

## Dissolution kinetics of calcined ulexite in ammonium sulfate solutions

Nizamettin Demirkiran<sup>a,✉</sup>, Mehmet Kayra Tanaydın<sup>b</sup>, G. Deniz Turhan Özdemir<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, Faculty of Engineering, İnönü University, Malatya, 44280, Turkey

<sup>b</sup> Department of Chemical Engineering, Faculty of Engineering, Tunceli University, Tunceli, 62000, Turkey

<sup>✉</sup>Corresponding author: [nizamettin.demirkiran@inonu.edu.tr](mailto:nizamettin.demirkiran@inonu.edu.tr)

Submitted: 19 April 2016; Accepted: 16 February 2017; Available On-line: 19 March 2018

**ABSTRACT:** Ulexite is one of the boron minerals, which include a respectable amount of hydration water. It can be used as a raw material in the production of boron compounds. Some part of water in the composition of ulexite can be removed from the solid matrix applying dehydration treatment, and a porous structure can be obtained to increase the reaction rate. In the present study, the effect of dehydration temperature on dissolution kinetics of ulexite in ammonium sulfate solutions was researched in a batch reactor utilizing the parameters of solution concentration, solid-to-liquid ratio, stirring speed and reaction temperature. It was determined that the dissolution rate of calcined material increased with increasing solution concentration and reaction temperature and with decreasing solid-to-liquid ratio. The highest dissolution rate was attained with the sample calcined at 150 °C. It was found that the dissolution rate fit to the first order pseudo-homogeneous model. The activation energy of the dissolution process was estimated to be 42 kJ·mol<sup>-1</sup>.

**KEYWORDS:** Ammonium sulfate; Dehydration; Dissolution kinetics; Ulexite

**Citation/Citar como:** Demirkiran, N.; Tanaydın, M.K.; Turhan Özdemir, G.D. (2018). "Dissolution kinetics of calcined ulexite in ammonium sulfate solutions". *Rev. Metal.* 54(1): e112. <https://doi.org/10.3989/revmetalm.112>

**RESUMEN:** *Cinética de la disolución de ulexita calcinada en soluciones de sulfato de amonio.* La ulexita es uno de los minerales de boro, que incluye una cantidad considerable de agua de hidratación. Se puede usar como materia prima en la producción de compuestos de boro. Una parte del agua existente en la composición química de la ulexita puede eliminarse de la matriz sólida aplicando tratamiento de deshidratación que permite obtener una estructura porosa, que aumenta la velocidad de reacción. En el presente trabajo, se estudió el efecto de la temperatura de deshidratación sobre la cinética de disolución de ulexita en soluciones de sulfato de amonio, en un reactor discontinuo estudiando los parámetros de concentración de solución, relación sólido/líquido, velocidad de agitación y la temperatura de reacción. Se determinó que la velocidad de disolución del material calcinado aumentaba al aumentar la concentración de la solución y la temperatura de reacción y con la disminución de la relación de sólido/líquido. La velocidad de disolución más alta se alcanzó con la muestra calcinada a 150 °C. Se encontró que la velocidad de disolución se ajusta al modelo pseudohomogéneo de primer orden. La energía de activación del proceso de disolución se estimó en 42 kJ·mol<sup>-1</sup>.

**PALABRAS CLAVE:** Cinética de disolución; Deshidratación; Sulfato de amonio; Ulexite

**ORCID ID:** Nizamettin Demirkiran (<https://orcid.org/0000-0001-9021-2477>); Mehmet Kayra Tanaydın (<https://orcid.org/0000-0003-1696-0754>); G. Deniz Turhan Özdemir (<https://orcid.org/0000-0003-4749-1989>)

## 1. INTRODUCTION

Boric acid is an important boron compound because it is used as the starting material in production of many boron chemicals including synthetic organic borate salts, boron phosphate, fluoroborates, boron tri-halides, borate esters. 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 (Şahin, 2002; Biyikoğlu and Yeksan, 2008; Demirkıran, 2009).

Boric acid can be manufactured from boron minerals, such as colemanite and ulexite. Boric acid is currently produced by means of heterogeneous solid-fluid reaction of colemanite minerals with sulfuric acid, in Turkey. In the present process, colemanite reacts with sulfuric acid at 85–90 °C, while calcium and boric acid in the structure of mineral pass into solution. When calcium in the solution reaches the saturation value, it precipitates in the form of gypsum. Boric acid is found in the soluble state in solution throughout the reaction. After gypsum is removed by means of filtration from solution, boric acid is obtained in the form of crystal by cooling the filtrate to about 40 °C. The yield of this process is not very good because of difficulties that are especially encountered in the filtration step of this process. On the other hand, one of the by-products generated in consequence of filtration process is borogypsum. When this material is discharged into the environment, it can cause environmental pollution. Thus, in order to improve alternative boric acid production process, many studies have been carried out by researchers. The researchers have concentrated to clarify the kinetics and mechanism of boron minerals dissolution (particularly colemanite and ulexite) in various inorganic and organic leaching solutions (Taylan *et al.*, 2007; Bulutçu *et al.*, 2008; Ekmekyapar *et al.*, 2010; Künkül *et al.*, 2012).

Boron minerals involve generally the crystallization water in their structures. Hydrated boron minerals lose some part of hydrate water depending upon applied temperature when they are undergone a heat treatment. This treatment applied to remove the water in mineral is known as calcination or dehydration. A reduction in original weight of hydrated mineral due to water loss occurs during heat treatment, and the B<sub>2</sub>O<sub>3</sub> grade of mineral increases. A porous solid is obtained in consequence of dehydration treatment, and the material becomes more chemically active. The resulting porous structure allows occurring more readily the reaction between solid and fluid, and so the dissolution rate increases

(Çelik *et al.*, 1994; Erşahan *et al.*, 1995; Künkül *et al.*, 1997; Demirkıran and Künkül, 2008).

Ulexite is found in huge quantities in Turkey, and it is commercially one of important boron minerals. Ulexite is generally available together with other borates, and it can be used in addition to colemanite in the production of boric acid (Demirkıran, 2008). Dehydration of ulexite mineral has been investigated by some researchers in the literature (Şener and Özbayoğlu, 1995; Tunç *et al.*, 1997; Waclawska, 1998; Erdoğan *et al.*, 1999; Şener *et al.*, 2000; Flores and Valdez, 2007). The dissolution kinetics of calcined ulexite using various leach reagents has been studied by researchers in recent years (Künkül *et al.*, 1997; Tekin *et al.*, 1998; Alkan *et al.*, 2000; Alkan *et al.*, 2004; Demirkıran, 2007; Künkül and Demirkıran, 2007; Demirkıran *et al.*, 2013).

In this work, the dissolution of calcined ulexite obtained at different dehydration temperatures was examined in ammonium sulfate solutions. The effects of dehydration temperature, concentration of ammonium sulfate, reaction temperature, solid-to-liquid ratio, and stirring speed on the dissolution of calcined ulexite were investigated. Ammonium sulfate solutions have a weakly acidic character. When ammonium sulfate ionizes in aqueous media, it yields ammonium and sulfate ions. When the ammonium ion hydrolyzes, it provides the protons required for the dissolution reaction. The resulting leach solutions from the dissolution of ulexite in the aqueous ammonium sulfate contain calcium, sodium, sulfate, dissolved boric acid, and ammonia/ammonium. After solid calcium sulfate is separated as waste product, various products such as boric acid, sodium sulfate, sodium and ammonium borates from the remaining solution may be obtained using suitable crystallization conditions.

## 2. MATERIALS AND METHODS

### 2.1. Material

Ulexite sample was supplied from Kırka, Eskişehir, Turkey. The material was crushed, ground, and then sieved using standard test sieves to obtain different particle size fractions. The sample used in the study was analyzed, and it was found 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 result of the X-ray analysis of the sample is given in Fig. 1. The SEM image of mineral is illustrated in Fig. 2.

### 2.2. Method

The dehydration of mineral was performed isothermally in an oven at constant temperatures in the range of 100–250 °C for various times. After putting 1 g of the samples with average particle size

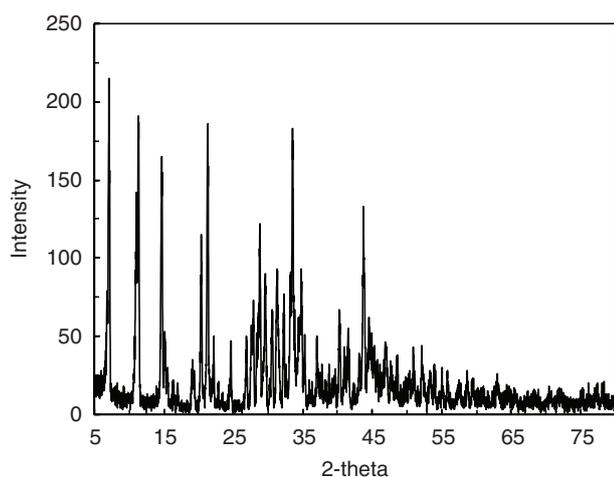


FIGURE 1. X-ray diffractogram of the uncalcined ulexite sample.

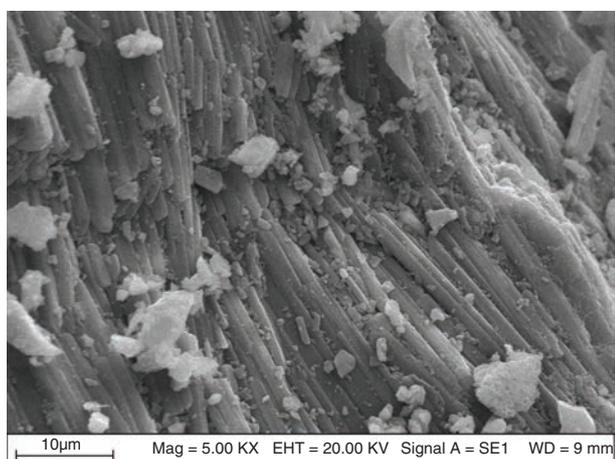


FIGURE 2. The SEM image of uncalcined ulexite mineral.

fractions of  $-0.840 + 0.420$  mm in a ceramic crucible, the ore was exposed to a given temperature for different dehydration times in the range of 0–180 min. After dehydration process, the calcined samples were cooled and weighed to determine the weight loss from ulexite mineral. The effects of dehydration temperature and time on the weight loss of ulexite were shown in Fig. 3. The weight loss, residual water content and  $B_2O_3$  content of the dehydrated mineral samples obtained after dehydration process at various temperatures were given in Table 1. Fig. 4 illustrates the X-Ray patterns of the calcined ulexite samples at temperatures of 150 and 200 °C. It can be observed from Fig. 4 that the crystal structure of ulexite was transformed into an amorphous state due to thermal effect during the dehydration process. Fig. 5 demonstrates the SEM images relating to calcined ulexite samples at temperatures of 150 and 200 °C.

The dissolution tests were performed in a 500 mL cylindrical glass reactor. The reactor content was

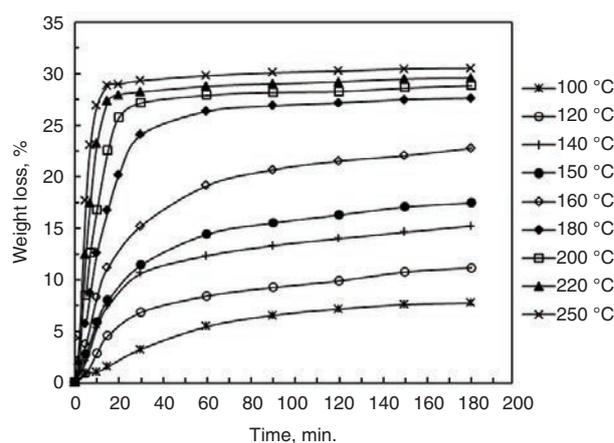


FIGURE 3. The weight loss of samples for various dehydration temperatures and times.

TABLE 1. The weight loss and the  $B_2O_3$  content of ulexite after dehydration process at various temperatures

Calcination Temperature (°C)	Weight Loss (%)	$B_2O_3$ Content (%)
Original (uncalcined)	—	42.08
100	7.52	46.46
120	10.50	48.00
140	14.75	50.40
150	17.37	52.00
160	21.56	54.77
180	27.66	59.34
200	28.6	60.17
220	29.2	60.68
250	30.42	61.75

mixed by a mechanical stirrer. To keep constant, the temperature during the dissolution reaction, a constant temperature circulator connected with reactor was used. After a total 200 mL of an ammonium sulfate solution of known concentration was poured into the reactor, the solution was heated to the desired temperature by means of reactor jacket. A given amount of dehydrated ulexite was added to the solution, and the reactor content was mixed by mechanical stirrer. Aliquots from solution in the reactor were withdrawn at regular intervals during the reaction and were analyzed to determine the dissolved boron content. After adding mannitol into the solution to be analyzed, the dissolved  $B_2O_3$  content was determined by titration using sodium hydroxide solution as titrant. The conversion fraction of calcined ulexite was calculated as follows:

$$X = \frac{\text{amount of dissolved } B_2O_3 \text{ in the solution}}{\text{amount of } B_2O_3 \text{ in the calcined ulexite}}$$

The data obtained were plotted as a function of conversion versus time.

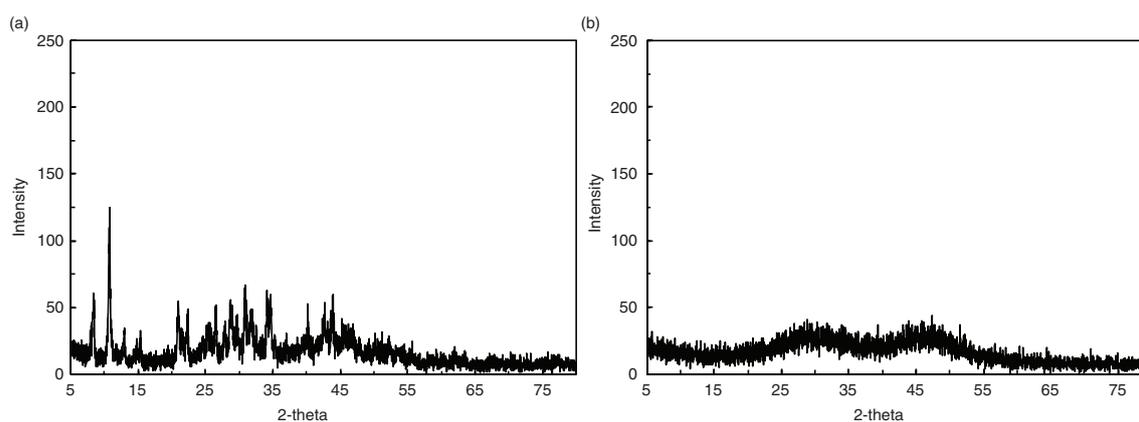


FIGURE 4. X-ray diffractogram of the calcined ulexite samples at 150 °C (a) and 200 °C (b).

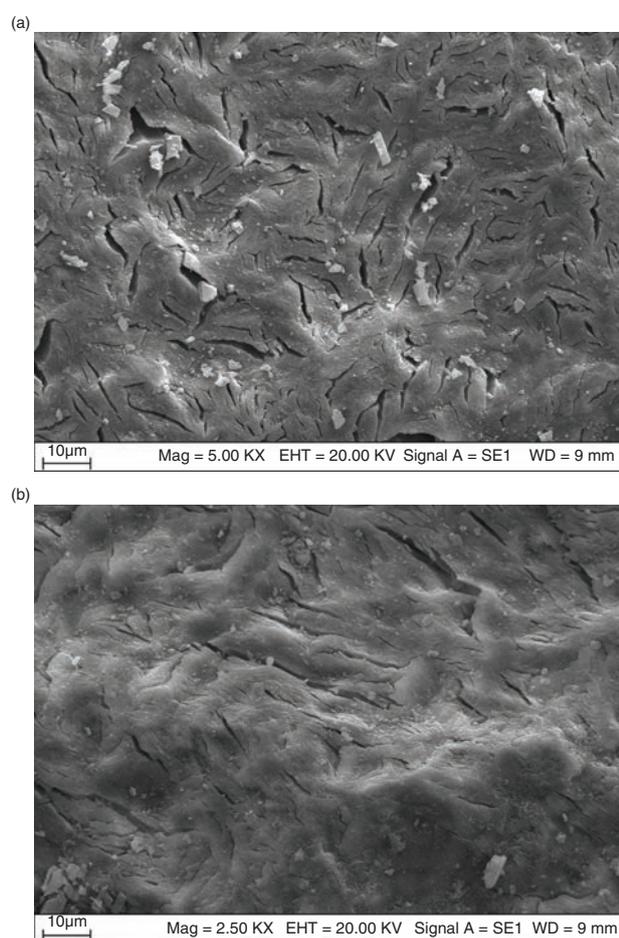
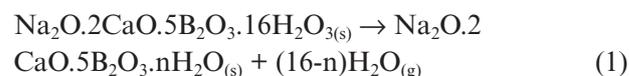


FIGURE 5. The SEM images of calcined ulexite samples at 150 °C (a) and 200 °C (b).

### 3. RESULTS AND DISCUSSION

The effect of thermal treatment at various temperatures on the weight loss of ulexite was given

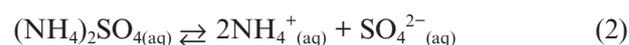
in Fig. 3. As can be seen from this figure, ulexite loses a portion of its hydrate water content during the thermal treatment. This figure shows that the dehydration rate is quite rapid within first 60 min for each temperature, thereafter the weight loss occurs more slowly. The weight loss increases with an increase in the dehydration temperature. The dehydration reaction of ulexite can be written as follows, Eq (1):



where  $n$  is the number of moles of water remaining after dehydration.

By increasing the weight loss, the hydrate water content per unit mass of calcined sample decreases, and the  $\text{B}_2\text{O}_3$  content increases. Relationship between the mass loss and  $\text{B}_2\text{O}_3$  content after dehydration can be seen in Table 1. This table was constructed using the values obtained at the end of 180 min in Fig. 3. It can be seen from Table 1 that the  $\text{B}_2\text{O}_3$  content increased with increasing mass loss as the calcination temperature arises. At temperature higher than 200 °C, the weight loss was not significant.

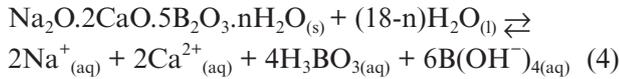
Ammonium sulfate ionizes in aqueous medium according to the following reactions:



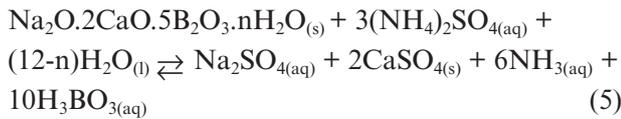
The hydrolysis reaction of ammonium ions with water gives hydronium ions and ammonia as shown in the following equation:



The reaction of calcined ulexite in aqueous medium is:



When calcined ulexite is added into ammonium sulfate solution, the overall reaction taking place in the aqueous medium containing ammonium sulfate can be written as follows (Eq. (5)):



In addition to the above reactions,  $\text{Ca}^{2+}$  ions pass in the solution as the mineral dissolves in ammonium sulfate solution. At the beginning of the dissolution, the concentration of  $\text{Ca}^{2+}$  in the solution increases until  $[\text{Ca}^{2+}][\text{SO}_4^{2-}] \geq K_{\text{sp}(\text{CaSO}_4)}$ , then,  $\text{CaSO}_4$  precipitate forms. Thus, the following precipitation reaction can be written (Eq. (6)):



### 3.1. Effects of parameters

To see the effect of dehydration process on the dissolution of ulexite, some experiments were carried out by using the calcined samples at dehydration temperatures of 100, 120, 140, 150, 160, 180, 200 and 250 °C. In these tests, the values of the solution concentration, stirring speed, solid-to-liquid ratio, and reaction temperature were chosen to be  $1 \text{ mol} \cdot \text{L}^{-1}$ , 400 rpm,  $2/200 \text{ g} \cdot \text{mL}^{-1}$ , and 30 °C, respectively. The results obtained these tests were plotted in Fig. 6. It can be seen from Fig. 6 that the dissolution rate of ulexite increased with increasing dehydration temperature up to 150 °C. It was observed that the conversion fraction of the calcined material decreased further increasing the dehydration temperature above 150 °C. This decrement can be attributed to the sintering of the particles with increasing dehydration temperature. Ulexite mineral loses more crystalline water at higher temperatures during the calcination process, and consequently the porosity of material can rise. At temperatures higher than 150 °C, the porosity of calcined ulexite can diminish due to sintering of particles. The sintering degree of particles may increase with increasing dehydration temperature.

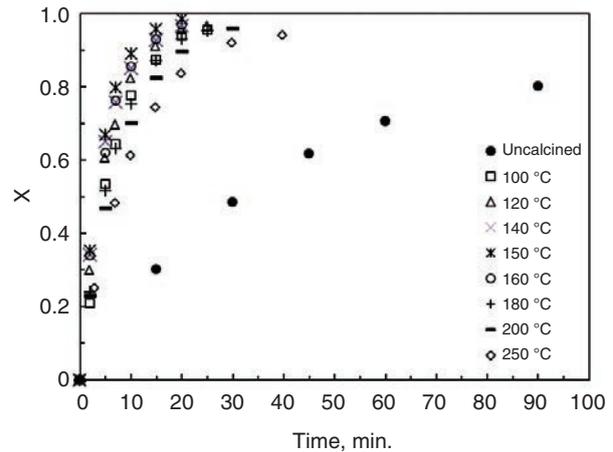


FIGURE 6. Effect of dehydration temperature on the dissolution rate of calcined ulexite.

Therefore, it can be said that there is a relation between particle porosity and dissolution rate. It can be observed from Fig. 5 above that micro-cracks and openings in the calcined ulexite sample at 150 °C arise. These gaps allow the leaching reagent to penetrate the calcined ulexite more easily, and so the dissolution rate of mineral increases. Due to the sintering of the particles at a dehydration temperature of 200 °C, it can be seen that the cracks closed partially. The fluid reactant cannot easily penetrate inwards the solid matrix by decreasing of pores, and the dissolution rate of the calcined ulexite decrease. Also, a test result performed using uncalcined ulexite was given in Fig. 6. It appears that it needs a longer reaction time to reach high conversion values for uncalcined sample. Thus, it is clearly understood that the dehydration process has significant effect on the dissolution of ulexite mineral. All further dissolution experiments were performed using the calcined samples at 150 °C.

The effect of ammonium sulfate concentration on the dissolution rate of calcined ulexite was studied at the concentrations of 0.10, 0.25, 0.50 and  $1.00 \text{ mol} \cdot \text{L}^{-1}$ , while a solid-to-liquid ratio of  $2/200 \text{ g} \cdot \text{mL}^{-1}$ , a stirring speed of 400 rpm and a reaction temperature of 30 °C were kept constant. The results obtained are presented in Fig. 7. It can be seen from Fig. 7 that the dissolution rate enhanced when the solution concentration increased from 0.10 to  $1.00 \text{ mol} \cdot \text{L}^{-1}$ . When ammonium sulfate ionizes in aqueous media, it provides ammonium ions according to Eq. 2, which contribute hydronium ions required for the dissolution of ulexite (in Eq. 3). Ulexite is a basic mineral, and hydronium ions are essentially responsible from dissolution of a basic mineral. Hydronium ion concentration increases with an increase in the concentration of ammonium sulfate. Thus, the dissolution rate of calcined sample increases with increasing concentration of solution.

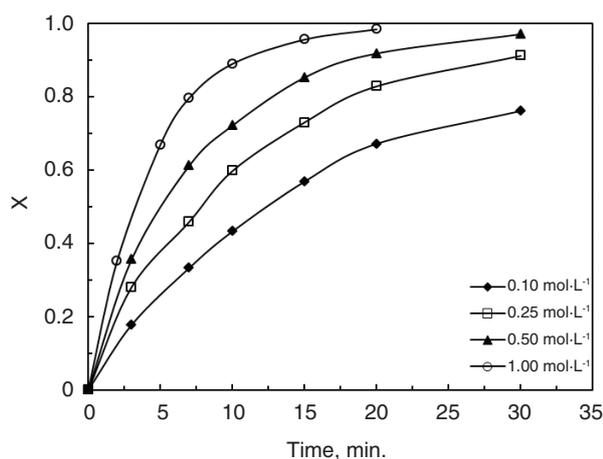


FIGURE 7. Effect of solution concentration on the dissolution of the calcined ulexite.

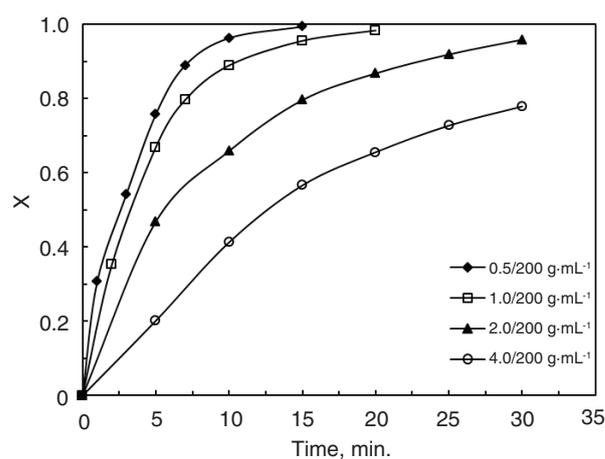


FIGURE 9. Effect of solid-to-liquid ratio on dissolution of calcined ulexite.

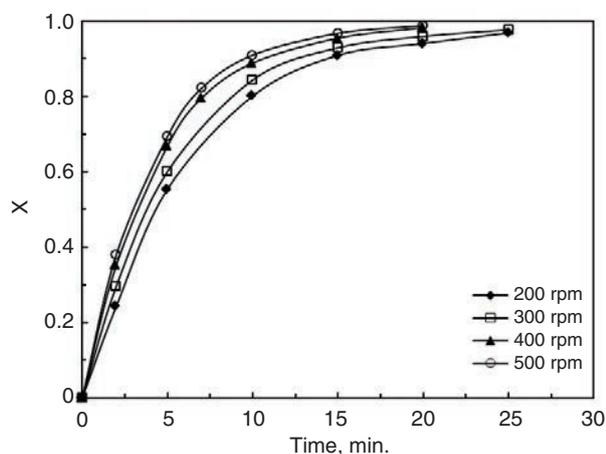


FIGURE 8. Effect of stirring speed on dissolution of calcined ulexite.

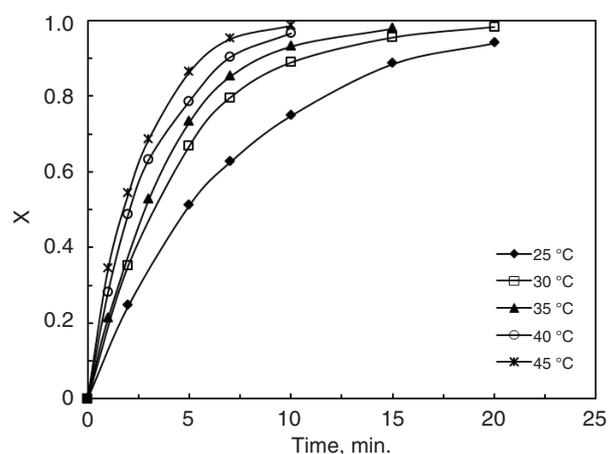


FIGURE 10. Effect of reaction temperature on dissolution of calcined ulexite.

The diffusion through the boundary layer of the leach reagent toward the external surface of the particles can be facilitated by means of the agitation of solution. Thus, the dissolution rate can increase with an increase in stirring speed. The effect of stirring speed on the dissolution rate of ulexite was examined in the stirring speeds of 200, 300, 400, and 500 rpm. During these experiments, the solution concentration, solid-to-liquid ratio and reaction temperature were kept constant at  $1 \text{ mol}\cdot\text{L}^{-1}$ ,  $2/200 \text{ g}\cdot\text{mL}^{-1}$ , and  $30 \text{ }^\circ\text{C}$ , respectively. Fig. 8 illustrates the effect of stirring speed on the dissolution process. It can be concluded that the stirring speed has little effect on the dissolution rate.

To observe the effect of the solid-to-liquid ratio on the dissolution rate, the experiments were carried out at four different solid-to-liquid ratios in the range of  $0.5/200\text{--}4/200 \text{ g}\cdot\text{mL}^{-1}$ . In these

experiments, the values of solution concentration, stirring speed, and reaction temperature were kept constant at  $1 \text{ mol}\cdot\text{L}^{-1}$ , 400 rpm, and  $30 \text{ }^\circ\text{C}$ , respectively. According to results shown in Fig. 9, the dissolution rate decreased as the solid-to-liquid ratio raised. Because the amount of solid per amount of fluid reactant will increase with increasing solid-to-liquid ratio, the decrease in the leaching rate can be an expected result.

To see the effect of reaction temperature on the dissolution of calcined ulexite in ammonium sulfate solutions, the experiments were performed at temperatures of 25, 30, 35, 40, and  $45 \text{ }^\circ\text{C}$ . The values of other parameters were kept constant at  $1 \text{ mol}\cdot\text{L}^{-1}$ ,  $2/200 \text{ g}\cdot\text{mL}^{-1}$ , and 400 rpm. The variations of the dissolution rate for various reaction temperatures are given in Fig. 10. This figure shows that the dissolution rate increases as the reaction temperature increases.

### 3.2. Kinetic analysis

The kinetic analysis of dissolution reactions is required for the design of reactor to be used in a hydrometallurgical process. The heterogeneous and homogeneous reaction models can be used to analyze the kinetics of the fluid–solid reactions. The most important models suggested for the derivation of the rate expression of a non-catalytic fluid–solid reaction are the shrinking core model and the progressive conversion model. According to the shrinking core model, it is thought that the reaction takes place on the outer surface of the solid and this surface shrinks toward the center of the solid as the reaction proceeds. This model assumes that the reaction rate may be controlled by diffusion through a fluid film, by a surface chemical reaction, or by diffusion through the ash or product layer. The integrated rate equations for each control mechanisms can be written as follows:

$$x = k_f t \quad (\text{for the film diffusion control}) \quad (7)$$

$$1-(1-x)^{1/3} = k_r t \quad (\text{for the surface chemical reaction control}) \quad (8)$$

$$\frac{1-3(1-x)^{2/3}+2(1-x)}{2} = k_d t \quad (\text{for the product or ash layer diffusion control}) \quad (9)$$

Where,  $x$  is the conversion fraction of solid particle,  $k_f$  is the apparent rate constant for diffusion through the fluid film,  $k_d$  is the apparent rate constant for diffusion through the product layer,  $k_r$  is the apparent rate constant for the surface chemical reaction, and  $t$  is the reaction time.

In the progressive conversion model, the liquid reactant is assumed to enter the solid particle and react at all times throughout the particle. Under these conditions, the reaction rate can be defined by pseudo-homogeneous models such as first order, second order (Levenspiel, 1972). If the reaction rate is controlled by pseudo-homogeneous models, then integrated rate equations are as follows:

$$-\ln(1-x) = k_1 t \quad (\text{for the first order pseudo homogeneous model}) \quad (10)$$

$$\frac{x}{(1-x)} = k_2 t \quad (\text{for the second order pseudo homogeneous model}) \quad (11)$$

where  $k$  is the first or second order rate constant.

The application of the above models to the experimental data will help to find the kinetics of the dissolution process. The experimental data obtained were analyzed by using the shrinking core model, but it was determined that the data did not fit this model. Low regression coefficients were obtained when the heterogeneous reaction models were applied to experimental data. Later, pseudo-homogeneous models were applied to determine the rate equation of this dissolution process.

When homogeneous models were applied to the experimental data obtained, it was observed that the dissolution process can be explained by the first order pseudo homogeneous model given in Eq. (10).

If the reaction follows the kinetic model in Eq. (10), then the straight lines passing through the origin must be obtained from graphs plotted for the left side of Eq. (10) versus time for each experimental parameter. Thus, the left side of Eq. (10) versus reaction time was plotted by using the conversion fraction values obtained from the experiments. After the graphs  $-\ln(1-x)$  versus time for each experimental parameter were drawn, it was seen that the straight lines passing through the origin with high correlation coefficients were obtained. The apparent rate constant values obtained from the plots and the correlation coefficients are provided in Table 2. Therefore, it can be said that the dissolution kinetics of calcined ulexite in ammonium sulfate solutions fit the first-order pseudo-homogeneous model.

The dependence of the rate constant on the solution concentration, solid-to-liquid and reaction temperature may be given by Eq. (12).

$$k = k_0 (C)^a (S/L)^b \exp(-E/RT) \quad (12)$$

TABLE 2. The apparent rate constants for the kinetic model and correlation coefficient values

Parameter	Pseudo-first order kinetic model	
	$k$ ( $\text{min}^{-1}$ )	$R^2$
Concentration, $\text{mol}\cdot\text{L}^{-1}$		
0.10	0.0516	0.980
0.25	0.0842	0.993
0.50	0.1214	0.995
1.00	0.2091	0.997
Solid-to-liquid ratio, $\text{g}\cdot\text{mL}^{-1}$		
0,5/100	0.3267	0.994
1/100	0.2091	0.997
2/100	0.1038	0.996
4/100	0.0519	0.996
Temperature, $^{\circ}\text{C}$		
25	0.1413	0.999
30	0.2091	0.997
35	0.2612	0.998
40	0.3330	0.998
45	0.4219	0.997

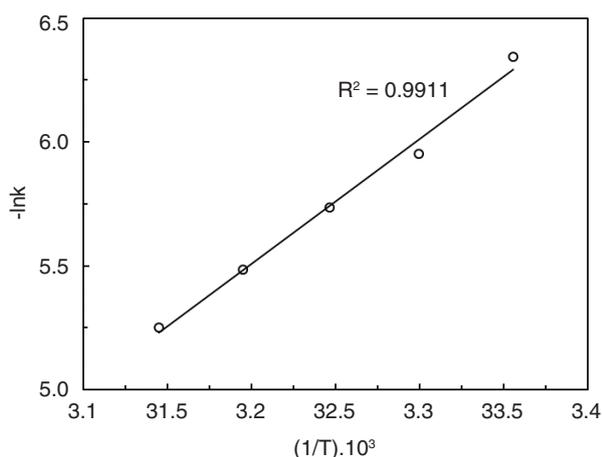


FIGURE 11. Arrhenius plot for the dissolution process.

The constants  $a$  and  $b$  in Eq. (12) were estimated using the apparent rate constant values given in Table 2 for the concentration and the solid-to-liquid ratio. The values of the constants  $a$  and  $b$  were calculated to be 0.55 and -0.89, respectively.

In order to calculate the activation energy of dissolution process, the Arrhenius plot in Fig. 11 was constructed using the apparent rate constants seen in Table 2. The slope of straight line in Fig. 11 gives the  $E/R$  value, and the intercept can be used to calculate  $k_0$ . The values of  $E/R$  and  $k_0$  were found to be 5045 and  $4.16 \times 10^4$ , respectively. Consequently, the following mathematical model can be suggested to represent the kinetics of this dissolution process.

$$-\ln(1-x) = 4.16 \times 10^4 (C)^{0.55} (S/L)^{-0.89} \exp(-5045/T).t \quad (13)$$

The activation energy for the reaction was calculated to be  $42 \text{ kJ} \cdot \text{mol}^{-1}$ .

#### 4. CONCLUSIONS

- In the present experimental study, the effect of dehydration process on the dissolution of ulexite mineral was examined. For this aim, the calcined ulexite samples at different dehydration temperatures were dissolved in ammonium sulfate solutions.
- It was observed that the calcination process possessed an important effect on the dissolution rate of ulexite. The effects of dehydration temperature, solution concentration, reaction temperature, solid-to-liquid ratio, and stirring speed on the dissolution of calcined ulexite were searched. It was determined that the dissolution rate of calcined samples was higher than that of the uncalcined samples.

- The highest conversion values were attained from the calcined samples at dehydration temperature of  $150 \text{ }^\circ\text{C}$ . At higher calcination temperatures above  $150 \text{ }^\circ\text{C}$ , it was observed that the conversion fraction decreased due to sintering of material.
- It was found that the dissolution rate increased with increasing solution concentration and reaction temperature, and decreasing solid-to-liquid ratio.
- A mathematical model was constructed to represent the dissolution process. The activation energy of the process was estimated to be  $42 \text{ kJ} \cdot \text{mol}^{-1}$ .
- The leach solutions obtained from the dissolution of the calcined ulexite in the ammonium sulfate contain calcium/calcium sulfate, sodium, sulfate, dissolved boric acid, and ammonia/ammonium. Various products, such as boric acid, sodium borates, and ammonium borates may be produced by applying appropriate separation processes.

#### REFERENCES

- Alkan, M., Çifçi, C., Ayaz, F., Doğan, M. (2000). Dissolution kinetics of ulexite in aqueous EDTA solutions. *Can. Metall. Quart.* 39 (4), 433–440. <https://doi.org/10.1179/cmq.2000.39.4.433>.
- Alkan, M., Doğan, M., Namli, H. (2004). Dissolution kinetics and mechanism of ulexite in oxalic acid solutions. *Ind. Eng. Chem. Res.* 43 (7), 1591–1598. <https://doi.org/10.1021/ie0302746>.
- Biyikoğlu, A., Yeksan, E. (2008). Production of anhydrous borax from borax pentahydrate. *Int. J. Hydrogen Energ.* 33 (23), 7103–7109. <https://doi.org/10.1016/j.ijhydene.2008.09.006>.
- Bulutçu, A.N., Ertekin, C.O., Kuskay Celikoyan, M.B. (2008). Impurity control in the production of boric acid from colemanite in the presence of propionic acid. *Chem. Eng. Process.* 47 (12), 2270–2274. <https://doi.org/10.1016/j.ccep.2007.12.012>.
- Çelik, M.S., Uzunoglu, H.A., Arslan, F. (1994). Decrepitation properties of some boron minerals. *Powder Technol.* 79 (2), 167–172. [https://doi.org/10.1016/0032-5910\(94\)02811-7](https://doi.org/10.1016/0032-5910(94)02811-7).
- Demirkiran, N. (2007). Leaching kinetics of calcined ulexite in ammonium nitrate solutions. *J. Chem. Eng. Jpn.* 40 (9), 755–760. <https://doi.org/10.1252/jcej.07WE027>.
- Demirkiran, N. (2008). A study on dissolution of ulexite in ammonium acetate solutions. *Chem. Eng. J.* 141 (1–3), 180–186. <https://doi.org/10.1016/j.ccej.2007.12.012>.
- Demirkiran, N. (2009). Dissolution kinetics of ulexite in ammonium nitrate solutions. *Hydrometallurgy* 95 (3–4), 198–202. <https://doi.org/10.1016/j.hydromet.2008.05.041>.
- Demirkiran, N., Künkül, A. (2008). Dissolution kinetics of ulexite prepared under different calcination temperatures. *Braz. J. Chem. Eng.* 25 (4), 751–758. <https://doi.org/10.1590/S0104-66322008000400012>.
- Demirkiran, N., Bayrakçı, N., Asin, C. (2013). Dissolution of thermally dehydrated ulexite in ammonium acetate solutions. *T. Nonferr. Metal. Soc. China* 23 (6), 1797–1803. [https://doi.org/10.1016/S1003-6326\(13\)62663-1](https://doi.org/10.1016/S1003-6326(13)62663-1).
- Ekmekyapar, A., Künkül, A., Demirkiran, N. (2010). Kinetic investigation of reaction between mineral ulexite and citric acid. *Min. Proc. Ext. Met. Rev.* 31 (4), 250–255. <https://doi.org/10.1080/08827508.2010.508961>.

- Erdoğan, Y., Zeybek, A., Şahin, A., Demirbaş, A. (1999). Dehydration kinetics of howlite, ulexite, and tunellite using thermogravimetric data. *Thermochim. Acta* 326 (1–2), 99–103. [https://doi.org/10.1016/S0040-6031\(98\)00591-7](https://doi.org/10.1016/S0040-6031(98)00591-7).
- Erşahan, H., Tunç, M., Ekmekyapar, A., Yapıcı, S. (1995). Flash dehydration of ulexite and investigation of dehydration kinetics from thermogravimetric data. *Thermochim. Acta* 250 (1), 125–135. [https://doi.org/10.1016/0040-6031\(94\)01978-P](https://doi.org/10.1016/0040-6031(94)01978-P).
- Flores, H.R., Valdez, S.K. (2007). Thermal requirements to obtain calcined and frits of ulexite. *Thermochim. Acta* 452 (1), 49–52. <https://doi.org/10.1016/j.tca.2006.10.007>.
- Künkül, A., Demirkıran, N. (2007). Dissolution kinetics of calcined ulexite in ammonium carbonate solutions. *Korean J. Chem. Eng.* 24 (6), 947–952. <https://doi.org/10.1007/s11814-007-0103-x>.
- Künkül, A., Tunç, M., Yapıcı, S., Erşahan, H., Kocakerim, M.M. (1997). Dissolution of thermally dehydrated ulexite in sulfuric acid solution. *Ind. Eng. Chem. Res.* 36 (11), 4847–4851. <https://doi.org/10.1021/ie9702136>.
- Künkül, A., Aslan, N.E., Ekmekyapar, A., Demirkıran, N. (2012). Boric acid extraction from calcined colemanite with ammonium carbonate solutions. *Ind. Eng. Chem. Res.* 51 (9), 3612–3618. <https://doi.org/10.1021/ie202388x>.
- Levenspiel, O. (1972). *Chemical Reaction Engineering*. John Wiley, New York.
- Şahin, S. (2002). A mathematical relationship for the explanation of ion exchange for boron adsorption. *Desalination* 143 (1), 35–43. [https://doi.org/10.1016/S0011-9164\(02\)00219-9](https://doi.org/10.1016/S0011-9164(02)00219-9).
- Şener, S., Özbayoğlu, G. (1995). Separation of ulexite from colemanite by calcination. *Miner. Eng.* 8 (6), 697–704. [https://doi.org/10.1016/0892-6875\(95\)00030-T](https://doi.org/10.1016/0892-6875(95)00030-T).
- Şener, S., Özbayoğlu, G., Demirci, Ş. (2000). Changes in the structure of ulexite on heating. *Thermochim. Acta* 362 (1–2), 107–112. [https://doi.org/10.1016/S0040-6031\(00\)00584-0](https://doi.org/10.1016/S0040-6031(00)00584-0).
- Taylan, N., Gürbüz, H., Bulutcu, A.N. (2007). Effects of ultrasound on the reaction step of boric acid production process from colemanite. *Ultrason. Sonochem.* 14 (5), 633–638. <https://doi.org/10.1016/j.ultsonch.2006.11.001>.
- Tekin, G., Onganer, Y., Alkan, M. (1998). Dissolution kinetics of ulexite in ammonium chloride solution. *Can. Metall. Quart.* 37 (2), 91–97. <https://doi.org/10.1179/cm.1998.37.2.91>.
- Tunç, M., Erşahan, H., Yapıcı, S., Çolak, S. (1997). Dehydration kinetics of ulexite from thermogravimetric data. *J. Therm. Anal.* 48 (2), 403–411. <https://doi.org/10.1007/BF01979284>.
- Waclawska, I. (1998). Controlled rate thermal analysis of hydrated borates. *J. Therm. Anal. Calorim.* 53 (2), 519–532. <https://doi.org/10.1023/A:1010101727380>.