

The Dissolution Kinetics of Ulexite in Sulphuric Acid Solutions

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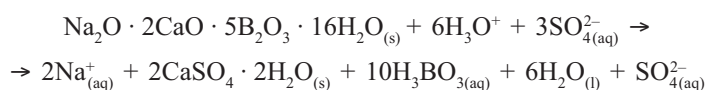
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This technical note presents an investigation on the dissolution kinetics of ulexite, a boron mineral, in H_2SO_4 solutions as a function of particle diameter, mass concentration, stirring speed, acid concentration, and reaction temperature. It was determined that the dissolution rate increased with increasing reaction temperature and decreasing particle diameter, mass concentration and acid concentration, while no important effect of stirring speed was observed. Ulexite could be dissolved up to 100 percent in the sulphuric acid solutions. The following overall reaction was suggested for the process



The analysis of the experimental data showed that the dissolution process was controlled by the diffusion of H_3O^+ ions to the mineral surface through the product and by-product layer, and the reaction kinetics can be expressed as

$$-\ln(1-x) = kt^n$$

where x is the dissolution amount fraction, k the function of the experimental quantities, and rate coefficient and t the reaction time.

Key words:

Dissolution kinetics, ulexite, boron minerals

Introduction

Boron is an element having the ability to form a large number of complex chemical compounds. Boron compounds are important raw materials in many branches of industry, and its use has been increasing and expanding continuously. Its compounds are used in the production of medicines, disinfectants, cosmetics, detergent materials, and in the industries of glass, polymer, dye and plating, steel, refractory materials etc. Furthermore, they have applications in nuclear technology as a radiation trapper, in rockets as fuel and in some production industries as catalysts¹. Ulexite, which is a sodium-calcium borate with a chemical formula of $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$, is available in huge quantities in nature, and is commercially important. Turkey has the largest boron resources in the world, and ulexite is available together with other borates around the regions of Balıkesir-Bigadiç and Kütahtaya-Emet.

The dissolution of ulexite in acidic solutions is of economic interest. Imamutdinova studied the dissolution of ulexite in H_2SO_4 , H_3PO_4 , HNO_3 and HCl solutions². The dissolution process in these acidic solutions was determined to be diffusion controlled. Zdanovskii and Biktagirova³ carried out a

study of the dissolution of ulexite in H_3PO_4 solutions and found that acid mass fraction of 5 %, a solid film of H_3BO_3 , formed on the ulexite crystals, and the dissolution rate of this product restricted the dissolution rate of the mineral. In the works on the dissolution of ulexite in aqueous SO_2 and CO_2 solutions⁴⁻⁷, the dissolution process was found to be diffusion controlled in the case of CO_2 while it is chemically reaction-controlled in SO_2 solutions. Imamutdinova and Abdrashitova⁸ investigated the dissolution of ulexite in acetic acid solutions, and they found that the dissolution rate was maximum at relatively low acid concentrations (10–20 %), and over these concentrations the dissolution rate decreased with increasing acid concentration. The dissolution of ulexite in perchloric acid solutions (Imamutdinova and Vladykina) was also investigated and it was determined that the dissolution is faster than that of HNO_3 solutions⁹. Künkül et al. studied the dissolution of ulexite in NH_3 solutions saturated with CO_2 , and found that the dissolution kinetics could be expressed with a pseudo-homogeneous first order reaction rate model¹⁰. Tunç et al¹¹ reported that the dissolution of ulexite in H_2SO_4 was controlled by the diffusion of H_3O^+ through the H_3BO_3 product layer and the by-product layer of $CaSO_4$ and /or $CaSO_4 \cdot 2H_2O$. In addition to these, there are many studies on ulexite in different aque-

ous media containing various acids.^{12,13} Ulexite is generally being used together with colemanite in the production of boron compounds. A study of the dissolution conditions of ulexite and the dissolution kinetics in H₂SO₄ solutions will be beneficial to the resolution of some problems encountered, in the production of boric acid, such as decreasing reaction yield and filtration. When taking into consideration the studies in the literature, there is no detailed work on the dissolution kinetics of ulexite in H₂SO₄ solution. The work of *Imamutdinova*² considered only the effect of temperature and acid concentration. For this reason the aim of the present work is to study the reaction kinetics by taking into consideration the experimental quantities of granulometric operation, mass concentration, and stirring speed in addition to reaction temperature and acid concentration on the dissolution process.

Experimental

Ulexite mineral used was provided from the resources in the Eskisehir–Kirka region. After cleaning the mineral from visible impurities manually, it was crushed and then ground followed by sieving, using ASTM standard sieves, to obtain the particle fractions of d : –2000+1000, –1000+710, –600+425, –425+300, and –300+250 μm . The chemical analysis and X-ray diffractogram of the sample is given in Table 1 and Figure 1, respectively.

Table 1 – Chemical analysis of the ulexite mineral

Component	Composition %
CaO	13.84
B ₂ O ₃	42.44
Na ₂ O	7.24
H ₂ O	35.63
Others	0.85

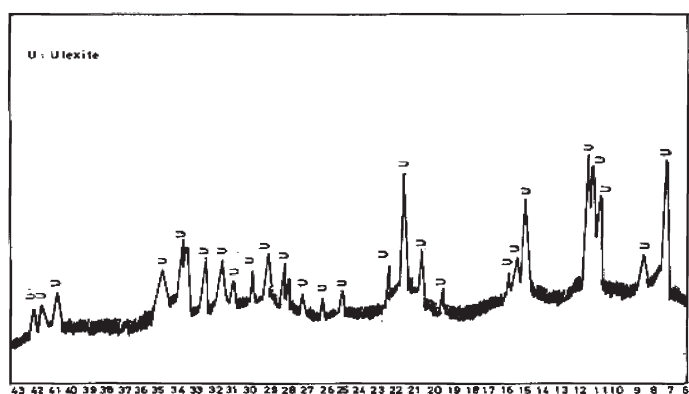


Fig. 1 – X-ray diffractogram of original ulexite mineral

The dissolution process was carried out in a 250 mL-spherical glass vessel at atmospheric pressure. For stirring the reactor contents, a mechanical stirrer was used, and a thermostat was employed to maintain reaction medium at a given temperature. To counteract evaporation, a cooler was attached to the reactor. The quantities investigated and their ranges are given in Table 2.

Table 2 – Quantities and their ranges used in the experiments

Quantities	Values
Particle diameter, mm	–2000 + 1000*, –1000 + 710, –710 + 600, –600 + 425, –425 + 300, –300 + 250
Acid concentration, mol · L ⁻¹	0.25, 0.49, 0.76, 0.90, 2.0*, 4.90
Mass concentration, g · mL ⁻¹	1 : 112, 2 : 112, 4 : 112
Stirring speed, s ⁻¹	21, 31, 42*, 63, 84
Reaction temperature, °C	3, 12, 18, 25, 30*, 40

*Values kept constant, when other quantities studied.

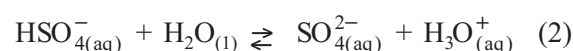
In the leaching experiments, 100 mL of H₂SO₄ was put into the reactor, and heated to a desired temperature. Subsequently, a known amount of the sample was added into the solution while the stirring was started. At the end of a given reaction period, the stirring was stopped and the contents was filtered. The B₂O₃ content of the filtrate was determined by a potentiometric method (*Nemodruk and Karolova*)¹. The fraction of mineral dissolved into the solution was calculated as follows

$$x_{\text{B}_2\text{O}_3} = \frac{\text{dissolved amount of B}_2\text{O}_3}{\text{total amount of B}_2\text{O}_3 \text{ in sample}}$$

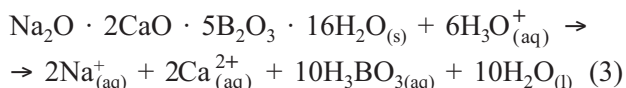
Results and discussions

Dissolution reactions

H₂SO₄ yields the following reactions in an aqueous medium



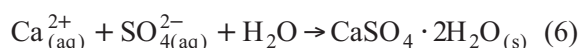
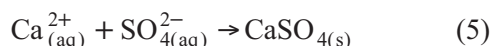
The equilibrium constant of the reaction (2) is $K_a = 0.012$. It is suggested that when ulexite is added into solution the following reaction takes place



When Ca^{2+} concentration reaches a limit value determined by

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{sp} \quad (4)$$

it gives the following reactions with SO_4^{2-} ions formed via the reaction (2) depending upon the experimental conditions.



The X-ray diffractogram of the original mineral sample and the sample subjected to dissolution process for 5 minutes at the experimental conditions of $d = -1000 + 710 \mu\text{m}$ particle diameter, mass concentration, 42 s^{-1} stirring speed, $30 \text{ }^\circ\text{C}$ reaction temperature and $4.90 \text{ mol} \cdot \text{L}^{-1}$ H_2SO_4 concentration are given in Figure 1 and 2, respectively. Although only ulexite is seen in X-ray diffractogram of the original ulexite mineral in Figure 1, Sassolite (H_3BO_3), anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are seen in Figure 2 in the X-ray diffractogram of the sample subjected to dissolution process. This situation confirms the occurrence of reactions (3), (5) and (6). Additional information about the dissolution mechanisms of the process is given by Tunç et al.¹¹

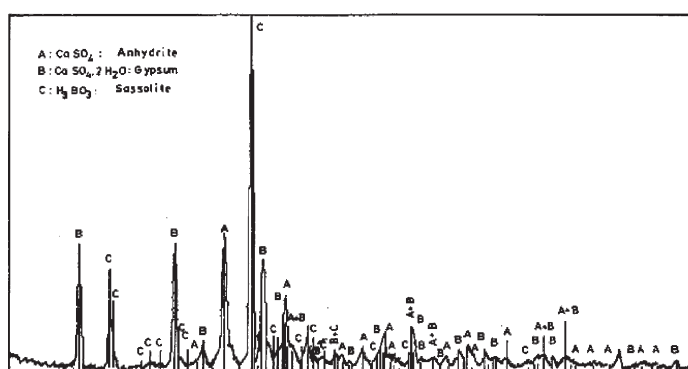


Fig. 2 – X-ray diffractogram of solid sample subjected to dissolution process for 5 minutes at a mass ratio of 4 : 122 $g \cdot \text{mol}^{-1}$

The effect of the quantities on the dissolution process

The effect of the granulometric characteristic on the dissolution rate was investigated using particle diameter fractions, given in Table 2, and the experiments were carried out at the conditions marked by an asterisk, called standard conditions here, in Table 2. As seen from the data in Figure 3, the dissolution rate

increases with decreasing particle diameter due to increasing a specific area of the sample.

The effect of H_2SO_4 concentration on the dissolution process was investigated using acid concentrations ranges, given in Table 2, and at the standard experimental conditions. The experimental results are presented in Figure 4 which shows that the increase of the acid concentration decreases the dissolution rate. This behaviour can be explained by the formation of H_3O^+ , HSO_4^- and SO_4^{2-} ions via the dissolution of H_2SO_4 in water. Since at high acid concentrations the amount of SO_4^{2-} per volume is higher than at low concentrations, the formation of a CaSO_4 film creates difficulty for H_3O^+ ions to diffuse to the unreacted mineral surface, resulting in a reduction in the dissolution rate.

The effect of the mass concentration was investigated using the ranges given in Table 2 at the standard conditions. As seen from the experimental data shown in Figure 5, increasing the mass concentration decreases the dissolution rate as expected.

The effect of the reaction temperature in the range of $3\text{--}40 \text{ }^\circ\text{C}$ was investigated at the standard conditions. Because the reaction between ulexite and H_2SO_4 solutions was fairly rapid, the temperatures in the range of $3\text{--}40 \text{ }^\circ\text{C}$ were chosen to study the effect of reaction temperature on dissolution rate. The experimental results in Figure 6 show that increasing reaction temperature substantially increases the dissolution rate.

The effect of the stirring speed was investigated in the range of $21\text{--}84 \text{ s}^{-1}$. Figure 7 shows that the stirring speed has no pronounced effect on the dissolution rate, and the complete dissolution was almost reached in 20 minutes at all stirring speeds.

Dissolution kinetics

The kinetics model of the dissolution process was analysed by applying shrinking particle models of solid–fluid heterogeneous reaction^{14,15}. But, the experimental results fitted none of these models. Further attempts to fit the results to a kinetic model led to the following expression

$$-\ln(1-x) = kt^n \quad (7)$$

which is called the Avrami model¹⁶. The regression analysis with 113 experimental data gave

$$-\ln(1-x) = kt^{0.79} \quad (8)$$

where

$$k = f(d_0, c_0, s_0, w, T) \quad (9)$$

The multiple regression analysis, including the effect of all the parameters gave the following kinetic expression, with a regression coefficient of 0.9905

$$-\ln(1-x) = \{1150 (d_0)^{-1.24} c_0^{-0.401} s^{-0.65} w^{0.14} e^{-4400/T}\} t^{0.79} \quad (10)$$

where

d_0 – the initial particle size, μm

c_0 – initial acid concentration, mol L^{-1}

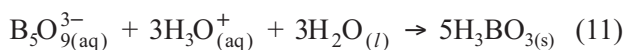
s_0 – initial mass concentration ratio, g mL^{-1}

w – stirring speed, s^{-1}

t – reaction period, s.

T – reaction temperature, K

The Avrami model¹⁶ is applied to explain the diffusion process through the gypsum layer on the mineral surface. As seen from X-ray analysis, CaSO_4 and/or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ solid by-products form during the reaction. The protonization of the boron-oxygen ring on the surface



produces boric acid as shown in Figure 8 and 1 mole of water is consumed as one mole hydronium ion attaches to the ring. This results in an instantaneous saturation of solution with H_3BO_3 , and thus the crystallisation of H_3BO_3 . Furthermore CaSO_4 is formed due to lack of water in the vicinity of the surface, in the Region I, while $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is formed in the Region II. The precipitation of these products creates difficulty for the diffusion of H_3O^+ to the surface, and due to crystallisation, the dissolution process can be expressed using the Avrami model. For a more detailed kinetic analysis beyond this empirical model and the standard models, a much more comprehensive and complex mathematical analysis accompanied by a more comprehensive experimental work program, could be performed. To test the agreement between the experimental results and the calculations by the model, the dissolution fractions are presented in Figure 9.

A good agreement was found with a relative root mean squares of the errors of 4.75 % calculated using

$$\text{ER} = \left[\frac{1}{N} \sum_{i=1}^N \frac{(x_{\text{pr}} - x_{\text{ex}})^2}{(x_{\text{pr}})^2} \right]^{1/2} \cdot 100 \quad (12)$$

where

N – the number of the experimental data

x_{pr} – predicted dissolution amount fraction

x_{ex} – experimental dissolution amount fraction.

Conclusions

This work showed that the kinetic model for the dissolution process of the ulexite mineral in

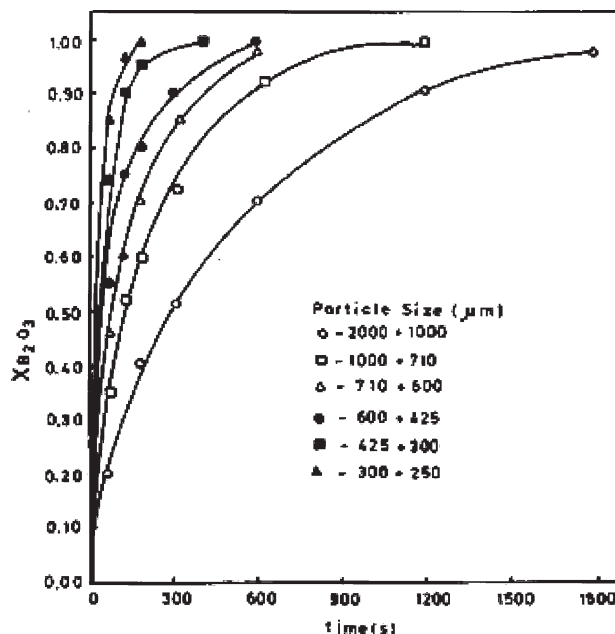


Fig. 3 – Effect of particle diameter on dissolution process

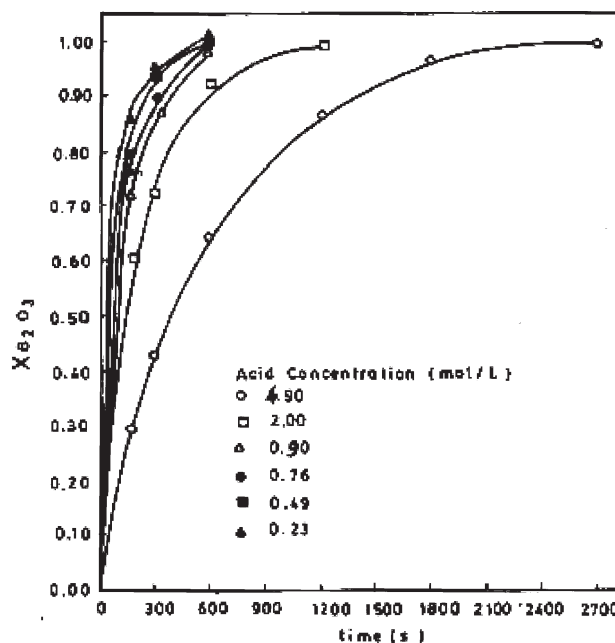


Fig. 4 – Effect of acid concentration on dissolution process

sulphuric acid solutions can be expressed by the Avrami model due to crystallisation of the product and by-products on the mineral surface. It was also determined that the precipitation of CaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on the mineral surface created difficulty for H_3O^+ to diffuse to the unreacted mineral surface. It was observed that the dissolution rate increased substantially with increasing temperature and slightly with increasing stirring speed, while it decreased with increasing particle size, solid-to-liquid ratio and acid concentration.

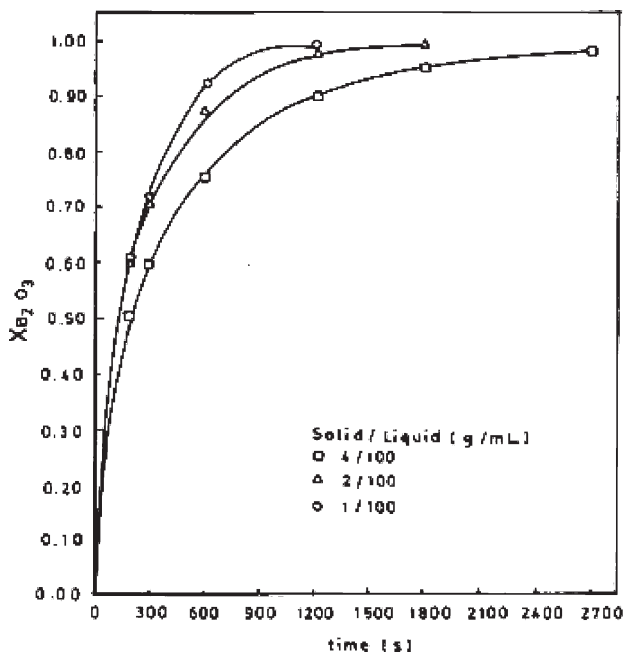


Fig. 5 – Effect of solid-to-liquid ratio on dissolution process

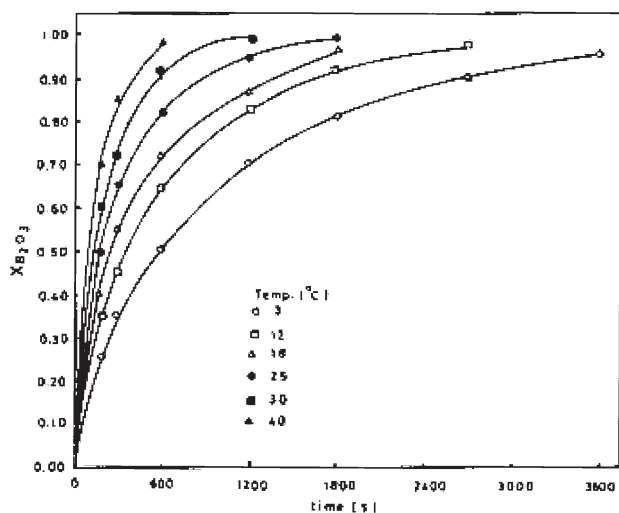


Fig. 6 – Effect of reaction temperature on dissolution process

List of symbols

- c – concentration, mol L⁻¹
- d – particle diameter, μm
- k – rate coefficient, s⁻¹
- N – number of experiments
- s – mass concentration, g mol⁻¹
- T – temperature
- t – reaction time
- w – stirring speed, rps
- x – dissolution amount fraction, n_d/n_t

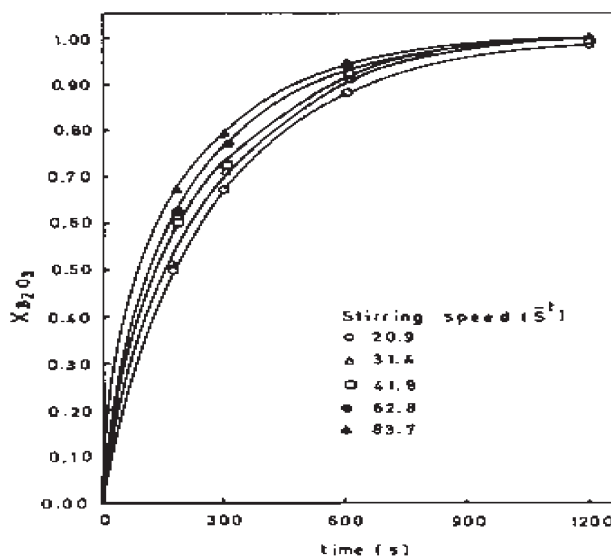


Fig. 7 – Effect of stirring speed on dissolution process

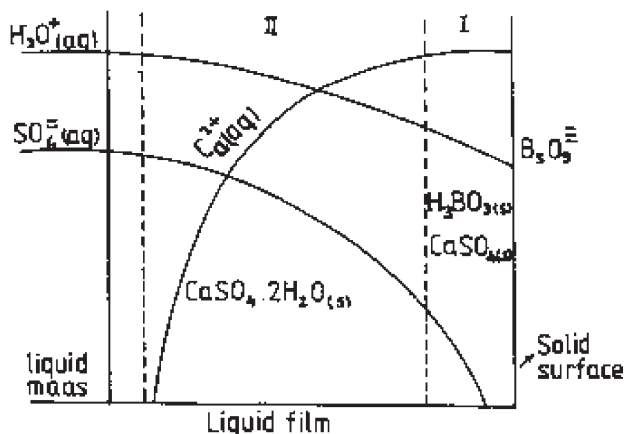


Fig. 8 – Schematic representation of dissolution process

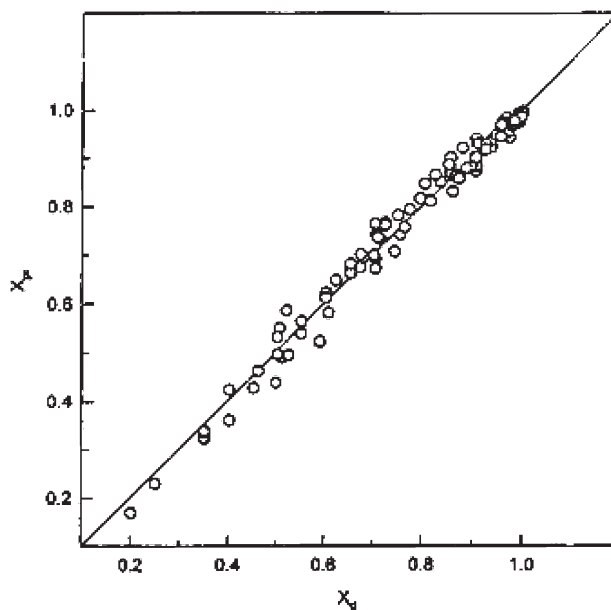


Fig. 9 – Agreement between predicted and experimental dissolution amount fractions

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