Korean J. Chem. Eng., **24**(4), 588-591 (2007)

SHORT COMMUNICATION

Dissolution mechanism of colemanite in sulphuric acid solutions

Aycan Gür†

Yuzuncu Yil University, Faculty of Science and Art, Department of Chemistry, 65100, VAN-TURKEY

(*Received 10 November 2006 • accepted 20 December 2006*)

Abstract−Boron compounds are very important raw materials in many branches of industry and their uses have been increasing and expanding continuously. Colemanite, one of the most common boron minerals, has a monoclinic crystal structure with a chemical formula of $2CaO\cdot 3B_2O_3\cdot 5H_2O$ and is used usually in the production of boric acid. The present study concerns an investigation of the dissolution mechanism of colemanite in H_2SO_4 solution and the effect of acid concentration, the effect of SO_4^{-2} ion on the dissolution process, using H_2SO_4, $HCI+H_2SO_4$ and $H_2SO_4+Na_2SO_4$ solutions. 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 $CaSO_4\cdot H_2O$.

Key words: Boron Minerals, Colemanite, Dissolution Mechanism

INTRODUCTION

Boron is available as B_2O_3 together with the oxides of same other elements in nature. The most common borates are sodium, calcium and sodium-calcium borates. These boron compounds are called borates. Boron is never found free in nature but invariably occurs as its oxide, B_2O_3, in combination with the oxides of the other elements forming borates of complexity. Boron compounds used in many branches of industry are produced from boron-containing ores [1].

In the boron reserves, colemanite is one of the most important underground riches of Turkey, which has approximately 60% of the world boron deposits, and colemanite has a large portion in these deposits. When colemanite is mined naturally, it contains various clay minerals. Huge portions of the Turkey's commercially recoverable boron reserves are colemanite, ulexite and tincal. Colemanite has a monoclinic crystal structure with a chemical formula of $2CaO\cdot 3B_3O_3\cdot 5H_2O$. Although the boron is not used directly, its compounds are widely consumed in the production of glass, fibers, heat resistant materials, material processing, nuclear reactors, fire retardants, catalysis and detergents, etc. [2] Colemanite is available in huge amounts together with some other borates in the Balikesir-Bigadic and Kütahya-Emet regions in Turkey [3]. The increasing demand and new industrial use of boron compounds have increased their importance and these compounds have been used as raw material in various areas of industry.

Some researchers have studied the dissolution of colemanite in H_2SO_4, H_3PO_4, HCI and HNO_3 solutions. The dissolution process in these solutions was found to be diffusion controlled, and HNO_3 solution gave the highest dissolution rate while H_2SO_4 solution gave the lowest. In the case of H_2SO_4 solution, it was claimed that the diffusional process was affected negatively by the formation of $CaSO_4\cdot 2H_2O$ [4]. Some studies on the use of ammonium salt for the leaching ores are found in literature. Dissolution of colemanite in $(NH_4)_2SO_4$ was investigated and it was seen that when the concentration of SO_4^{-2} increases the dissolution rate decreases [5]. Dissolution kinetics of of Calcined ulexite in ammonium chloride solutions and dissolution kinetics of calcined ulexite in ammonium chloride solutions at high solid-to-liquid ratios were investigated [6,7]. Furthermore the Taguchi method was used to determine optimum conditions for the dissolution of ulexite in NH_4CI solution [8]. Ammonium carbonate solutions were used as leachant for malachite, because basic ores often consume acids, and therefore a basic matter more lixiviant than sulphuric acid, may be attractive [9]. In another study the leaching of malachite with ammonium sulphate solutions has been investigated [10]. The leaching of magnesite with ammonium chloride solution has also been investigated [11].

The dissolution of ulexite was investigated in acetic acid solutions, and found that the dissolution rate was maximum at relatively low acid concentration (10-20 wt%) and over this concentration the dissolution rate decreased. It was also reported that the process was controlled by diffusion [12]. Work carried out on the dissolution of ulexite in H_3PO_4 solution reported that in the dissolutions of ulexite in 5 wt% H_3PO_4 solutions H_3BO_3 solid film formed on crystals; this restricted the dissolution rate of the mineral [13]. The dissolution of ulexite in perchloric acid solutions [14] and NH_3 solutions saturated with CO_2 [15] was reported to be diffusion controlled. In the studies in which the dissolution of ulexite in aqueous SO_2 and CO_2 solutions were investigated, it was claimed that the dissolution rate process was found to be diffusion-controlled in CO_2 solutions while it was chemical reaction-controlled in SO_2 solution [16-19]. In the other work the dissolution kinetics of colemanite in oxalic acid solutions was studied and it was found that the dissolution rate was controlled by product layer (ash layer) diffusion process; the activation energy of the process was to be 9.50 cal mol^{-1} [20]. Despite these dissolution studies in acidic solutions, no detailed study on dissolution of colemanite has been found in the literature. For this reason, the purpose of this present work was to clarify the dissolution process of colemanite in H_2SO_4 solutions.

EXPERIMENTAL

---

†To whom correspondence should be addressed.
E-mail: aycangurbor@yahoo.com

Table 1. Chemical composition of the colemanite sample used in the study

Main mineral	Percent
CaO	25.34
B_2O_3	47.27
H_2O	20.37
SiO_2	4.11
Al_2O_3	0.80
Fe_2O_3	0.37

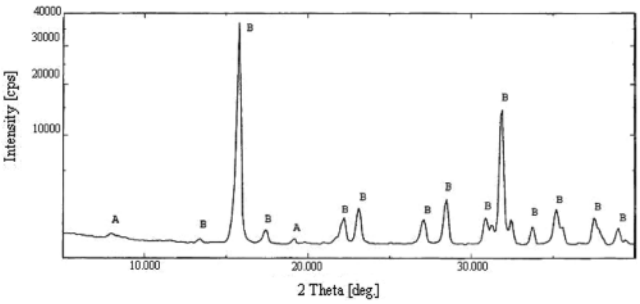

Fig. 1. X-Ray diffractogram of colemanite ore: (A) SiO_2; (B) $Ca_2B_6O_{11}\cdot 5H_2O$.

1. Preparation of Materials

Colemanite mineral used in the experimental study was provided from the Kütahya-Emet region in Turkey. After the mineral was manually cleaned from the visible impurities, it was crushed then ground, followed by sieving, using ASTM standard sieves, to obtain a particle size fraction of –600+425 μm. The chemical analysis and X-Ray diffractogram of the sample are given in Table 1 and Fig. 1, respectively.

2. Apparatus and Procedure

Dissolution experiments were carried out in a 250 ml-spherical glass vessel at atmospheric pressure. For stirring the reactor contents a mechanical stirrer was used, and thermostat was employed to keep reaction medium at constant temperature. To avoid the loss of reactor content by evaporation, a reflux cooler was attached to the reactor.

In the dissolution experiment, 100 ml of H_2SO_4 solution was first put into the reactor and after reaching a desired temperature, a given amount of simple was added to solution and stirring was started. At the of the reaction period, the stirring was stopped and the reactor contents were filtered off. The B_2O_3 content of the filtrate was determined by a potentiometer method [21]. The dissolution fraction was calculated as follows:

$$XB_2O_3\text{=the amount of dissolved } B_2O_3 \text{ /the amount of } B_2O_3 \text{ in original sample}$$

RESULTS AND DISCUSSION

1. Dissolution Reactions

H_2SO_4, used in the dissolution process, gives the following reaction in aqueous medium:

$$H_2SO_4(aq)+H_2O(s)\rightarrow HSO_4^-+H_3O^+(aq) \quad (1)$$

$$HSO_4^-(aq)+H_2O(s)\rightarrow SO_4^=+H_3O^+(aq) \quad (2)$$

The equilibrium constant of reaction (2) is Ka=0.012. It is suggested that when ulexide is added to this solution the following reaction takes place:

$$2CaO\cdot 3B_2O_3\cdot 5H_2O(s)+4H_3O^+(aq) \rightarrow 2Ca^{+2}(aq)+6H_3BO_3(aq)+2H_2O(s) \quad (3)$$

When Ca^{+2} concentrations reaches a limiting value determined by the solubility product

$$[Ca^{+2}][SO_4^{-2}]=Ksp \quad (4)$$

This gives the following reaction with ion formed via reaction (2)

$$Ca^{+2}(aq)+SO_4^{-2}(aq)\rightarrow CaSO_{4(s)} \quad (5)$$

Thus, a solid precipitate is formed. Finally, the dissolution reaction of colemanite in H_2SO_4 solution can be written as:

$$2CaO\cdot 3B_2O_3\cdot 5H_2O_{(s)}+2H_2SO_{4(aq)}+2H_2O_{(s)} \rightarrow 2CaSO_{4(s)}+6H_3BO_{3(aq)} \quad (6)$$

2. The Effect of H_2SO_4 Concentration on Dissolution Rate

The effect of the H_2SO_4 concentration on dissolution rate was investigated by using the acid concentration of 0.50, 0.75, 1,00 and 2.00 mol·l^{-1}. In the experiments, the dissolved amount of the mineral was determined at the reaction temperature of 35 °C, solid-to-liquid ratio of 1/100 (g/ml) and stirring speed of 41, 87 s^{-1}. The experimental results exhibited in Fig. 2 show that the dissolution decreased with increasing H_2SO_4 concentration. This finding can be explained by the increase in the formation of SO_4^{-2} ion per unit volume with increasing acid concentration. This leads to the occurrence of reaction (5), that is, precipitation of solid $CaSO_4$ and $CaSO_4\cdot 2H_2O$ on the particle surface. This solid side-product layer creates difficulty for H_3O^+ ion to diffuse to the mineral, decreasing the dissolution rate of the sample.

The X-ray diffractogram of the solid sample, subjected to the dissolution process with H_2SO_4 solution of 0.50 mol·l^{-1} for 30 min for ulexite mineral, confirmed the occurrence of reaction (5). In addition, X-ray diffractogram of the sample subjected to dissolution at a solid-to-liquid rate of 5/100 (g/ml) showed the formation of $CaSO_{4(s)}$ and $CaSO_4\cdot 2H_2O_{(s)}$ [22].

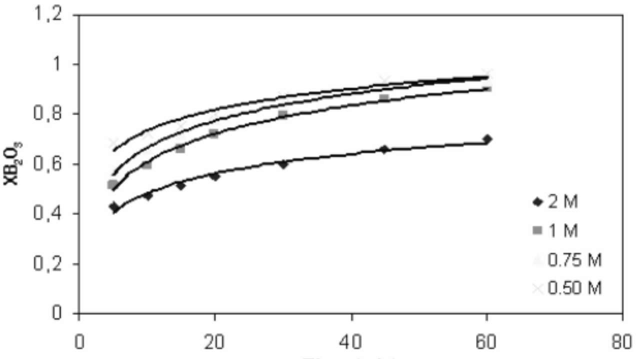

Fig. 2. The effect of the solution concentration on dissolution fraction.

Table 2. Effect on the conversion rate of HCI, H_2SO_4, H_2SO_4+HCI, and H_2SO_4+Na_2SO_4 solutions

Compound of solution	Time (min)	B_2O_3 in the solution (mg)	Conversion ratio (XB_2O_3)	CaO in the solution (mg)	Conversion ratio (XCaO)
1 $mol\cdot l^{-1}$ HCI	5	430,7	0.9080	242,6	0.8987
	15	458,0	0.9663	258,7	0.9579
	30	469,8	0.9911	269,8	0.9990
2 $mol\cdot l^{-1}$ HCI	5	407,2	0.8589	230,3	0.8530
	15	422,8	0.8910	239,0	0.8849
	30	428,5	0.9248	252,6	0.9355
2 $mol\cdot l^{-1}$ H_2SO_4	30	304,1	0.6008	42,1	0.1562
2 $mol\cdot l^{-1}$ H_2SO_4+1 mol^{-1} HCI	30	324,9	0.6855	54,1	0.2006
2 $mol\cdot l^{-1}$ H_2SO_4+2 mol^{-1} Na_2SO_4	30	211,4	0.4459	24,6	0.0910

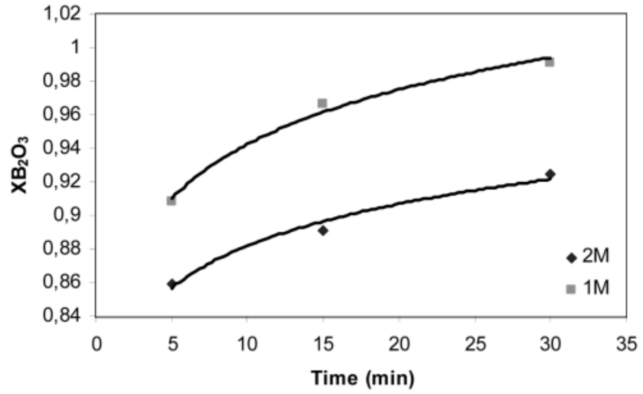

Fig. 3. Effect of HCI concentration on dissolution fraction.

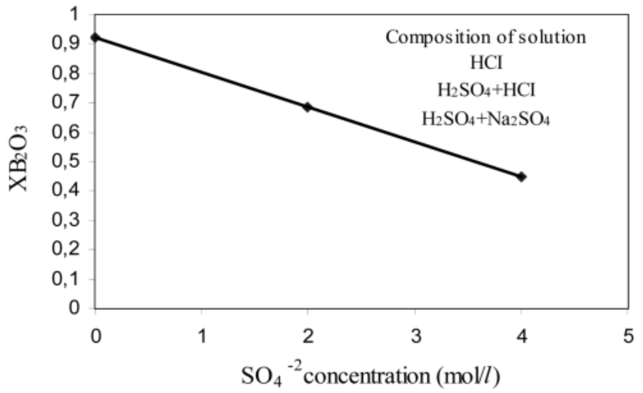

Fig. 4. Effect of SO_4^{-2} concentration on dissolution fraction.

3. Dissolution Rate in HCI Solutions

The effect of the HCI solution on the dissolution of colemanite was investigated for experimental conditions of the particle size of –600+425 μm, reaction temperature of 35 °C, stirring speed of 41.87 s^{-1}, solid-to-liquid rate of 1/100 (g/ml), and HCI concentration of 1 and 2 $mol\cdot l^{-1}$. As seen from Table 2 and Fig. 3, increasing the HCI concentration increased the formation of the solid H_3BO_3 product layer on the surface of the mineral, and this caused slowing down of the diffusion of H_3O^+ ion to the undissolved part of the mineral. Therefore, this situation prevented the dissolution of the mineral reaching 100%.

When the dissolution of the mineral in HCI solution is compared with the mineral in H_2SO_4 solution at the same concentration, it can be seen that almost 92.48% dissolution was reached in 30 min for HCI solution, while the dissolution process with H_2SO_4 solution has 60.08%. Therefore, it was concluded that the negative effect of the $CaSO_4$ and $CaSO_4\cdot 2H_2O$ solid film formed of the surface is much more pronounced that the H_3BO_3 film. The result showed that almost all of CaO in the mineral dissolved in HCI solution, while Ca^{2+} ions partly converted to $CaSO_4$ and/or $CaSO_4\cdot 2H_2O$ in the case of H_2SO_4 solutions.

4. The Effect of HCI, H_2SO_4+HCI and H_2SO_4+Na_2SO_4 Solutions on the Dissolution

To understand the effect of SO_4^{2-} concentration on the solubility, some experiments were carried out with the solutions of 2 $mol\cdot l^{-1}$ H_2SO_4+1 $mol\cdot l^{-1}$ HCI and 2 $mol\cdot l^{-1}$ H_2SO_4+2 $mol\cdot l^{-1}$ Na_2SO_4 solution, keeping other experimental parameters constant. The best result was obtained with a solution of 2 $mol\cdot l^{-1}$ H_2SO_4+1 $mol\cdot l^{-1}$ HCI, followed by a solution of 2 mol^{-1} H_2SO_4, and lowest dissolution was obtained with a solution of 2 $mol\cdot l^{-1}$ H_2SO_4+2 $mol\cdot l^{-1}$ Na_2SO_4.

The experimental results are shown in Table 2 and in Fig. 4. These show that the dissolution decreased as the concentration of SO_4^{2-} ions increased. These results clarified the tendency of the formation of $CaSO_4$ and/or $CaSO_4\cdot 2H_2O$ as the concentration of SO_4^{2-} ions increases. Of all the solutions, the 2 mol^{-1} H_2SO_4+1 $mol\cdot l^{-1}$ HCI solution had the minimum SO_4^{2-} concentration, since the presence of HCI caused reaction (2) to shift to the left, reducing SO_4^{2-} concentration. Therefore, the dissolution in this case was much more than in the other solution. The reason why the 2 mol^{-1} H_2SO_4 dissolution is less than the first solution can be explained by higher SO_4^{2-} concentration. In the case of the third solution, the SO_4^{2-} concentration was the highest of all solutions; thus the precipitation of $CaSO_4$ and $CaSO_4\cdot 2H_2O$ film is much more pronounced.

These result proved how important the formation of this side-product is to the dissolution process. When further experiments with 1 $mol\cdot l^{-1}$ HCI solutions for 30 min are compared with results of three solutions, it is seen that this solution gave better results than the solution of 2 mol^{-1} H_2SO_4+1 mol^{-1} HCI solution since it has no SO_4^{2-} ion, and this confirms the conclusion above. X-ray diffractogram analysis showed that both $CaSO_4$ and $CaSO_4\cdot 2H_2O$ formed on surface [22]. The dissolution of magnesium borates in H_2SO_4 solution was investigated and it suggested that the dissolution took place as a result of H_3O^+ ion to the mineral surface and the protonation of the boron-oxygen [23].

When taking into consideration this explanation and tendency of the present study, the dissolution process can be shown according to the following reaction:

$$B_5O_9^{3-}+3H_3O^{+}+3H_2O \rightarrow 5H_3BO_3 \tag{7}$$

In case of a shortage of water in the medium, the following reaction occurs:

$$Ca^{2+}_{(aq)}+SO^{2-}_{4(aq)} \rightarrow CaSO_{4(s)}$$

In case of the availability of enough water, the following reaction takes place:

$$Ca^{2+}_{(aq)}+SO^{2-}_{4(aq)}+2H_2O_{(l)} \rightarrow CaSO_4 \cdot 2H_2O_{(s)} \tag{8}$$

Consequently, it can be concluded that $CaSO_4$ crystals formed simultaneously with H_3BO_3 crystals result in higher diffusional resistance to the diffusion of H_3O^+ to the mineral surface than the case of only H_3BO_3 crystals.

CONCLUSIONS

The present study has explained the dissolution process of colemanite in H_2SO_4 solution. It was seen that increasing H_3O^+ concentration increased the dissolution, and that increasing SO_4^{2-} concentration decreased the dissolution due to the formation of $CaSO_4$ and/or $CaSO_4 \cdot 2H_2O$ which substantially slowed down the diffusion of H_3O^+ ion to the mineral surface. The effect of $CaSO_4$ and $CaSO_4 \cdot 2H_2O$ in diffuse anal resistance to H_3O^+ ion is much more pronounced than that of solid H_3BO_3 crystals precipitated as a thin film on the surface.

NOMENCLATURE

x : fraction of solid reacted
T : temperature [°C]
C : concentration of solution [mol·l^{-1}]
t : reaction time [min]

REFERENCES

1. H. P. Kemp, *The chemistry of borates: Part I*, Borax Consolidated Ltd., London (1956).
2. D. E. Garred, *Borates*, Academic Press, New York, 421 (1998).
3. M. Polat, Turkiye'de ve Dunya'da Bor ve Bor Teknolojisi Uygulamalarının Arastırılması, No: FBE/MAD-87 AR 037, 1987, Izmir.
4. V. M. Imamutdinova, *Zh. Prikl. Khim.*, **40**, 2593 (1967).
5. M. Tunç, M. M. Kocakerim, Ö. Kuçuk and M. Aluz, *Korean J. Chem. Eng.*, **43**, in press (2007).
6. Ö. Kuçuk, *Korean J. Chem. Eng.*, **23**, 21 (2006).
7. A. Gür A. Yıldız and H Ceylan, *Asian Journal of Chem.*, **18**, 2002 (2006).
8. A. Gür, *Acta Phys.-Chim. Sin.*, **22**, 1287 (2006).
9. P. D. Oudenne and F. A. Olson, *Metal. Trans.*, **14B**, 34 (1983).
10. K. G. Bryden, *Dis. Abstr. Int.*, **41**, 337 (1980).
11. A. M. Renjithan and P. R. Khangoankor, *Hydrometallurgy*, **23**, 177 (1990).
12. V. M. Imamutdinova and N. Abdrashidova, *Zh. Prikl. Khim.*, **43**, 452 (1970).
13. A. B. Zdonovoskii and L. G. Biktagirova, *Zh. Prikl. Khim.*, **40**, 2659 (1967).
14. V. M. Imamutdinova and A. N. Vladykina, *Zh. Prikl, Khim.*, **42**, 1172 (1969).
15. A. Kunkul, S. Yapici, M. M. Kocakerim and M. Copur, *Hydrometallurgy*, **44**, 135 (1997).
16. M. Alkan and M. M. Kocakerim, *J. Chem. Tech. Biotechnol.*, **40**, 215 (1987).
17. H. Gulensoy and M. M. Kocakerim, *Bull. Miner. Res. Explor. Inst. Turk.*, **90**, 1 (1978).
18. M. M. Kocakerim, S. Colak, T. Davies and M. Alkan, *Canadian Metallurgical Quarterly*, **32**, 393 (1993).
19. S. Yapici, M. M. Kocakerim and A. Kunkul, *J. Eng. Environ. Sci.*, **18**, 91 (1990).
20. M. Alkan and M. Dogan, *Chemical Engineering and Processing*, **43**, 867 (2004).
21. A. A. Nemodruk and Z. K. Karalova, *Israel Program for Scientific Translations, Jerusalem*, **1**, 33 (1965).
22. M. Tunc, M. M. Kocakerim, A. Gür and A. Yartasi, *Energy, Education, Science and Technology*, **3**, 32 (1999).
23. G. N. Kononova and E. S. Nazhko, *Zh. Prikl. Khim.*, **54**, 397 (1981).