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Studies on the Ulexite Breakdown Process of Sulfuric Acid

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ABSTRACT

The highest fraction of the boron deposits in the world are found in India. Ulexite, one of the most commonly available boron minerals, has the chemical formula $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 16\text{H}_2\text{O}$ and the shape of triclinic crystals and is generally used in the manufacture of boric acid. This research explores the dissolution mechanism of ulexite in H_2SO_4 solution for high solid to liquid ratios and the influence of acid concentration on the dissolution process using H_2SO_4 , $\text{HCl} + \text{H}_2\text{SO}_4$ and $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ solutions. This study investigates the effect of SO_4^{2-} on the dissolution process. The study of the experimental results reveals that increasing SO_4^{2-} concentration decreased the dissolution rate due to the precipitation of a solid CaSO_4 and $\text{CaSO}_4\cdot\text{H}_2\text{O}$ film, but the dissolution rate improved by increasing H_3O^+ acid concentration.

Keywords-- Effect of SO_4^{2-} , boron minerals, Sulfuric Acid

I. INTRODUCTION

Ulexite is one of India's most significant underground mines, with approx. 60 percent of all boron deposits worldwide. It contains different clay minerals as ulexite is extracted naturally. Colemanite, ulexite and tincal are significant parts of the commercially recoverable boron reserves in India. Ulexite has the chemical formula of $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 16\text{H}_2\text{O}$ and the triclinic crystal composition, which is one of the most readily available boron minerals. While boron is not specifically used its compounds are commonly used in the manufacture of glass, fabrics, heat-resistant products, manufacturing materials, nuclear reactors, fire retardants, detergents and catalysts, etc¹. Ulexite, along with some other borates, is present in significant quantities in the Balikesir-Bigadic and Kütahya-Emet regions of Turkey². Increasing demand and modern industrial uses for boron compounds have expanded their significance, and these compounds have been used in

different sectors of industry as raw materials. The dissolution of colemanite in solutions of H_2SO_4 , H_3PO_4 , HCl and HNO_3 has been studied by several researchers. The dissolution method in these solutions was found to be diffusion regulated and the highest dissolution rate was given by HNO_3 solution while the lowest was given by H_2SO_4 solution. In the case of the H_2SO_4 solution, it was claimed that the development of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ had a negative effect on the diffusion process.

Dissolution kinetics of calcined ulexite is studied at high solid-to-liquid ratios in NH_4Cl solutions^{4,5}. As leachant for malachite, ammonium carbonate solutions were used because simple ores often absorb acids and can thus be attractive to a basic matter that is more lixiviant than sulphuric acid⁶. Another research studied the leaching of malachite with solutions of ammonium sulphate⁷. Magnesite leaching was also examined with ammonium chloride solution⁸.

The dissolution of ulexite was studied in acetic acid solutions and found that at a moderately low acid concentration (10-20 w percent) the dissolution rate was optimum and the dissolution rate decreased over these concentrations. It was also reported that diffusion controlled the process⁹. Dissolution of ulexite in H_3PO_4 solution was performed and dissolution of ulexite in 5 Wt was confirmed. H_3BO_3 solid film formed on crystals for one percent H_3PO_4 solutions. The dissolution rate of the mineral was constrained by this¹⁰. Dissolution of ulexite in perchloric acid solutions and CO_2 -saturated NH_3 solutions was stated to be regulated by diffusion¹². In studies that investigated the dissolution of ulexite in aqueous SO_2 and CO_2 solutions, it was observed that the phase of dissolution rate was diffusion-regulated in CO_2 solutions while the chemical reaction was controlled in SO_2 solution¹³⁻¹⁶. In addition, studied the degradation process of solutions for colemanite sulphuric acid. No systematic research on the dissolution mechanism of ulexite for high solid to liquid

ratios has been found in the literature, despite the dissolution mechanism of ulexite in sulphuric acid solution. Therefore the purpose of this present work was to explain the dissolution mechanism of ulexite for high solid to liquid ratios in H_2SO_4 solutions.

II. EXPERIMENTAL

In order to get samples with a particle size of 40 ± 60 mesh, the sample mineral was first broken into small parts, ground and sieved with ASTM regular sieves. For chemical composition, the initial sample was tested and found to have 35.85 % B_2O_3 , 15.22 % CaO, 15.22 % CaO,

6.38% Na_2O , 29.67% H_2O , 5.38% MgO , and 7.5% of the other elements.

The X-ray diffractogram is displayed in Fig.1 for the initial study in a 250 mL jacketed glass reactor fitted with gas inlet and outlet tubing, dissolution tests were conducted. With a mechanical stirrer with a tachometer, the reactor material was stirred and the temperature was regulated with a steady circulator temperature. The vessel constant was purified at the end of the desired time as soon as the process was completed and B_2O_3 was analysed titrimetrically using a wireless titrator in the solution. The reaction fraction of the present sample is described as:

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

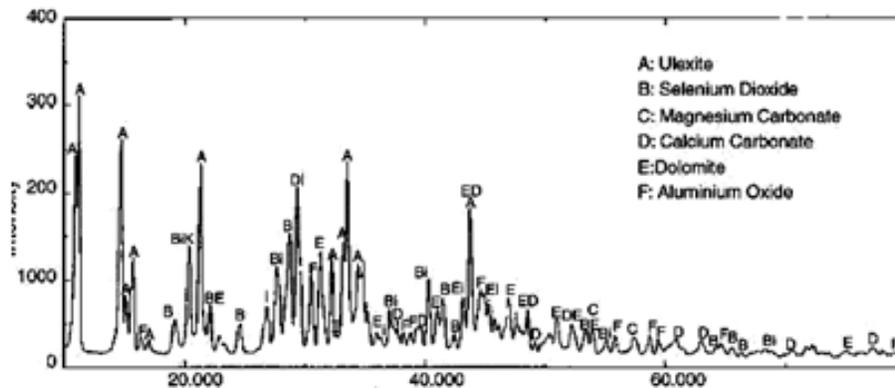
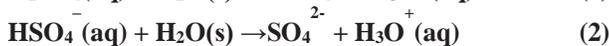


Figure 1: X-ray diffractogram of the ulexite ore

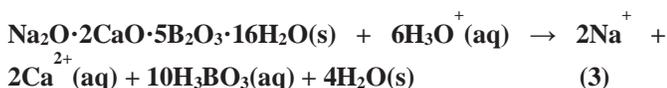
III. RESULTS AND DISCUSSION

Dissolution reactions:

In aqueous medium, the sulphuric acid used in the dissolution process gives the following response.



The reaction equilibrium constant (2) is $K_a = 0.012$. It is proposed that the following reaction occurs when ulexite is added to this solution.



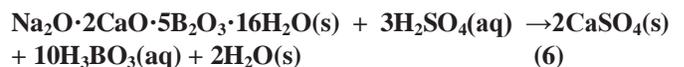
When the concentrations of Ca^{2+} exceed a limiting value established by the solution-bility product

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

This supplies the following reaction with reaction-formed ions (2)



Therefore the formation of strong precipitates. Finally, the H_2SO_4 solution dissolution reaction of ulexite can be written as:



Impact of concentration of H_2SO_4 on rate of dissolution:

An acid concentration of 0.50, 1, 1.50 and 2 mol L^{-1} was used to research the influence of the H_2SO_4 concentration on the dissolution rate. The dissolved quantity of the mineral was calculated in the experiments at a reaction temperature of $35^\circ C$, a solid to liquid ratio of 10/100 (g/mL) and a stirring rate of 41, 87 s^{-1} . Experimental effects shown in Fig. 2 suggest that the dissolution decreased with increased concentration of H_2SO_4 . This result can be explained by the rise in the output of SO_4^{2-} per unit volume with rising concentrations of acid. This contributes to the occurrence of reaction, i.e. solid $CaSO_4$ and $CaSO_4 \cdot 2H_2O$ precipitation on the particle surface. This strong side-product coating causes trouble diffusing the H_3O^+ ion to the mineral, limiting the sample's dissolution rate.

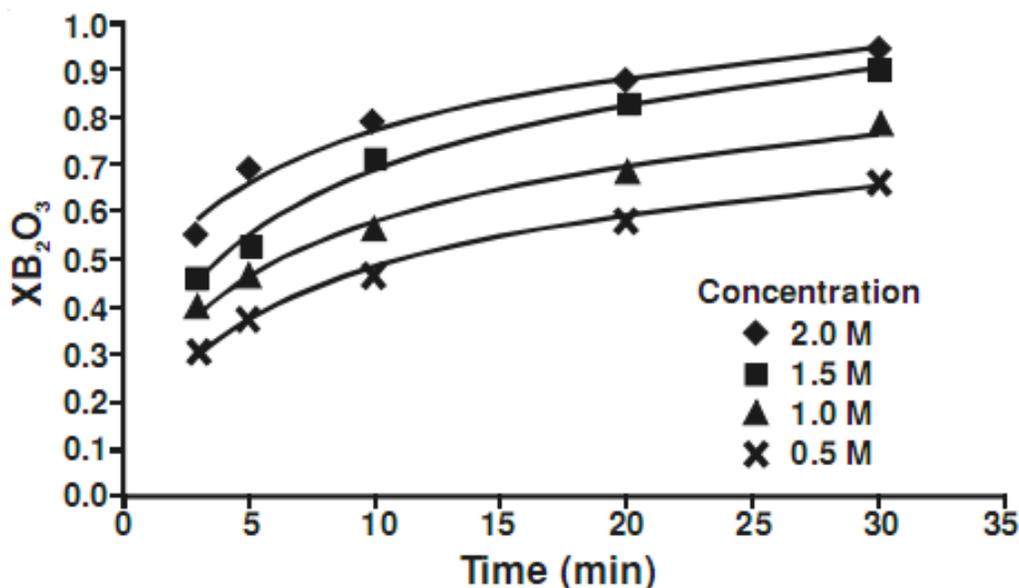


Figure 2: Effect of the solution concentration on dissolution rate

The solid sample X-ray diffractogram subjected to the dissolution process with H_2SO_4 0.50 mol L^{-1} solution for 0.5 h for ulexite mineral confirmed the presence of a reaction (5). In addition, the X-ray diffractogram of the sample subjected to dissolution demonstrated the formation of $\text{CaSO}_4(\text{s})$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ at a solid-to-liquid average of $5/100 \text{ (g/mL)}$ ¹⁹.

Rate of dissolution in HCl solutions:

The effect of the HCl solution on ulexite dissolution was investigated for experimental conditions of 600 ± 425

μm particle size, 35°C reaction temperature, 41.87 s^{-1} stirring rate, $10/100 \text{ (g/mL)}$ solid-to-liquid rate, and 1 and 2 mol L^{-1} HCl concentration.

As can be seen from Table-1 and from Fig. 3 Increasing the concentration of HCl increased the deposition on the surface of the mineral of the strong H_3BO_3 substance layer and allowed the diffusion of the H_3O^+ ion to slow down to the undissolved portion of the mineral. Therefore the mineral dissolution stopped this condition from reaching 100%.

Table 1: Effect on the Conversion Rate of HCl, H_2SO_4 , $\text{H}_2\text{SO}_4 + \text{HCl}$ and $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ Solutions

		(X B ₂ O 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 ₂ SO ₄	10	0.5594
1.5 mol L ⁻¹ H ₂ SO ₄ + 1 mol ⁻¹ HCl	10	0.6579
1.5 mol L ⁻¹ H ₂ SO ₄ + 1 mol ⁻¹ Na ₂ SO ₄	10	0.4828

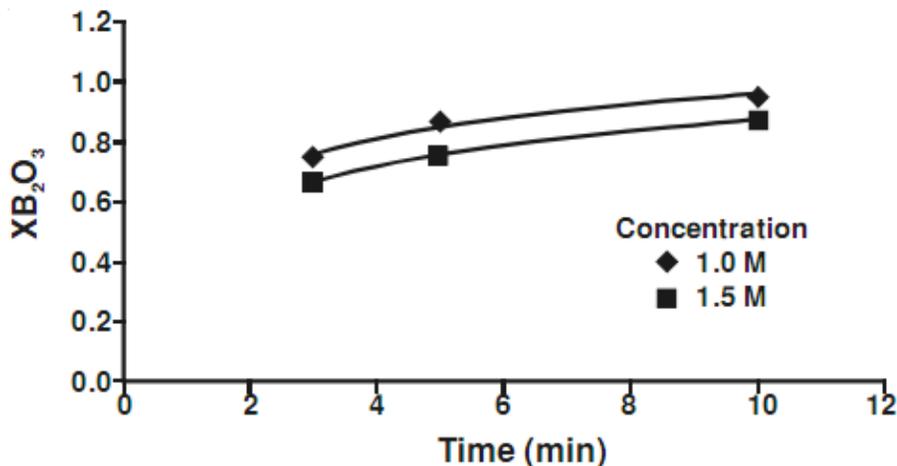


Figure 3: Effect of HCl concentration on dissolution fraction

When the dissolution of the mineral in HCl solution is compared at the same concentration with the mineral in H₂SO₄ solution, it can be found that almost 94.32% dissolution was achieved with HCl solution in 10 minutes, while 70.55% is the dissolution phase for H₂SO₄ solution. It was therefore concluded that the negative influence of the surface solid film produced by CaSO₄ and CaSO₄•2H₂O was even more pronounced than that of the H₃BO₃ film. The result revealed that almost all CaO in the mineral dissolved in the solution of HCl, while in the case of H₂SO₄ solutions, Ca²⁺ ions partially converted to CaSO₄ and/or CaSO₄•2H₂O.

Effect of HCl, H₂SO₄ + HCl and H₂SO₄ + Na₂SO₄ solutions on the dissolution:

Some tests were conducted with the solutions of the solutions to understand the effect of SO₄²⁻ concentration on the solubility of the solution. 1.5 mol L⁻¹ H₂SO₄+1 mol L⁻¹ HCl and 1.5 mol L⁻¹ H₂SO₄+1 mol L⁻¹ Na₂SO₄ solution, ensuring a steady presence of other experimental parameters.

The highest result was obtained with 1.5 mol L⁻¹ H₂SO₄+1 mol L⁻¹ HCl solution, followed by 2 mol L⁻¹ H₂SO₄ solution and the lowest dissolution was obtained with 1.5 mol L⁻¹ H₂SO₄+1 mol L⁻¹ Na₂SO₄ solution. Table-1 and Fig. 4 demonstrate the experimental effects. These shows that as the SO₄²⁻ ion concentration increased, the dissolution decreased. These findings explained the propensity of CaSO₄ and/or CaSO₄•2H₂O to form as the SO₄²⁻ ion concentration rises. In all the solutions, the minimum SO₄²⁻ concentration was 1,5 mol L⁻¹ H₂SO₄+1 mol L⁻¹ HCl solution, as the presence of HCl caused the reaction (2) to move to the left, decreasing the SO₄²⁻ concentration. Therefore in this situation, the dissolution was even stronger than in the other solution. Higher SO₄²⁻ concentration may explain the explanation for the 1.5 mol L⁻¹ H₂SO₄ dissolution is less than the first solution. The SO₄²⁻ concentration was the strongest of all solutions in the case of the third solution, so the precipitation of CaSO₄ and CaSO₄•2H₂O film is even more pronounced.

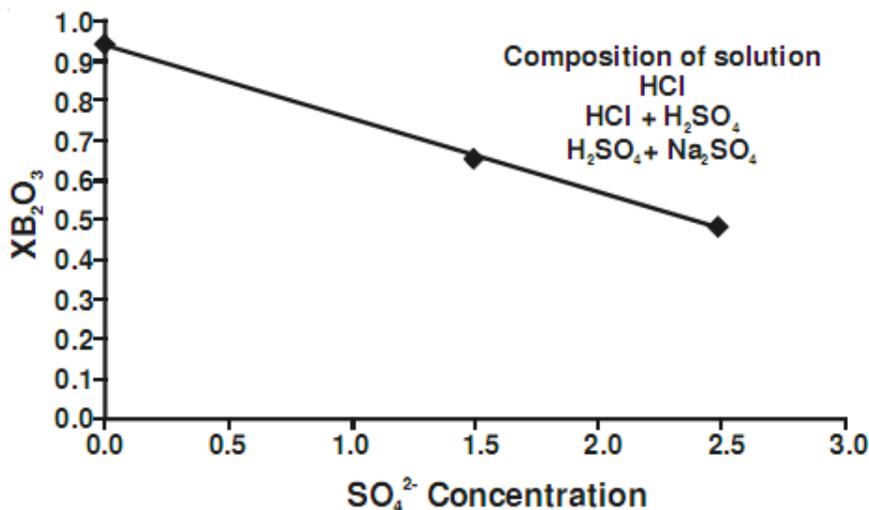


Figure 4: Effect of the SO₄²⁻ concentration on the dissolution rate

These findings showed that the formation of this side-product is essential for the process of dissolution. Compared with the results of three solutions, as further tests of 1 mol L⁻¹ HCl solutions for 10 min were compared with the results of three solutions, it is shown that this solution yielded stronger results than the 1.5 mol⁻¹ H₂SO₄+1 mol⁻¹ HCl solution since it does not have a SO₄²⁻ ion and this reinforces the above inference. Analysis of the X-ray diffractogram showed that both CaSO₄ and CaSO₄•2H₂O were formed on the surface. The dissolution of magnesium borates in the H₂SO₄ solution was investigated, suggesting that the dissolution took place as a result of the mineral surface of the H₃O⁺ ion and the protonation of boron-oxygen¹⁹.

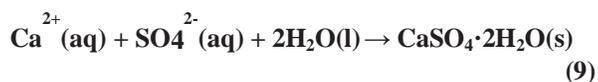
The dissolution process can be shown according to the following reaction when taking this explanation and trend of the present study into account.



The following reaction occurs in the case of a lack of water in the medium;



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It can therefore be inferred that CaSO₄ crystals formed concurrently with H₃BO₃ crystals result in greater diffusion resistance to the mineral surface diffusion of H₃O⁺ than just H₃BO₃ crystals.

IV. CONCLUSION

In this article, in H₂SO₄ solutions, the dissolution process of ulexite for high solid to liquid ratios was investigated and it was shown that increasing H₃O⁺ concentration increased the dissolution and increased SO₄²⁻ concentration decreased the dissolution due to the formation of CaSO₄ and/or CaSO₄•2H₂O, which greatly slows down the diffusion of H₄O⁺ ion to the mineral surface. The effect of CaSO₄ and CaSO₄•2H₂O is far more pronounced in the diffuse anal resistance to H₃O⁺ ion than that of stable H₃BO₃ crystals precipitated on the surface as a thin film^{18,19}.

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