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$_2$O·2CaO·5B$_2$O$_3$·16H$_2$O 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$_2$SO$_4$ 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$_2$SO$_4$, HCl + H$_2$SO$_4$ and H$_2$SO$_4$ + Na$_2$SO$_4$ 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$_4$·H$_2$O, but increasing H$_3$O$^+$ 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$_2$O·2CaO·5B$_2$O$_3$·16H$_2$O 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 Turkey².

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$_2$SO$_4$, H$_3$PO$_4$, HCl and HNO$_3$ solutions. The dissolution process in these solutions was found to be diffusion
controlled and HNO₃ solution gave the highest dissolution rate while H₂SO₄ solution gave the lowest. In the case of H₂SO₄ solution, it was claimed that the diffusional process was affected negatively by the formation of CaSO₄·2H₂O.

Dissolution kinetics of calcined ulexite in NH₄Cl solutions at high solid-to-liquid ratios were investigated⁴,⁵. 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 attractive⁶. In another study the leaching of malachite with ammonium sulphate solutions has been investigated⁷. The leaching of magnesite with ammonium chloride solution has also been investigated⁸.

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 w %) and over these concentration the dissolution rate decreased. It was also reported that the process was controlled by diffusion⁹. It was carried out on the dissolution of ulexite in H₃PO₄ solution and reported that in the dissolutions of ulexite in 5 wt. % H₃PO₄ solutions, H₃BO₃ solid film formed on crystals. This restricted the dissolution rate of the mineral¹⁰. The dissolution ulexite in perchloric acid solutions¹¹ and NH₃ solutions saturated with CO₂ was reported¹² to be diffusion controlled. In the studies in which the dissolution of ulexite in aqueous SO₂ and CO₂ solutions were investigated and claimed that the dissolution rate process was found to be diffusion-controlled in CO₂ solutions while it was chemical reaction-controlled in SO₂ solution¹³-¹⁶. 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 process¹⁷ was to be 9.50 cal mol⁻¹. Furthermore, Gür¹⁸ 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 H₂SO₄ 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 % B₂O₃, 15.22 % CaO, 6.38 % Na₂O, 29.67 % H₂O, 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$_2$O$_3$ in the solution was analyzed as titrimetrically using a digital titrator. The fraction of present sample reacted is defined:

\[ X_{B_2O_3} = \frac{\text{the amount of dissolved } B_2O_3}{\text{the amount of } B_2O_3 \text{ in original sample}}. \]

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

\[ \text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O(s)} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+(aq) \]  
(1)

\[ \text{HSO}_4^- (aq) + \text{H}_2\text{O(s)} \rightarrow \text{SO}_4^{2-} + \text{H}_3\text{O}^+(aq) \]  
(2)

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

\[ \text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O(s)} + 6\text{H}_3\text{O}^+(aq) \rightarrow 2\text{Na}^+ + 2\text{Ca}^{2+}(aq) + 10\text{H}_3\text{BO}_3(aq) + 4\text{H}_2\text{O(s)} \]  
(3)

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

\[ [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = \text{Ksp} \]  
(4)

It gives the following reaction with ion formed via reaction (2)
Thus, forming a solid precipitates. Finally the dissolution reaction of ulexite in H$_2$SO$_4$ solution can be written as:

\[
\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}(s) + 3\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{CaSO}_4(s) + 10\text{H}_3\text{BO}_3(aq) + 2\text{H}_2\text{O}(s) \quad (6)
\]

**Effect of H$_2$SO$_4$ concentration on dissolution rate:** The effect of the H$_2$SO$_4$ 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$_2$SO$_4$ 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$_4$·2H$_2$O on the particle surface. This solid side-product layer creates difficulty for H$_3$O$^+$ ion to diffuse to the mineral, decreasing the dissolution rate of the sample.

![Fig. 2. Effect of the solution concentration on dissolution rate](image_url)

The X-ray diffractogram of the solid sample, subjected to the dissolution process with H$_2$SO$_4$ 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$_4$·2H$_2$O(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\(_3\)BO\(_3\) product layer on the surface of the mineral and this caused slowing down of the diffusion of H\(_3\)O\(^+\) ion to the undissolved part of the mineral. Therefore, this situation prevented the dissolution of the mineral reaching 100%.

<table>
<thead>
<tr>
<th>Compound of solution</th>
<th>Time (min)</th>
<th>Conversion ratio (X B(_2)O(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mol L(^{-1}) HCl</td>
<td>3</td>
<td>0.7250</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.8621</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.9432</td>
</tr>
<tr>
<td>1.5 mol L(^{-1}) HCl</td>
<td>3</td>
<td>0.6512</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.7522</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.8645</td>
</tr>
<tr>
<td>1.5 mol L(^{-1}) H(_2)SO(_4)</td>
<td>10</td>
<td>0.5594</td>
</tr>
<tr>
<td>1.5 mol L(^{-1}) H(_2)SO(_4) + 1 mol L(^{-1}) HCl</td>
<td>10</td>
<td>0.6579</td>
</tr>
<tr>
<td>1.5 mol L(^{-1}) H(_2)SO(_4) + 1 mol L(^{-1}) Na(_2)SO(_4)</td>
<td>10</td>
<td>0.4828</td>
</tr>
</tbody>
</table>

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\(_2\)SO\(_4\) 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\(_2\)SO\(_4\) solution has 70.55%. Therefore, it was concluded that the negative effect of the CaSO\(_4\) and CaSO\(_4\)·2H\(_2\)O solid film formed of the surface is much more pronounced that the H\(_3\)BO\(_3\) 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}·2H_{2}O in the case of H_{2}SO_{4} solutions.

**Effect of HCl, H_{2}SO_{4} + HCl and H_{2}SO_{4} + Na_{2}SO_{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_{2}SO_{4} + 1 mol L^{-1} HCl and 1.5 mol L^{-1} H_{2}SO_{4} + 1 mol L^{-1} Na_{2}SO_{4} solution, keeping other experimental parameters constant. The best result was obtained with the solution 1.5 mol L^{-1} H_{2}SO_{4} + 1 mol L^{-1} HCl, followed by the solution of 2 mol L^{-1} H_{2}SO_{4} and lowest dissolution was obtained with the solution 1.5 mol L^{-1} H_{2}SO_{4} + 1 mol L^{-1} Na_{2}SO_{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}·2H_{2}O as the concentration of SO_{4}^{2-} ions increases. Of all the solution, the 1.5 mol L^{-1} H_{2}SO_{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_{2}SO_{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}·2H_{2}O film is much more pronounced.

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 L^{-1} H_{2}SO_{4} + 1 mol L^{-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$_4$·2H$_2$O formed on surface. It was investigated the dissolution of magnesium borates in H$_2$SO$_4$ solution suggested that the dissolution took place as a result of H$_3$O$^+$ 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.

$$\text{B}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}^+ + 3\text{H}_2\text{O} \rightarrow 5\text{H}_3\text{BO}_3 $$ (7)

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

$$\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CaSO}_4(\text{s})$$

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

$$\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O}(\text{s})$$ (8)

Consequently, it can be concluded that CaSO$_4$ crystals formed simultaneously with H$_3$BO$_3$ crystals result in higher diffusional resistance to the diffusion of H$_3$O$^+$ to the mineral surface than the case of only H$_3$BO$_3$ crystals.

**Conclusion**

In this paper, the dissolution mechanism of ulexite for high solid to liquid ratios has been investigated in H$_2$SO$_4$ solutions and It was seen that increasing H$_3$O$^+$ concentration increased the dissolution and that increasing SO$_4^{2-}$ concentration decreased the dissolution due to the formation of CaSO$_4$ and/or CaSO$_4$·2H$_2$O which substantially slow down the diffusion of H$_3$O$^+$ ion to the mineral surface. The effect of CaSO$_4$ and CaSO$_4$·2H$_2$O in diffuse anal resistance to H$_3$O$^+$ ion is much more pronounced than that of solid H$_3$BO$_3$ crystals precipitated as a thin film on the surface.$^{18,21}$

**REFERENCES**


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