to the reaction system can be very effective in masking these ions and greatly improve the selectivity [20].

Table 1: Chemical composition of the colemanite ore used, %.

Composition	%	Composition	%
B_2O_3	39.4286	Fe_2O_3	0.6870
CaO	25.3863	As_2O_3	0.4294
Na_2O	0.3352	SiO	1.6958
MgO	2.4586	TiO_2	0.5078
Al_2O_3	1.2550	K_2O	0.6352
SiO_2	2.8674	BaO	0.0261
SO_3	1.2776	Moisture	0.3743

All chemicals must be analytical grade or better and deionized water has to be used to prepare all the solutions. Optimal results are obtained when the azomethine H solution is prepared fresh.

Boron concentrations were measured in 1.00-cm sample cells, at 420 nm, according to Azomethine H method [21,22] by a Shimadzu double beam UV-VIS spectrophotometer, Model UV 1601.

3. RESULTS AND DISCUSSIONS

It is known from the literature that, boron may be extracted as one of its organic complexes such as (a) the boron-2-ethyl-1,3-hexanediol complex of boron into chloroform or benzene,[23,24] (b) the 2,4-dinitro-1,8-naphthalenediol complex of boron into toluene,[25] or (c) the complex of boron with a 24% solution of 2,4-dimethyl-2,4-octanediol into isopentanol [26].

In the present study, boron has been leached from colemanite, by the application of different aqueous-organic solvent systems, such as, glycerol (**G**), ethylene glycol (**EG**), ethanolamine (**EA**) and diethylene glycol (**DEG**). The determination of the amount of extracted boron has been measured by the application of the azomethine H method, which is reported to give no significant differences with the high cost spectroscopic methods, like ICP-OES spectrometry [27]. The detection limit for the Azomethine-H method has been found to be 1.5 % B_2O_3 , the present case.

Presently, three parameters have been considered for the design of the leaching process from colemanite. These are (i) Type of the organic solvent and the solvent/water ratio, (ii) Acidity of the leaching solution, (iii) Temperature of the leaching medium.

(i) The effects of solvent and organic solvent/water ratio on the leaching

At first, the leaching experiments have been performed with aqueous (water only) and organic (glycerol only) solvent systems. The amount of extracted boron has been increased from 15.9 % to 26.6 %, by the use of glycerol as the leaching solvent. However, mixing of the leaching solution was difficult in the case of glycerol, due to its very viscous character. Therefore, aqueous-organic solvent mixture systems were used.

Another important parameter in leaching of boron from colemanite was the organic solvent/water ratio. The achievement of the same leaching of boron with lower organic solvent ratios would be more economic for industrial applications. Therefore, boron leaching experiments have been performed with different water/organic solvent ratios and the results have been reported in Table 2. But unfortunately, lowering the ratio of the organic component in the leaching solution leads to decrease in the percentage of boron leached for all cases.

Table 2: Effect of acidity of the leaching solution on the leaching of boron^a.

	EG	G	EA	DEG
No acid	10.6 ± 0.03	26.6 ± 0.01	4.0 ± 0.02	14.9 ± 0.03
10⁻² M HCl	20.2 ± 0.02	50.5 ± 0.02	7.3 ± 0.04	23.5 ± 0.01
1.2 M HCl	20.4 ± 0.03	50.9 ± 0.03	7.4 ± 0.03	23.9 ± 0.02

a: Average of five measurements.

Table 3: Effect of aqueous/organic solvent ratio on the percentage of boron leached (at 1 hour mixing)^a.

Organic Solvent	% Organic Component			
	100	50	30	20
G	26.6 ± 0.01	50.5 ± 0.03	38.8 ± 0.02	35.2 ± 0.05
DEG	13.4 ± 0.04	23.5 ± 0.04	18.2 ± 0.02	12.3 ± 0.02
EG	16.1 ± 0.02	15.6 ± 0.02	14.4 ± 0.01	12.9 ± 0.01
EA	2.5 ± 0.01	7.3 ± 0.01	3.2 ± 0.02	0.9 ± 0.01

a: Average of five measurements

In the rest of the study, all the experiments have been performed with the aqueous solutions of the organic solvents with 1:1 ratio (see Table 2).

After the achievement of an increase in the percentage of boron leached by glycerol, other alcoholic organic solvents (ethylene glycol, ethanolamine and diethylene glycol) have

been considered as the organic component of the leaching solution. Among the four organic solvents considered, maximum and minimum the percentage of boron leached have been observed in the cases of glycerol and ethanolamine, respectively (see Table 3).

(ii) The effect of HCl concentration on the leaching

It is well known from the theoretical literature that leaching performance becomes greater in acidic solutions [3,28]. Therefore, the leaching solutions were acidified with the use of different amounts of concentrated HCl. Acidifying the leaching solution has effectively increased the percentage of boron leached and the amount of leached boron has been increased almost double. However, making the solution more and more acidic than 10^{-2} M, had a very little effect on the amount of leached boron (see Table 2). Figure 1 shows the graph for the amount of B_2O_3 vs. time for the four solvents used at 10^{-2} M HCl concentration.

Figure 1: Effect of the type of the organic solvent on the percentage of boron leached at 10^{-2} M HCl concentration. (2.5 g colemanite is mixed in 50 mL of solution which is 1:1 organic solvent-aqueous mixture).

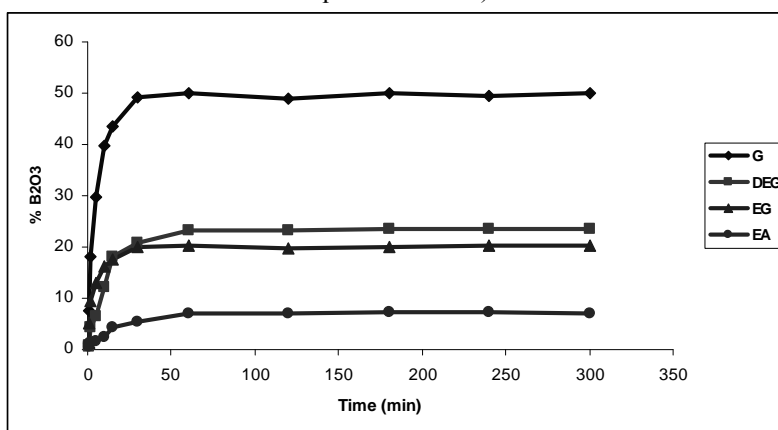
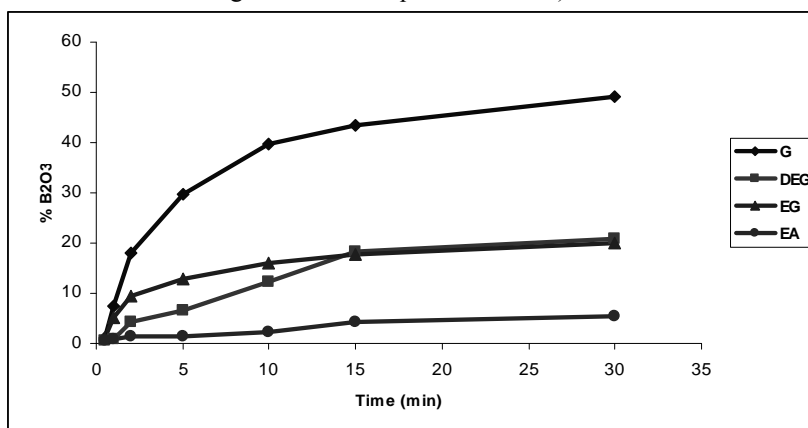


Figure 2: Effect of the type of the organic solvent on the percentage of boron leached at 10^{-2} M HCl concentration (at initial times). (2.5 g colemanite is mixed in 50 mL of solution which is 1:1 organic solvent-aqueous mixture).



As can be seen from the figure, water-glycerol (in 10^{-2} M HCl) system has been found to be the best among all for the leaching of boron from the colemanite ore samples. Figure 2 shows the change in the amount of B_2O_3 leached at initial times.

(iii) Effect of temperature on the leaching of boron

Increasing the temperature of a solution will lower the intermolecular attraction (hydrogen bonding in this case) between solvent molecules. This may result in lowering the viscosity of the leaching solution and the problems with mixing the leaching solution would be overcome. Thus, the present leaching experiments have been performed at 25 °C and 60 °C. The percentage of boron leached at 60 °C has been found to be slightly higher than that of leaching at 25 °C.

4. CONCLUSIONS

In the present study, leaching of boron from colemanite ore has been performed with different aqueous-organic solvent systems. The azomethine H method has been used for the determination boron. The detection limit for this method is found to be 1.5 % B_2O_3 . The results showed that, glycerol-water system is the best solvent to leach boron from colemanite. The amount of B_2O_3 extracted from colemanite has been reached to 50.5 % with the glycerol-water system while 23.5 %, 15.6 % and 7.3 % leaching has been achieved by the use of **DEG**, **EG** and **EA**, respectively.

It is necessary to perform the leaching process in acidic medium. However, it is found to be unnecessary to use very strongly acidic solutions. The ratio of the aqueous and organic components is important, since the decrease of the percent of the organic solvent decreases the percentage of boron leached and the increase of the percent of the organic solvent increases the cost of leaching process for the industrial applications. The maximum percentage of boron leached has been achieved when the ratio of the organic-aqueous mixture is 1:1 by volume.

During the design of the experiments, the viscosity problem of organic components has been thought to be overcome by heating the leaching solution. But then, it is found that leaching process at higher temperatures is not essential, since the viscosity problem has been solved by mixing the organic solvents with water.

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REFERENCES

1. Betekhtin A.; A Course of Mineralogy, Mir Pub. Moscow, **1970**.
2. Kocakerim M.M.; Alkan M. Dissolution kinetics of colemanite in SO_2 saturated water. *Hydrometallurgy* **1988**, *19*, 385-392.

3. Küçük Ö.; Kocakerim M.M., Yartaşı A., Çopur M. Optimization of dissolution of ulexite saturated with sulphur dioxide. *Ind. Eng. Chem. Res.* **2002**, *41*, 2853-2857.
4. Boncukçuoğlu R.; Kocakerim M.M., Erşahan H. Upgrading of the reactor waste obtained during borax production from tincal. *Miner. Eng.* **1999**, *12*, 1275-1280.
5. Lynn L.; *Borax, Ger. Offen.* 2, 337, 506 A1 19740221, *Chem Abs.* **1974**, *81*, 5128e.
6. Dinu G.; Mohai S., Adam I. Boric Acid from Borax. *Rom.* 67, 967, *Chem. Abs.* **1979**, *94*, 194376m.
7. Davies T.W.; Çolak S., Hooper R.M. Boric Acid Production by The Calcination and Leaching of Powdered Colemanite. *Powder Technol.* **1991**, *65*, 433-440.
8. Imamutdinova V.M.; Rate of borate dissolution in acetic acid solutions. *Zh. Prikl. Khim.* **1970**, *43*, 452-5.
9. Kononova G.N.; Nozhko E.S. Nature of the sulfuric acid dissolution of magnesium borates. *Zh. Prikl. Khim.* **1981**, *54*, 397-9.
10. Alkan M. M.; Kocakerim M.M., Çola S. Dissolution kinetics of colemanite in water saturated by carbon dioxide. *J. Chem. Technol. Biotechnol.* **1985**, *35A*, 382-6.
11. Tunç M.; Kocakerim M.M., Gür A., Yartaşı A., A semi-empirical kinetic model for dissolution of ulexite in aqueous acetic acid solutions. *Energy, Educ., Sci. Technol.* **1999**, *3*, 1-10.
12. Tunç M.; Gür A., Kocakerim M.M., Yartaşı A., Dissolution of ulexite in sulphuric acid solutions for high solid-to-liquid ratios. *Energy, Educ., Sci. Technol.* **1999**, *3*, 32-41.
13. Morales G.V., Capretto M.E., Fuentes L.M., Quiraga O.D. Dissolution kinetics of hydroboracite in water saturated with carbon dioxide. *Hydrometallurgy* **2000**, *58*, 127-133.
14. Demirbaş A.; Recycling of lithium from borogypsum by leaching with water and leaching kinetics. *Resour., Conserv. Recycl.* **1999**, *25*, 125-131.
15. Erdoğan Y.; Aksu A., Demirbaş, Abalı Y. Analyses of boronic ores and sludges and solubilities of boron minerals in CO₂-saturated water. *Resour., Conserv. Recycl.* **1998**, *24*, 275-283.
16. Shanina T.M.; Gelman N.E., Mikhailovskaya V.S., Quantitative analysis of organometallic compounds. Spectrophotometric microdetermination of boron. *Fresenius' Zeitschrift fuer Analytische Chemie* **1967**, *22*, 782-7.
17. Basson W.D.; Bohmer R.G., Stanton D.A. An automated procedure for the determination of boron in plant tissue, *Analyst.* **1969**, *34*, 1135-1141.
18. Basson W.D.; Pille P.P., Du Preez A.L. Automated in situ preparation of azomethine H and the subsequent determination of boron in aqueous solution. *Analyst* 1974, *99*, 168-170.
19. Evans S.; Krahenbuhl U., Boron analysis in biological material: microwave digestion procedure and determination by different methods. *Fresenius J. of Anal. Chem.* 1994, *349*, 454-549.
20. Saygıdeğer Demir B.; Serindağ O. Determination of boron in grape (*Vitis vinifera*) by Azomethine H spectrophotometric method *Eurasian J. of Anal. Chem.* 2006, *1*, 1.
21. John M.K.; Chuah H.H., Neufeld J.H., Application of improved Azomethine-H method to the determination of boron in soils and plants. *Analytical Letters* 1975, *8*, 559-568.

22. Wolf B.; Determination of boron in soil extracts, plant materials, composts, manures, water and nutrient solutions. *Soil Science and Plant Analysis* 1971, 2, 363-374.
23. Agazzi E.J.; Extraction-flame photometric determination of boron. *Anal. Chem.* 1967, 39, 233-5.
24. Mezger G., Grallath E., Stix U., Tolg G., Bestimmung von borspuren in metallen durch emissionsspektrometrie mit ICP-Anregung nach abtrennung als borsäure-ester. *Fresenius Z., Anal. Chem.* 1984, 317, 765-773.
25. Kuwada K.; Motomizu S., Toei K. Solvent extraction-spectrophotometric determination of boron with 2,4-dinitro-1,8-naphthalenediol and Brilliant Green. *Anal. Chem.* 1978, 50, 1788-92.
26. Panov V.A.; Semenko K.A., Kuzyakov Y.Y. Extraction-flame molecular emission spectrometric determination of boron with pulsed nebulization of extract. *Zhurnal Analiticheskoi Khimii* 1989, 44, 1382-7.
27. Şimşek A.; Korkmaz D., Veliöglu Y.S., Ataman O.Y. Determination of boron in hazelnut (*Corylus avellana* L.) varieties by inductively coupled plasma optical emission spectrometry and spectrophotometry. *Food Chem.* 2003, 83, 293-296.
28. Türker L. ; Some boric acid esters of glycerol - an ab initio treatment. *Ind. J. of Chem.* 2006, 45A, 1339-1344.