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## Dissolution of thermally dehydrated ulexite in ammonium acetate solutions

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**Abstract:** Ulexite, a boron mineral, contains a substantial amount of hydration water. Using calcination method, some part of water in the composition of solid can be removed from the solid matrix, and a porous structure can be obtained to increase the reaction rate. The dissolution of the calcined ulexite samples at various temperatures was investigated. Ammonium acetate was used as a leach reagent. The effects of some reaction parameters on the dissolution of the calcined ulexite were examined. It is found that the dissolution rate of calcined samples is higher than that of the uncalcined sample. The dissolution rate of the calcined ulexite is enhanced with increasing calcination temperature up to 150 °C. It is determined that the reaction rate conforms to the chemical reaction model. The activation energy of the dissolution process was calculated to be 41.5 kJ/mol. **Key words:** calcination; dissolution kinetics; ulexite; boron mineral

## **1** Introduction

The borates are an unusually large group of minerals, but the number of commercially important borates is limited [1]. Most of the world's commercially recoverable reserves of boron are in the form of the hydrated metal borate minerals, such as pandermite, ulexite, tincal, and colemanite [2]. Boron is never found at free form in nature, and it is usually obtained in the form of boric acid and other compounds by acid leaching of boron-containing ores.

Boric acid and some other boron salts have an extensive industrial use in the production of glass, porcelain, leather, cosmetics and photographic chemicals, detergent materials, polymer, catalysts, steel and refractory materials, etc. Boron compounds are used in certain fertilizers for the treatment of boron-deficient soils. Boric acid, which has mild bactericidal and fungicidal properties, is also used as a disinfectant and food preservative [3,4]. Boric acid is also used as the starting material in the preparation of many boron chemicals, including synthetic organic borate salts, boron phosphate, fluoroborates, boron tri-halides and borate esters [5,6]. Boron minerals, such as colemanite and ulexite, are used as raw materials in the production of boric acid.

Boric acid can be produced by the solid-fluid

reaction of the borate minerals with a leach reagent. The production of boric acid is performed from a reaction involving colemanite and sulfuric acid, in Turkey. In this production process, the ground colemanite reacts with an excess amount of sulfuric acid at 85-90 °C. Gypsum is formed as a by-product and precipitates in the reactor, while boric acid, which is highly soluble in water, remains in the liquid phase throughout the reaction. Gypsum is removed by filtration, and boric acid is crystallized by cooling the filtrate to about 40 °C [7–9]. Ulexite, a sodium-calcium-borate hydrate, has a chemical formula of Na<sub>2</sub>O·2CaO·5B<sub>2</sub>O<sub>3</sub>·16H<sub>2</sub>O, which is found in huge quantities in Turkey, and is commercially an important boron mineral. Ulexite is generally available together with other borates, and it can be used in addition to colemanite in the production of boron compounds due to the rapidly growing demand for various boron products [3,10]. In order to produce boric acid from ulexite, many studies have been performed using different leach reagents by various researchers [11-20].

Most of boron minerals include crystallization water in their structures. When minerals containing the water of crystallization, like ulexite, are subjected a heat treatment, they lose some part of hydrate water depending upon applied temperature. This process is known as calcination or dehydration. One of the goals of dehydration process is to obtain a porous solid for

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increasing the reaction rate in a solid-fluid reaction. The resulting porous structure allows more readily the occurring of the reaction between solid and fluid, and so the dissolution rate increases [21–23]. But, the dehydration process on the leaching rate of ulexite becomes effective till a certain dehydration temperature. During the dehydration process, some changes in the crystal structure of ulexite occur depending upon applied temperature. The porosity of ulexite increases with increasing the dehydration temperature. This provides an increment at the leaching rate. After a certain temperature, the sintering fact is observed with further heating the mineral. The sintering causes a decrease in the porosity of particle. Hence, the dissolution rate of ulexite decreases as a result of sintering [13,17,22,24].

Dehydration or calcination of ulexite was investigated [25–34]. The dissolution kinetics of calcined ulexite using various leach reagents was examined in recent years [13,15,17,22,24,34].

In this study, the dissolution of calcined ulexite at different dehydration temperatures was investigated in ammonium acetate solutions. The effects of calcination temperature, solution concentration, reaction temperature, solid to liquid ratio, and stirring speed on the dissolution of calcined ulexite were examined.

## 2 Experimental

#### 2.1. Material

The ulexite sample used in the study was provided from Kırka, Eskişehir, Turkey. The sample was crushed, ground, and then sieved using standard test sieves to obtain different particle sizes. A fraction of 0.425-0.850mm size was used in the calcination process. The original ore sample (uncalcined) was analyzed, and it was determined that the mineral contained 42.08% B<sub>2</sub>O<sub>3</sub>, 13.94% CaO, 7.85% Na<sub>2</sub>O, 35.96% H<sub>2</sub>O, and 0.17 % insoluble matter. The XRD pattern of the sample is given in Fig. 1.



Fig. 1 XRD pattern of original (uncalcined) ulexite sample

#### 2.2 Method

Ulexite dehydration was performed isothermally in an oven at constant temperatures of 100–250 °C for 3 h. The aim of dehydration process essentially was to obtain calcined ulexite samples for use in the determination of the relationship between solubility and calcination. After putting 2 g of the sample with particle size of 0.425–0.850 mm in a ceramic crucible furnished with a cover, the sample was subjected to a given temperature. Following this procedure, the sample was cooled and weighed. Thus, calcination data of samples at various temperatures were obtained.

The dissolution experiments were performed in a 500 mL cylindrical glass reactor equipped with a mechanical stirrer, a reaction temperature control unit, and a condenser to avoid loss of solution by evaporation. The experimental procedure was initiated by adding 200 mL ammonium acetate solution into the glass reactor and bringing it to the desired reaction temperature. A given amount of calcined solid sample was then added to the solution. The dissolution process was carried out for various reaction time. 3 mL liquor were withdrawn at regular intervals during the reaction and were immediately filtered. The amount of dissolved calcium in the solution was determined complexometrically using TitriplexIII solution as titrant. The conversion fraction (x) of calcined ulexite was calculated.

In the dissolution experiments, the effects of calcination temperature, concentration of ammonium acetate solution, reaction temperature, solid to liquid ratio, and stirring speed were investigated.

## **3 Results and discussion**

During the thermal treatment, ulexite loses some hydrate water depending upon the dehydration temperature. The dehydration reaction of ulexite can be written as follows:

$$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O_3(s) \longrightarrow Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot nH_2O(s) + (16-n)H_2O(g)$$
(1)

where *n* is the mole number of water remaining after dehydration. Relationship between the mass loss and  $B_2O_3$  content by calcination process is given in Fig. 2. It can be seen from Fig. 2 that the  $B_2O_3$  content increases with increasing mass loss as the calcination temperature arises. At temperature higher than 200 °C, the mass loss was not significant.

When the calcined ulexite is added into ammonium acetate solution, the overall reaction occurring during the dissolution process is probably as follows:

$$\begin{aligned} \text{Na}_2\text{O}\cdot\text{2CaO}\cdot\text{5B}_2\text{O}_3\cdot n\text{H}_2\text{O}(s) + 6\text{NH}_4\text{CH}_3\text{COO}(aq) + \\ (12-n)\text{H}_2\text{O}(l) \longrightarrow 2\text{NaCH}_3\text{COO}(aq) + \\ 2\text{Ca}(\text{CH}_3\text{COO})_2(aq) + 6\text{NH}_3(aq) + 10\text{H}_3\text{BO}_3(aq) \end{aligned} (2)$$



Fig. 2 Remaining water amount in ulexite and  $B_2O_3$  content after dehydration process at various temperatures

#### 3.1 Effect of parameters

To examine the effect of dehydration temperature on the dissolution of calcined ulexite, experiments were carried out using the calcined samples at dehydration temperatures of 100, 120, 140, 150, 160, 170, 180, 200, and 250 °C. Figure 3 shows that the dissolution rate increases with increasing dehydration temperature up to 150 °C, and it decreases above this temperature. After 15 min of dissolution, the conversion fraction of the calcined ulexite increases from 85.28% to 97.83% when the dehydration temperature increases from 100 to 150 °C. Further increasing the dehydration temperature above 150 °C, the conversion fraction of the calcined solid decreases for the identical dissolution time. This decrement in the dissolution rate can be attributed to the sintering of the particles with increasing dehydration temperature. Figure 4 shows the XRD patterns of the calcined ulexite samples at various temperatures. It can



**Fig. 3** Effect of dehydration temperature on dissolution of calcined ulexite (Solution concentration: 1 mol/L; reaction temperature: 30 °C; solid to liquid ratio: 0.01 g/mL; stirring speed: 400 r/min)



**Fig. 4** XRD patterns of calcined ulexite samples at various temperatures: (a) 120 °C; (b) 150 °C; (c) 200 °C

be seen that the crystal structure of ulexite during the dehydration was transformed into an amorphous state due to the thermal effect. Figure 5 illustrates the SEM images relating to the original and calcined ulexite samples at various temperatures. As can be seen from Fig. 5, numerous micro-cracks and openings in the calcined ulexite samples exist at all calcination temperatures. These cracks and openings allow the leaching reagent to penetrate the calcined ulexite more easily, and so the



**Fig. 5** SEM images of ulexite samples: (a) Original (uncalcined) ulexite; (b) Calcined ulexite at 120 °C; (c) Calcined ulexite at 150 °C; (d) Calcined ulexite at 200 °C

rate of the dissolution reaction increases. However, it was observed that the cracks were partially closed due to the sintering of the particles at a calcination temperature of 200 °C (in Fig. 5(d)). Reduction of the microcracks due to effect of heat treatment leads to a decrease in the dissolution rate of the calcined mineral. Hence, the optimum dehydration temperature was selected to be 150 °C, and all further experiments were performed using the calcined samples at this temperature.

In addition to the above experiments, to see the effect of calcination process on dissolution of ulexite, an experiment was also performed using the uncalcined sample. The result concerning this experiment is given in Fig. 6. Compared Fig. 3 with Fig. 6, it can be seen that it needs a longer reaction time for dissolution of the uncalcined sample. Thus, it is clearly understood that the dehydration process has significant influences on the dissolution of ulexite. Dissolution of the uncalcined ulexite samples in ammonium acetate solutions was investigated in the previous study [9].



**Fig. 6** Dissolution of original (uncalcined) ulexite (Solution concentration: 1mol/L; reaction temperature: 30 °C; solid to liquid ratio: 0.01 g/mL; stirring speed: 400 r/min)

Experiments were carried out at concentrations of 0.10, 0.25, 0.50 and 1.00 mol/L to observe the effect of the concentration of ammonium acetate solution on the

dissolution of calcined ulexite. Figure 7 shows the experimental results concerning the effect of solution concentration. It can be seen from Fig. 7 that the dissolution rate is enhanced when the solution concentration increases from 0.10 to 1.00 mol/L. Hydronium ion concentration increases with an increase in the concentration of ammonium acetate. Thus, the dissolution rate of the calcined sample increases with increasing the concentration of solution.



**Fig. 7** Effect of solution concentration on dissolution of calcined ulexite (Reaction temperature: 30 °C; solid to liquid ratio: 0.01 g/mL; stirring speed: 400 r/min)

The effect of reaction temperature on the dissolution rate of calcined ulexite was studied at 25–45 °C. The variations of the dissolution rate at various reaction temperatures are given in Fig. 8. It shows that the dissolution rate increases as the reaction temperature increases.



**Fig. 8** Effect of reaction temperature on dissolution of calcined ulexite (Solution concentration: 1 mol/L; solid to liquid ratio: 0.01 g/mL; stirring speed: 400 r/min)

To determine the effect of the solid to liquid ratio on the dissolution rate, experiments were performed at four different solid to liquid ratios in the range of 0.0025–0.02 g/mL. The results obtained from these tests are shown in Fig. 9. According to the results given in Fig. 9, the dissolution rate decreases as the solid to liquid ratio increases. This can be explained by an increase in the amount of solid per amount of reagent in the reaction mixture.



**Fig. 9** Effect of solid to liquid ratio on dissolution of calcined ulexite (Solution concentration: 1 mol/L; reaction temperature: 30 °C; stirring speed: 400 r/min)

Figure 10 shows the effects of stirring speed on the dissolution rate of calcined ulexite at the stirring speeds of 200, 300, 400, and 500 r/min. It can be concluded that the effect of stirring speed on the dissolution rate can be practically neglected.



**Fig. 10** Effect of stirring speed on dissolution of calcined ulexite (Solution concentration: 1 mol/L; reaction temperature: 30 °C; solid to liquid ratio: 0.01 g/mL)

#### 3.2 Kinetic analysis

The rate expression of the reaction between a solid and fluid can be represented by homogeneous or heterogeneous reaction models. The experimental data obtained in this study were analyzed by both the heterogeneous and homogeneous models, and it was determined that the data did not fit the homogeneous 1802

models. Thus, heterogeneous models were applied to deriving the rate equation of this process. When heterogeneous kinetic models were applied to the experimental data, it was observed that the dissolution process can be expressed by the following chemical reaction model [35–37]:

$$1 - (1 - x)^{1/3} = k_r t$$
 (3)

If the dissolution reaction follows the kinetic model in Eq. (3), then the straight lines passing through the origin must be obtained from graphs plotted for the left side of Eq. (3) versus time for each experimental parameter. Thus, the graphs of the left side of Eq. (3) vs reaction time were constructed by the conversion fraction obtained from the dissolution experiments for each parameter. It was observed that the straight lines with high correlation coefficients were obtained for all parameters. For the reaction temperature, the plot of  $1-(1-x)^{1/3}$  vs reaction time is given in Fig. 11. Thus, it can be said that the rate of this process is controlled by chemical reaction.

In order to determine the activation energy of the process, it was benefited from the slopes of the straight lines in Fig. 11. Figure 12 shows the apparent rate





**Fig. 11** Plot of  $1-(1-x)^{1/3}$  vs *t* at various reaction temperatures

Fig. 12 Arrhenius plot for dissolution process

constants obtained from the slopes of these lines vs 1/T. From the slope of the line in Fig. 12, the activation energy for this dissolution reaction was calculated to be 41.5 kJ/mol. This activation energy confirms that the dissolution rate is controlled by chemical reaction.

## **4** Conclusions

The effect of dehydration process on the dissolution of ulexite mineral was investigated. The dissolution of calcined ulexite was examined in ammonium acetate solutions. It was observed that the calcination process influenced the dissolution rate of ulexite. It was determined that the calcined samples were dissolved in shorter reaction time according to the uncalcined sample. The highest conversion values were obtained from the calcined samples at dehydration temperature of 150 °C. These results confirm with those in the literature. In the literature, the calcination temperatures determined for the maximum conversion are generally between 140 and 170 °C. At higher calcination temperatures, reduction of the dissolution rate of the calcined ulexite can be attributed to the sintering of the calcined product. It was determined that the dissolution rate increased with increasing solution concentration and reaction temperature, and decreasing solid to liquid ratio. It was found that the rate of this dissolution process was controlled by chemical reaction. The activation energy for this study was calculated to be 41.5 kJ/mol.

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# 热脱水钠硼解石在醋酸铵溶液中的溶解

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**摘 要:** 钠硼解石含有大量的结晶水。采用煅烧法可以将固体组分中的一部水脱去,得到一种多孔结构物质,以 提高浸出反应速率。采用醋酸铵作为浸出溶剂,研究煅烧钠硼解石样品在不同温度下的溶解情况。研究了反应参 数对煅烧钠硼解石溶解的影响。研究发现,煅烧样品的溶解速率高于未煅烧样品的溶解速率。在煅烧温度低于 150 ℃时,煅烧钠硼解石的溶解速率随着煅烧温度的升高而加快。钠硼解石的浸出反应速率符合化学反应控制模型。 溶解过程中的活化能为 41.5 kJ/mol。

关键词: 煅烧; 溶解动力学; 钠硼解石; 硼矿

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