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Studies on Dissolution Mechanism of Ulexite in Sulphuric Acid

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There is the largest fraction of the world's boron reserves in Turkey. Ulexite, which is one of the most widely available boron minerals, has the chemical formula $Na_2O·2CaO· 5B_2O_3·16H_2O$ and triclinic crystal structure and is used usually in the production of boric acid. The present study concerns an investigation of the dissolution mechanism of ulexite in H_2SO_4 solution for high solid to liquid ratios and the effect of acid concentration, the effect of SO_4^{2-} on the dissolution process, using H_2SO_4, $HCl + H_2SO_4$ and $H_2SO_4 + Na_2SO_4$ solutions. The analysis of the experimental data show that increasing SO_4^{2-} concentration reduced dissolution rate because of the precipitation of a solid film of $CaSO_4$ and $CaSO_2·H_2O$, but increasing H_3O^+ acid concentration increased the dissolution rate.

Key Words: Ulexite, Dissolution mechanism, Sulphuric acid.

INTRODUCTION

Ulexite is one of the most important underground deposits in Turkey having *ca.* 60 % of the world boron deposits. When ulexite is mined naturally, it contains various clay minerals. Huge portions of the Turkey's commercially recoverable boron reserves are colemanite, ulexite and tincal. Ulexite, which is one of the most widely available boron minerals, has the chemical formula of $Na_2O·2CaO·5B_2O_3·16H_2O$ and triclinic crystal structure. 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.*[1]. Ulexite is available in huge amounts together with some other borates in Balikesir-Bigadic and Kütahya-Emet regions in Turkey[2].

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, HCl and HNO_3 solutions. The dissolution process in these solutions was found to be diffusion

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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[3] of $CaSO_4·2H_2O$.

Dissolution kinetics of calcined ulexite in NH_4Cl solutions at high solid-to-liquid ratios were investigated[4,5]. Ammonium carbonate solutions were used as leachant for malachite, because basic ores often consume acids and therefore a basic matter which is more lixiviant than sulphuric acid, may be attractive[6]. In another study the leaching of malachite with ammonium sulphate solutions has been investigated[7]. The leaching of magnesite with ammonium chloride solution has also been investigated[8].

The dissolution of ulexite was investigated in acetic acid solutions and found that the dissolutions rate was maximum at relatively low acid concentration (10-20 w %) and over these concentration the dissolutions rate decreased. It was also reported that the process was controlled by diffusion[9]. It was carried out on the dissolution of ulexite in H_3PO_4 solution and 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[10]. The dissolution ulexite in perchloric acid solutions[11] and NH_3 solutions saturated with CO_2 was reported[12] to be diffusion controlled. In the studies in which the dissolution of ulexite in aqueous SO_2 and CO_2 solutions were investigated and 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[13-16]. In the other work, the dissolution kinetics of colemanite in oxalic acid solutions were studied and founded that the dissolution rate was controlled by product layer (ash layer) diffusion process, the activation energy of the process[17] was to be 9.50 cal mol^{-1}. Furthermore, Gür[18] investigated dissolution mechanism of colemanite sulphuric acid solutions. In spite of dissolution mechanism of ulexite has been studied in sulphuric acid solution, no detailed study on dissolution mechanism of ulexite for high solid to liquid ratios has been found in literatures. Therefore, the goal of this present work was to clarify the dissolution process of ulexite in H_2SO_4 solutions for high solid to liquid ratios.

EXPERIMENTAL

The ulexite mineral used in the study was obtained from Bigadic¸ town of Balikesir Province in Turkey. The sample mineral was first broken into small pieces, ground and sieved with ASTM standard sieves to have sample with the particle size of 40 ± 60 mesh. The original sample was tested for chemical composition and found to have 35.85 % B_2O_3, 15.22 % CaO, 6.38 % Na_2O, 29.67 % H_2O, 5.38 % MgO and 7.5 % other components.The

X-ray diffractogram of the original sample is shown in Fig. 1. Dissolution experiments were performed in a 250 mL jacketed glass reactor equipped with gas inlet and outlet tubing. Reactor content was stirred with a mechanical stirrer with tachometer and the temperature was controlled with a constant temperature circulator. At the end of the desired period, the constant of the vessel was filtered as soon as the process finished and B_2O_3 in the solution was analyzed as titrimetically using a digital titrator. The fraction of present sample reacted is defined:

X B_2O_3 = the amount of dissolved B_2O_3/the amount of B_2O_3 in original sample.

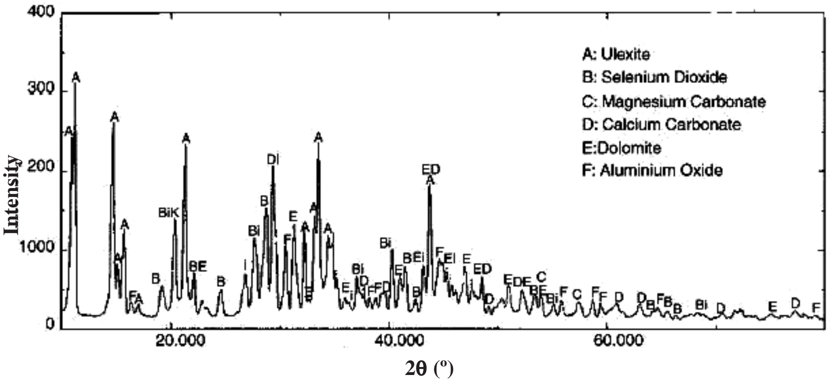

Fig. 1. X-ray diffractogram of the ulexite ore

RESULTS AND DISCUSSION

Dissolution reactions: Sulphuric acid used in the dissolution process give the following reaction in aqueous medium

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

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

The equilibrium constant of reaction (2) is Ka = 0.012. lt is suggestion that when ulexite is added to this solution the following reaction takes place

$$Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O(s) + 6H_3O^+(aq) \rightarrow 2Na^+ + 2Ca^{2+}(aq) + 10H_3BO_3(aq) + 4H_2O(s) \quad (3)$$

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

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

It gives the following reaction with ion formed *via* reaction (2)

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s) \quad (5)$$

Thus, forming a solid precipitates. Finally the dissolution reaction of ulexite in H_2SO_4 solution can be written as:

$$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O(s) + 3H_2SO_4(aq) \rightarrow 2CaSO_4(s) + 10H_3BO_3(aq) + 2H_2O(s) \quad (6)$$

Effect of H_2SO_4 concentration on dissolution rate: The effect of the H_2SO_4 concentration on dissolution rate have been studied using the acid concentration of 0.50, 1, 1.50 and 2 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 10/100 (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-} per unit volume with increasing acid concentration. This leads to the occurrence of reaction (5), *i.e.*, 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.

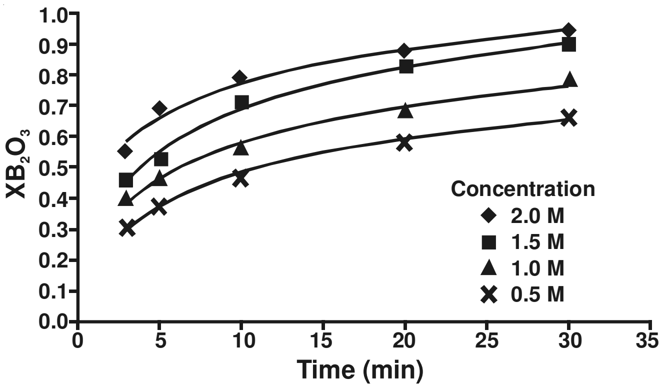

Fig. 2. Effect of the solution concentration on dissolution rate

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 0.5 h 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 $CaSO_4 \cdot 2H_2O(s)$[19].

Dissolution rate in HCl solutions: The effect of the HCl solution on the dissolution of ulexite was investigated for experimental condition 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 10/100 (g/mL) and HCl concentration of 1 and 2 mol L^{-1}. As seen from Table-1 and Fig. 3 increasing the HCl 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 %.

TABLE -1
EFFECT ON THE CONVERSION RATE OF
HCl, H_2SO_4, H_2SO_4 + HCl AND H_2SO_4 + Na_2SO_4 SOLUTIONS

Compound of solution	Time (min)	Conversion ratio ($X B_2O_3$)
1 mol L^{-1} HCl	3	0.7250
	5	0.8621
	10	0.9432
1.5 mol L^{-1} HCl	3	0.6512
	5	0.7522
	10	0.8645
1.5 mol L^{-1} H_2SO_4	10	0.5594
1.5 mol L^{-1} H_2SO_4 + 1 mol^{-1} HCl	10	0.6579
1.5 mol L^{-1} H_2SO_4 + 1 mol^{-1} Na_2SO_4	10	0.4828

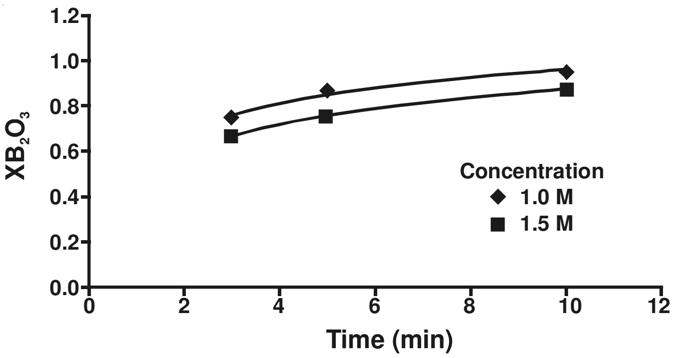

Fig. 3. Effect of HCl concentration on dissolution fraction

When the dissolution of the mineral in HCl solution is compared with the mineral in H_2SO_4 solution at the same concentration, it can be seen that almost 94.32 % dissolution was reached in 10 min for HCl solution, while the dissolution process with H_2SO_4 solution has 70.55 %. 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 HCl 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.

Effect of HCl, H_2SO_4 + HCl and H_2SO_4 + Na_2SO_4 solutions on the dissolution: To understand the effect of SO_4^{2-} concentration on the solubility of the are some experiments were carried out with the solutions of 1.5 mol L^{-1} H_2SO_4 + 1 mol L^{-1} HCl and 1.5 mol L^{-1} H_2SO_4 + 1 mol L^{-1} Na_2SO_4 solution, keeping other experimental parameters constant. The best result was obtained with the solution 1.5 mol L^{-1} H_2SO_4 + 1 mol L^{-1} HCl, followed by the solution of 2 mol L^{-1} H_2SO_4 and lowest dissolution was obtained with the solution 1.5 mol L^{-1} H_2SO_4 + 1 mol L^{-1} Na_2SO_4.

The experimental results are shown in Table-1 and Fig. 4. These showed 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 solution, the 1.5 mol L^{-1} H_2SO_4 + 1 mol L^{-1} HCl solution had the minimum SO_4^{2-} concentration, since the presence of HCl caused reaction (2) to shift to left, reducing SO_4^{2-} concentration. Therefore the dissolution in this case was much more than in the other solution. The reason for the 1.5 mol L^{-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 solution thus the precipitation of $CaSO_4$ and $CaSO_4 \cdot 2H_2O$ film is much more pronounced.

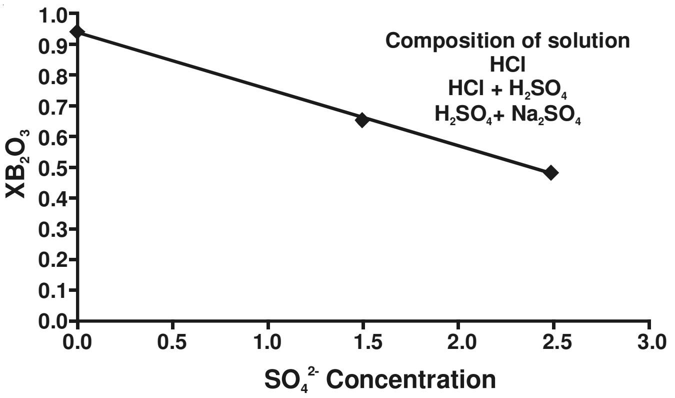

Fig. 4. Effect of the SO_4^{2-} concentration on the dissolution rate

These result proved the importance of the formation of this side-product is to the dissolution process. When the further experiments with 1 mol L^{-1} HCl solutions for 10 min were compared with results of three solution, it is seen that this solution gave better results than the solution of 1.5 mol^{-1} H_2SO_4 + 1 mol^{-1} HCl 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. It was investigated the dissolution of magnesium borates in H_2SO_4 solution suggested that the dissolution took place as a result of H_3O^+ ion to the mineral surface and the protonation of the boron-oxygen[20].

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

$$B_5O_3^{3-} + 3H_3O^+ + 3H_2O \rightarrow 5H_3BO_3 \quad (7)$$

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

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$$

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

$$Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(l) \rightarrow CaSO_4 \cdot 2H_2O(s) \quad (8)$$

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.

Conclusion

In this paper, the dissolution mechanism of ulexite for high solid to liquid ratios has been investigated in H_2SO_4 solutions and 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 slow down the diffusion of H_4O^+ 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[18,21].

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