

Dissolution Kinetics of Calcined Ulexite in Ammonium Chloride Solutions

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In this study, the leaching kinetics of calcined ulexite in ammonium chloride solutions were investigated. The effect of calcination temperature, solution concentration, reaction temperature and pre-hydration were chosen as parameters. It was observed that the rate of dissolution increased with increasing calcination temperature, solution concentration and reaction temperature, while it was not affected by prehydration. Employing graphical and statistical methods, the dissolution rate, based on homogeneous reaction model, can be shown as: $(1 - X)^{-1} - 1 = k(\text{NH}_4\text{Cl})^{4/5}$. The activation energy for the dissolution of the ulexite sample calcined at 160°C was found to be 62.65 kJ mol⁻¹.

Key Words: Kinetics, Calcined ulexite, Ammonium chloride solutions.

INTRODUCTION

Boron is found as compounds of metals, especially of sodium and calcium, in nature¹. The production of boron compounds has substantially increased recently due to increasing use of these compounds in nuclear technology, in rocket engines as fuel and in the production of heat-resistant technology materials such as refractories and ceramics, high-quality steel, heat resistant polymers, etc. Ulexite, a hydrated calcium-sodium borate having the chemical formula $\text{Na}_2 \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ is a commercially important boron mineral. It is commonly used in the production of fire-resistant chemical substances, in isolators and fibre-glass². Ulexite and colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) are used as the borate minerals in sulphuric acid leaching process; gypsum is formed as a by-product, which poses several environmental problems^{2,3}.

The dissolution kinetics of ulexite in CO₂-saturated water³ and in SO₂-saturated water were studied earlier⁴. There are some studies on the boron minerals in the dissolution of hydrochloric acid⁵, nitric acid-acetic acid⁶, sulphuric acid⁷, the dissolution kinetics of colemanite in CO₂-saturated water⁸. In the other work⁹, the dissolution kinetics of colemanite in oxalic acid solutions were also studied and found that the dissolution rate was controlled by product layer (ash layer) diffusion process.

Some studies on the use of ammonium salt for leaching ores are also carried out. Ammonium carbonate solutions¹⁰ and ammonium sulphate solutions¹¹ were

used as leachant for malachite. The leaching of magnesite with ammonium chloride solution¹² has also been investigated. No work has been found in the literature relating to the dissolution of ulexite using ammonium chloride solutions. In this work, the effects of calcination temperature, concentration of NH_4Cl solution, reaction temperature and pre-hydration on the rate of dissolution were examined and kinetic parameters were also evaluated.

EXPERIMENTAL

The ulexite sample was provided from deposits around Eskişehir-Kirka in Turkey. After cleaning, ulexite was ground and the $-150\ \mu\text{m}$ size fraction was used for the present study. To prepare the calcined samples, some of the ulexite was calcined at 80, 120 and 160°C for 5 h in an ash furnace. The composition of the sample was determined by X-ray diffraction (Fig. 1) and their chemical composition is given in Table-1.

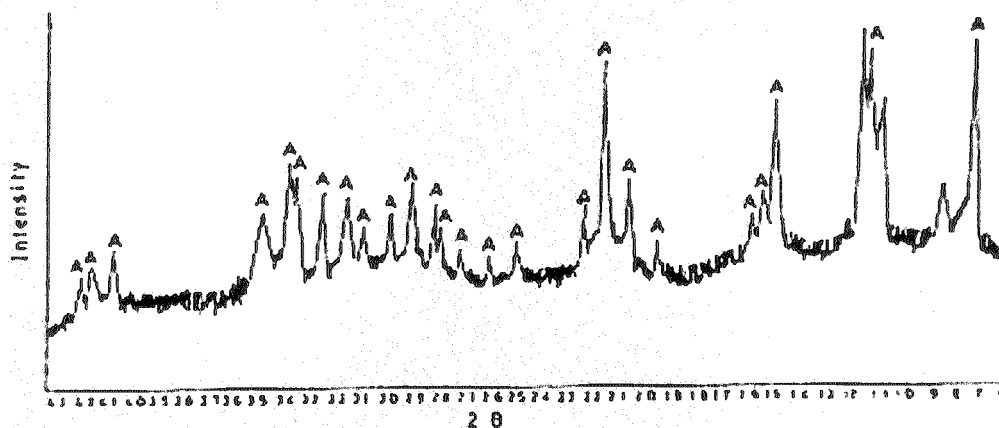


Fig. 1. X-ray diffractogram of original mineral (A: ulexite)

TABLE-1
CHEMICAL COMPOSITION OF THE ULEXITE SAMPLE

Calcination temperature ($^\circ\text{C}$)	Chemical decomposition (%)			
	Na_2O	CaO	B_2O_3	H_2O
Room temperature	7.64	13.83	42.92	35.56
80	8.30	14.45	44.42	32.22
120	8.57	15.39	47.71	28.28
160	9.41	17.03	52.86	20.67

Leaching experiments were carried out in 250 mL glass flasks equipped with condensers. The reaction mixture was stirred by a magnetic stirrer and kept at the required temperature by a constant temperature circulator. A 100 mL aliquot of leachant solution was equilibrated at the desired temperature and leaching was initiated by adding 1 g of the sample. At the end of the desired period of time, the contents of the vessel were filtered as soon as the process finished and B_2O_3 in the solution was analyzed titrimetrically using a digital titrator. The fraction of our sample reacted is defined as:

$$x = w/w_0$$

where w = mass of B_2O_3 in solution at time t and w_0 = total B_2O_3 in the sample.

RESULTS AND DISCUSSION

In initial tests the string speed was varied from 200–800 min^{-1} . The reaction rate proved to be insensitive to change in stirring speed, so all further experiments were performed at 500 min^{-1} .

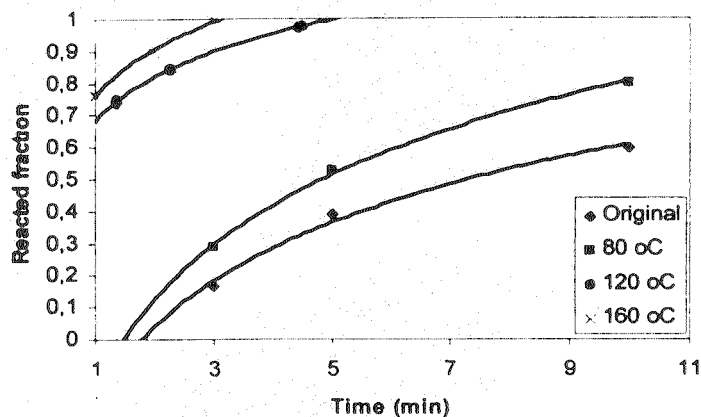


Fig. 2. Effect of calcination temperature on the dissolution rate

Effect of calcination temperature: The samples calcined at temperatures of 80, 120 and 160°C were used to study the influence of calcination temperature on the rate. The concentration and temperature of NH_4Cl solution were 2 M and 70°C, respectively. Fig. 2 shows that the pre-calcination of ulexite has strongly beneficial effect on the dissolution rate, during subsequent leaching the calcine. During the calcination process the way in which ulexite loses its crystal water depends on the temperature.

Effect of the solution concentration: Measurements were taken for 1, 2 and 3 M initial concentrations of NH_4Cl at 35°C with a $-150 \mu\text{m}$ fraction calcined at 160°C. The fraction reacted under the above conditions is shown in Fig. 3, indicating that the dissolution rate increased with increasing solution concentration.

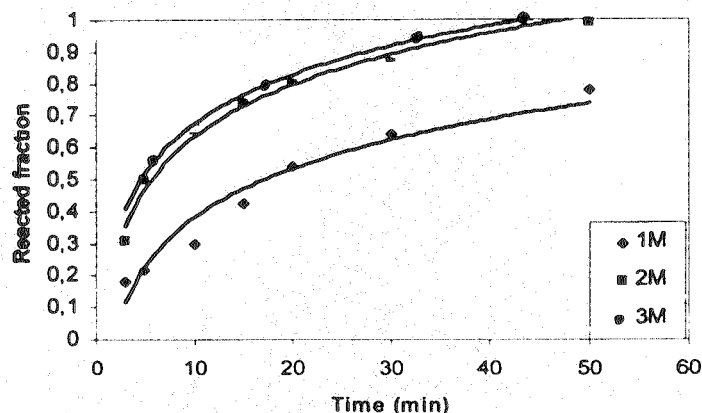


Fig. 3. Effect of the concentration of NH_4Cl solution on the dissolution rate

Effect of reaction temperature: The leaching was performed within the temperature range 20–70°C, concentration of 2 M NH₄Cl and with a –150 μm fraction calcined at 160°C. It was seen that the results given in Fig. 4 at the various temperatures have an important effect on the dissolution rate.

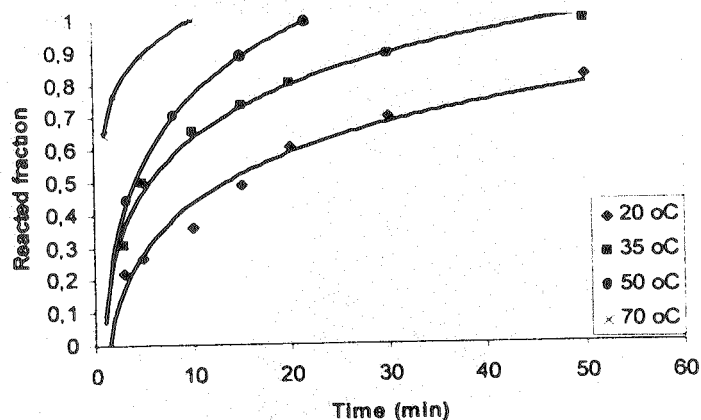
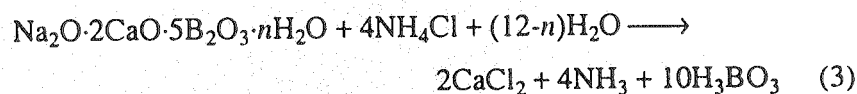


Fig. 4. Effect of the reaction temperature on the dissolution rate

Effect of pre-hydration: The sample calcined at 160°C was kept for 1 h in 50 mL of distilled water at 35°C before it was leached with 2 M NH₄Cl solution at the same temperature for different reaction periods. It was observed that the pre-hydration had no significant effect on the leaching rate, agreeing with the result of Renjitham and Khangaonkar¹² on leaching of calcined magnesite with ammonium chloride solution.

Dissolutions kinetics: The rate of reaction between a solid and a fluid can be expressed according to the heterogeneous or homogeneous reaction model¹³. According to the heterogeneous reaction model, the rate may be controlled by fluid film diffusion and product layer diffusion of chemical reaction. The fact that the dissolution rate was independent of stirring speed, as mentioned above, indicated that the diffusion through a fluid film does not act as a rate-controlling step. The dissolution reaction of colemanite in ammonium chloride solution can be described by the following equation:



where n = a number which can change from 0 to 16 depending on the calcination temperature.

Eqn. (3) assumes that there is no solid product layer formed during the leaching reaction; hence the possibility of product layer diffusion being the rate-controlling step is ruled out. If the surface reaction is the rate-controlling step, the relationship between the fractional conversion and time is

$$t/t^* = 1 - (1 - X)^{1/3} \quad (4)$$

The kinetic data of the present study were analyzed using graphical and statistical methods. As the experimental results were analyzed using fluid-solid heterogeneous reaction models by graphical and statistical methods, it was found that the data fit none of the heterogeneous kinetic model. When the experimental

data were analyzed using the homogeneous model, it was found that the process can be expressed by

$$t/t^* = (1 - X)^{1-m} - 1$$

For the homogeneous reaction model, the rate can be described by Bronikowski¹³:

$$t/t^* = (1 - X)^{1-m} \quad (5)$$

or

$$t/t^* = -\ln(1 - X) \quad (6)$$

where $t^* = 1/k_L$.

Equations (5) and (6) are for reaction orders $m \neq 1$ and $m = 1$, respectively. The experimental data were plotted in terms of eqn. (5) and as seen from Fig. 5, straight lines are obtained for the calcined samples. Fig. 6 shows similar plots for different

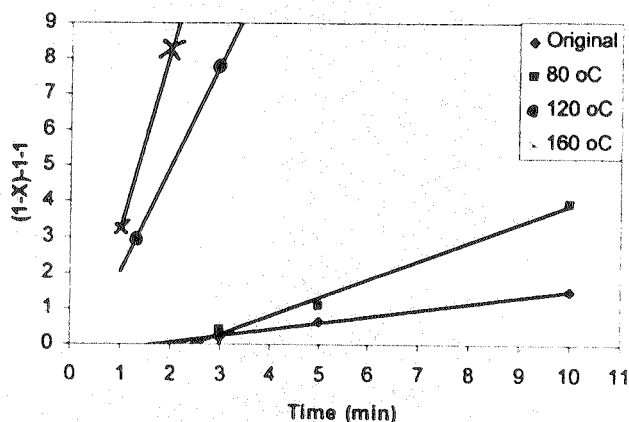


Fig. 5. Plot of $(1 - X)^{-1} - 1$ against t for samples calcined at different temperatures concentration of the solution and Fig. 7 for various temperatures. From these it was concluded that the rate is controlled by the homogeneous reaction for $m = 2$.

The slopes of the lines in Figs. 5-7 give the rate constant, k_1 . By assuming that the relationship between k_1 and C is:

$$k_1 = kC^n \quad (7)$$

The values of k for the sample calcined at 160°C and n were determined by plotting $\log k_L$ against $\log C$ using the k_L and C values from Table-2. By using

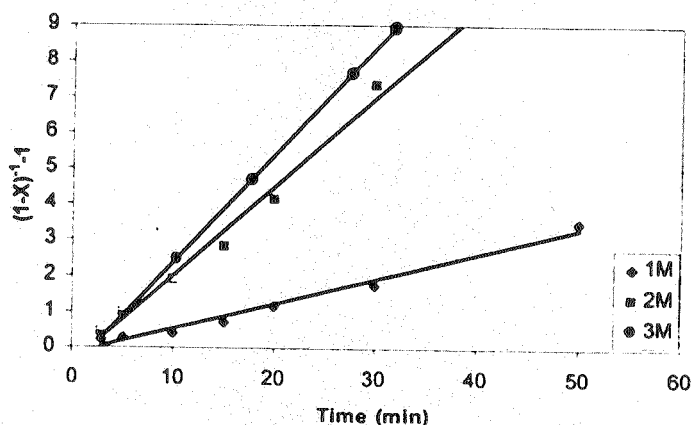


Fig. 6. Plot of $(1 - X)^{-1} - 1$ against t for various NH_4Cl concentrations

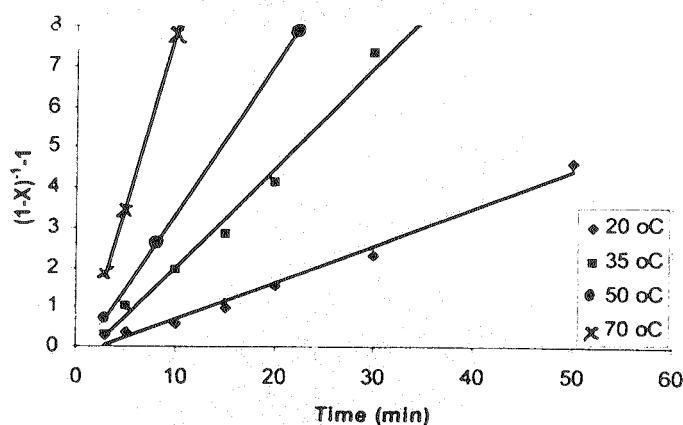
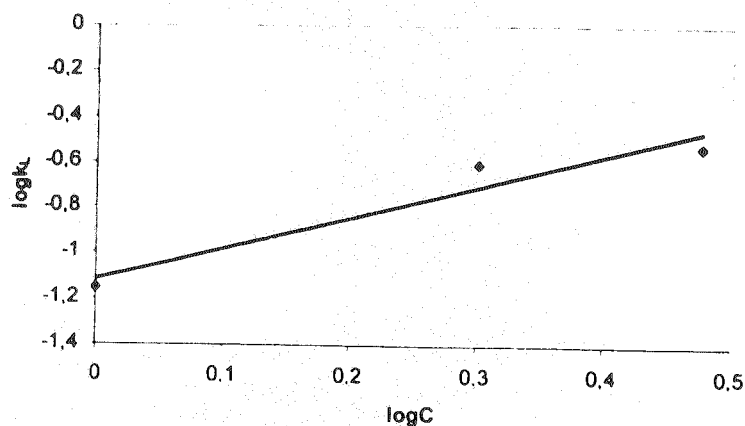
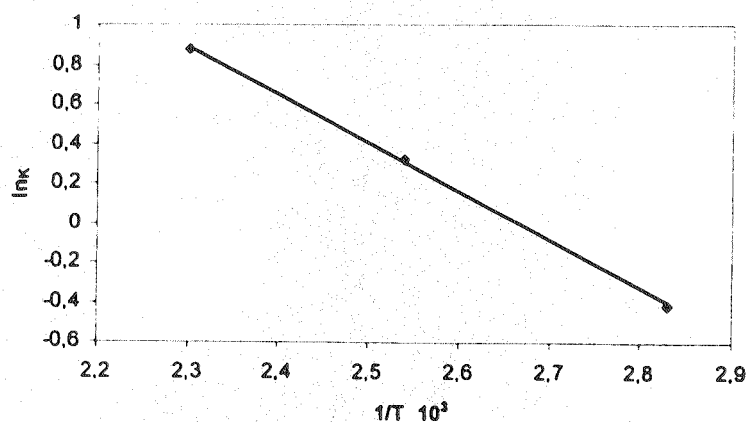
Fig. 7. Plot of $(1 - X)^{-1} - 1$ against t for various reaction temperaturesFig. 8. Plot of $\log k_L$ against $\log C$ 

Fig. 9. Arrhenius plot

k_L and n values in eqn. (7), k values at different temperatures for the sample calcined at 160°C were determined. The results obtained (Table-2) for different temperatures were used to construct the Arrhenius plot (Fig. 9), from which the activation energy and pre-exponential factor were found to be $62.65 \text{ kJ mol}^{-1}$ and $2.18 \cdot 10^{14} (\text{mol}^{-1})^{-3/4}$, respectively, showing that the dissolution rate is chemically controlled¹⁴.

TABLE-2
RATE CONSTANTS

Calcination temperature (°C)	Concentration of NH ₄ Cl solution (mol L ⁻¹)	Reaction temperature (°C)	k _L (min ⁻¹)	k [(mol L ⁻¹) ^{-3/4} min ⁻¹]
Room temperature	2	70	0.1807	0.1356
80	2	70	0.5200	0.3903
120	2	70	2.8916	2.1158
160	2	70	10.0272	7.5262
160	1	35	0.0702	0.0720
160	2	35	0.2476	0.1858
160	3	35	0.2929	0.1858
160	2	20	0.0911	0.0683
160	2	50	0.3728	0.2798

Conclusions

The investigation of leaching conditions and kinetics of ulexite in ammonium chloride solution will help to solve possible problems, which can be faced in the plant of boric acid production. The conclusions drawn from the present study are that ulexite can be dissolved completely in ammonium chloride solution. The dissolution rate increases as the calcinations temperature increases and is extremely sensitive to calcination temperature. The higher value of activation energy indicates that the dissolution is a chemically controlled reaction.

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