

DISSOLUTION KINETICS OF ULEXITE PREPARED UNDER DIFFERENT CALCINATION TEMPERATURES

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Abstract - Ulexite is one of the boron minerals used as a raw material in the production of boron compounds. It contains a substantial amount of hydration water. Using calcination methods, the B_2O_3 grade of ulexite can be increased. In this study, the effect of calcination temperature on dissolution kinetics of ulexite in ammonium chloride solutions was investigated in a batch reactor employing the parameters of concentration, solid-to-liquid ratio and reaction temperature. It was found that the dissolution rate increased with increasing concentration and reaction temperature and with decreasing solid-to-liquid ratio. The highest dissolution rate was obtained with the sample calcined at 413 K. It was determined that the dissolution rate fit to the second-order pseudo-homogeneous model. The activation energy of this dissolution process was found to be 64.3 kJ/mol.

Keywords: Calcination; Ulexite; Dissolution kinetics; Ammonium chloride.

INTRODUCTION

From strategic and industrial points of view, boron is one of the most important elements in the world. Although the element is not used directly, its compounds have a wide range of applications. Boron is found in nature in the form of metal borates, mostly as sodium, calcium and magnesium borates. Boron compounds are produced from boron-containing ores. Commercially, the most-used compound of boron is boric acid. Boric acid is used in many branches of industry, such as in the medical, pharmaceutical and electronic sectors. Boric acid is also used as a starting material in the preparation of many boron chemicals including synthetic organic borate salts, boron phosphate, fluoroborates, boron tri-halides, borate esters, boron carbide and metal alloys such as

ferroboron. Ulexite and colemanite are used as raw materials in the production of boric acid (Çetin et al., 2001; Künkül et al., 2003; Temur et al., 2000).

Most boron minerals, like ulexite, tincal, colemanite and pandermite, include water of crystallization in their composition. They give off such water of crystallization on heating, a process known as dehydration. The dehydration of the hydrated boron minerals is an important preparation stage prior to the production of boron compounds (Erşahan et al., 1995), because transportation costs are reduced and the grade is increased. Besides, the mineral becomes more porous after the calcination process is applied and it is attacked by the leaching reagent more easily when subjected to a leaching process. Therefore, a high rate of extraction of boric acid can be obtained from the calcined mineral.

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Ulexite is a sodium-calcium-borate hydrate with a chemical formula of $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$. During the thermal dehydration process, ulexite loses part of its hydration water content, depending upon the dehydration temperature. Erşahan et al. (1995) observed that the dehydration of ulexite began at 100°C , and the dehydration rate was high up to 230°C . Above this temperature, the dehydration continued at a quite low rate up to 530°C , at higher temperatures, there was almost no loss of weight. Şener et al. (2000) reported that amorphisation was observed above 160°C .

Several studies on the dissolution of ulexite in various solutions can be found in literature. Kocakerim et al. (1993) studied the dissolution kinetics of ulexite in CO_2 -saturated water. Künkül et al. (1997a) examined the dissolution of thermally dehydrated ulexite in sulfuric acid solutions and determined that the dissolution process fit the first-order pseudo-homogeneous kinetic model. The dissolution kinetics of ulexite in ammonia solutions saturated with carbon dioxide was investigated by Künkül et al. (1997b). It was found that the dissolution rate of ulexite can be described by a first-order pseudo-homogeneous reaction. The activation energy of the process was calculated to be approximately 55 kJ/mol. The dissolution kinetics of ulexite in ammonium chloride (Tekin et al., 1998) and in ammonium sulfate (Künkül et al., 2003) solutions were investigated. In ammonium sulphate solutions, it was determined that the dissolution rate of ulexite can be described by a heterogeneous diffusion-controlled ash or product layer. The activation energy of the reaction was found to be 83.5 kJ/mol. Dissolution of ulexite in aqueous EDTA solutions was examined by Alkan et al. (2000). Alkan et al. (2004) studied the dissolution kinetics and mechanism of ulexite in oxalic acid solutions and determined that the reaction rate was controlled by product-layer diffusion. The activation energy was calculated to be 59.8 kJ/mol for this process. Recently, some studies relating to the leaching kinetics of calcined and uncalcined ulexite have been published in the literature. In these studies, ammonium chloride (Gür et al., 2006; Kucuk, 2006), perchloric acid (Demirkıran and Kunkul, 2007) and ammonium nitrate (Demirkıran, 2007) solutions were used as leaching reagents.

In most of the hydrometallurgical processes, inorganic acids are often used as the leaching reactant. When inorganic acids are used as leaching reagent, some undesired impurities can pass into the leaching media. Also, basic ores cause excess acid consumption in the leaching process. Therefore,

more basic lixivants may be a more attractive extracting agent. For this reason, ammonium salts can be used in the leaching studies of ores. The use of ammonium chloride solution has some advantages. One of the important characteristics of leaching in ammonium chloride solution is that pH 6.5 is maintained almost constant during the leaching. In addition, ammonium chloride provides chloride ion and the ammonium ions furnish the protons required for the dissolution reaction. When ammonium chloride is used as leachant in the leaching of ulexite, the final solution contains Na^+ , Ca^{2+} , and Cl^- ions in addition to dissolved boric acid. Boric acid is crystallized from the final solution, and Na^+ , Ca^{2+} and Cl^- ions remain in the solution.

As mentioned above, the B_2O_3 grade of ulexite is increased upon calcination, a porous solid can be obtained, and the material becomes more active chemically. Therefore, the leaching rate of the mineral can increase. In this study, the dissolution kinetics of calcined ulexite at different temperatures was examined in ammonium chloride solutions. The effect of calcination temperature, concentration of solution, reaction temperature and solid-to-liquid ratio were investigated and kinetic parameters are reported.

EXPERIMENTAL

Ulexite samples were obtained from Kirka, Eskisehir, Turkey. The material was first cleaned from visible impurities. Afterwards, the samples were sieved to obtain different particle size fractions. The original ore sample was analyzed and it was found that the mineral contained 42.08% B_2O_3 , 13.98% CaO , 7.95% Na_2O , 35.98% H_2O and 0.17% insoluble matter.

The aim of this process is essentially to obtain calcined ulexite samples for use in the determination of the relationship between solubility and calcination. The dehydration of ulexite was performed isothermally in an oven at constant temperatures between 373 K and 523 K for different periods of time until the weight loss was practically constant. After putting 1 g of the sample with particle size fractions of $-0.840+0.420$ mm in a ceramic crucible, the sample was subjected to the given temperature. Following this procedure, the sample was cooled and weighed. For various calcination temperatures and times, the weight loss of sample is presented in Fig.1. This figure shows that the weight loss is quite rapid up to a certain value at each temperature. Thereafter, the weight

loss is negligible. Therefore, ulexite calcined for 120 min was used in the dissolution tests. At each temperature, the maximum loss of weight (at 180 minutes) and the B_2O_3 grade are shown in Fig. 2. It can be seen in this figure that the B_2O_3 grade increases with increasing loss of weight. After the calcination tests, the calcined samples were used in the dissolution reactions.

Parameters that were expected to affect the dissolution rate were chosen, including the calcination temperature, solution concentration, reaction temperature, and solid-to-liquid ratio. The ranges of parameters are presented in Table 1. The dissolution experiments were carried out in a 500 mL cylindrical glass reactor equipped with a mechanical stirrer (a 45-mm-diameter Teflon stirring blade), a reaction temperature control unit (a constant-temperature bath), and a condenser to avoid loss of

solution by evaporation. The experimental procedure was as follows: 200 mL of a 99.5% pure ammonium chloride solution at a definite concentration were placed in the glass reactor. The reactor jacket was heated to the desired temperature and stirring speed was set. A given amount of calcined solid sample was added to the solution. The dissolution process was carried out for various reaction times. At the end of each reaction, the contents of the reactor were filtered and the amount of B_2O_3 in the solution was determined (Scott, 1963). B_2O_3 in the solution was analysed titrimetrically using a digital titrator. Since the aqueous solutions of boric acid have too weak of an acidic character, direct titration with a basic solution is not possible. For this reason, mannitol is added to the solution to give weak acid character, thus permitting direct analysis of boric acid by titration with a basic solution like sodium hydroxide.

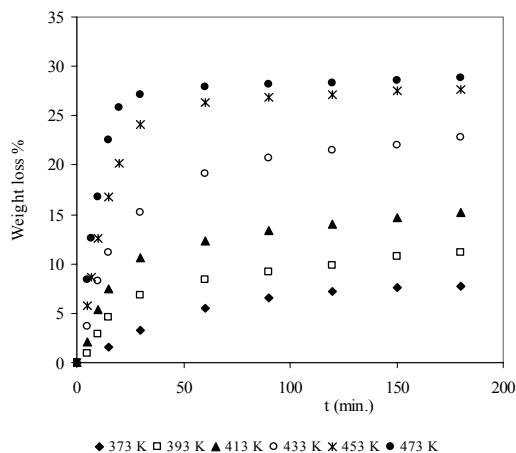


Figure 1: The weight loss of samples for various dehydration temperatures and times

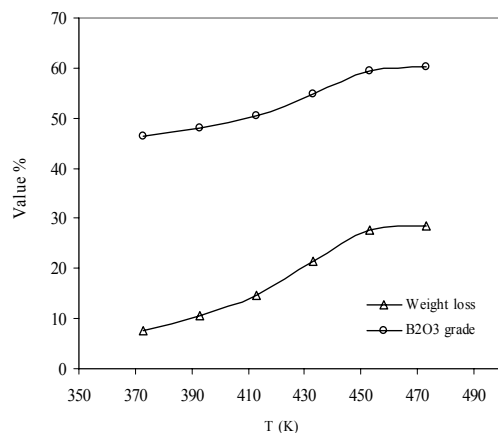


Figure 2: The maximum loss of weight (at 180 min.) and the B_2O_3 grade

Table 1: The ranges of parameters used in the experiments

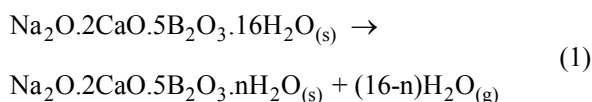
Parameter	Value					
	Dehydration temperature, (K)	373	393	413*	433	453
Concentration, (mol/L)	0.50	1.00	1.75*	2.50		
Solid/liquid ratio, (g/mL)	1/200	2/200*	4/200	6/200		
Temperature, (K)	298	303	308*	313	318	
Particle size, (mm)	-0.840+0.420*					
Stirring speed, (rpm)	400*					
Dehydration time, (min.)	120*					

* The constant values used when the effect of the parameters was investigated.

RESULTS AND DISCUSSION

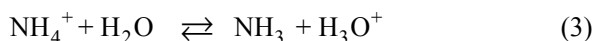
Dehydration and Dissolution Reactions

During the thermal dehydration process, ulexite loses part of its hydration water content depending upon the dehydration temperature. The dehydration reaction of ulexite is as follows:

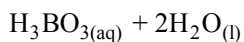
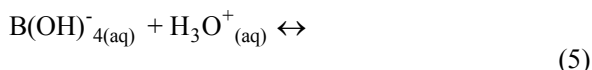
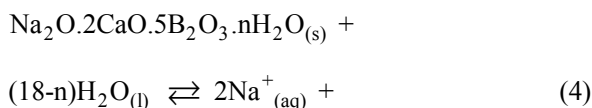


Where n is the number of moles of water remaining after dehydration.

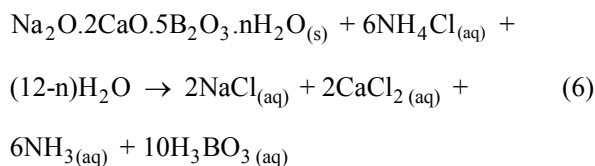
Ammonium chloride ionizes in aqueous medium according to the following reactions,



When the calcined ulexite is added into the ammonium chloride solution, the reactions occurring during the dissolution process are probably as follows.



Thus, the overall reaction can be written as follows.



Effects of Parameters

The effect of the dehydration temperature on the dissolution rate was examined at 373, 393, 413, 433, 453, and 473 K, while a concentration of solution of 1.75 mol/L, a solid-to-liquid ratio of 2 g/200 mL, a reaction temperature of 308 K and a stirring speed of 400 rpm were kept constant. The results are shown in Fig. 3. It can be seen that the dissolution rate increases with the dehydration temperature up to 413 K and decreases with the dehydration temperature above this temperature. This behavior can be explained on the basis of the changes in the crystal structure of ulexite that occur during calcination. During the calcination process, ulexite loses more crystalline water at higher temperatures, thus increasing its porosity. At temperatures higher than 413 K, the porosity of ulexite diminishes due to sintering. Sintering can be expected after 413 K, and the sintering rate of ulexite may increase rapidly with increasing calcination temperature. A similar behavior has also been observed by Künkül et al. (1997a), Tekin et al. (1998) and Alkan et al. (2000). Therefore, it appears that there is a direct relation between particle porosity and dissolution rate. In the absence of pores, the fluid does not penetrate easily inwards into the solid matrix.

The effect of ammonium chloride concentration on the dissolution rate was examined at the concentrations of 0.50, 1.00, 1.75 and 2.50 mol/L, while a calcination temperature of 413 K, a solid-to-liquid ratio of 2 g/200 mL, a stirring speed of 400 rpm and a reaction temperature of 308 K were kept constant. The results are presented in Fig. 4. This

figure shows that dissolution rate increases with an increase in solution concentration.

To observe the effect of the solid-to-liquid ratio on dissolution rate, the experiments were carried out at 1/200, 2/200, 4/200, 6/200 g/mL. During the experiments, the calcination temperature, the concentration, the stirring speed and the reaction temperature were kept constant at 413 K, 1.75 mol/L, 400 rpm, and 308 K, respectively. The results plotted in Fig. 5 show that the dissolution rate decreases with an increase in the solid-to-liquid ratio. This situation can be explained by the increase in the amount of solid per

amount of reagent in the reaction mixture.

In order to determine the effect of the reaction temperature on the dissolution rate, the experiments were performed with five different reaction temperatures in the range of 298-318 K. The temperature of calcination, the concentration of solution, the solid-to-liquid ratio and the stirring speed were kept constant at 413 K, 1.75 mol/L, 2 g/200 mL, and 400 rpm, respectively. The experimental results are plotted in Fig. 6. From this figure, it is seen that the conversion rate increases with the reaction temperature.

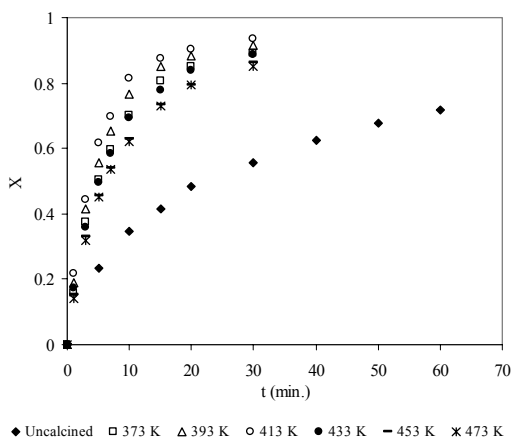


Figure 3: The effect of dehydration temperature on the dissolution rate

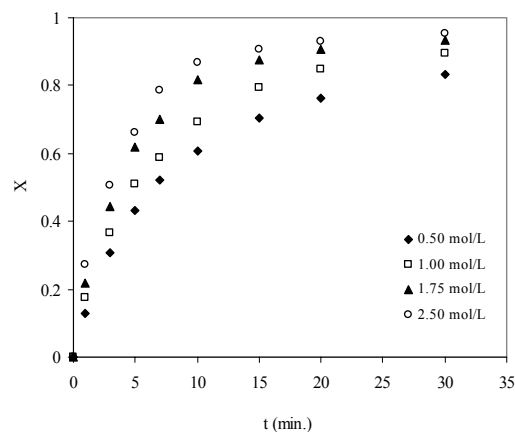


Figure 4: The effect of concentration on the dissolution of ulexite

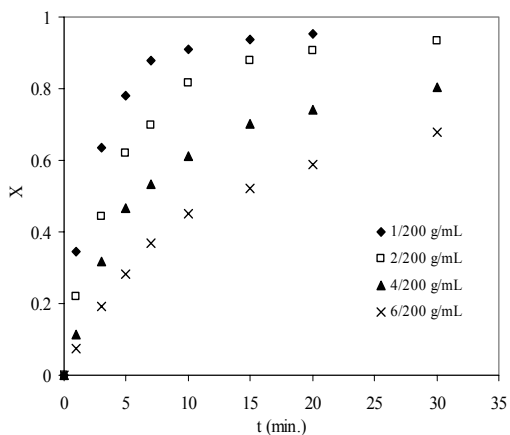


Figure 5: The effect of solid-to-liquid ratio on the dissolution of ulexite

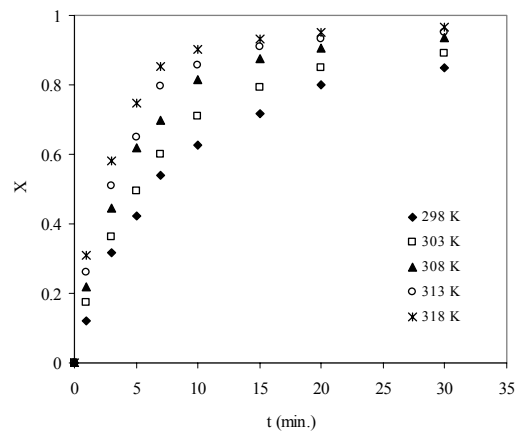


Figure 6: The effect of reaction temperature on the dissolution of ulexite

Kinetic Analysis

Fluid-solid heterogeneous reaction systems have many applications in chemical and hydrometallurgical processes. The reaction between a solid and a fluid may be represented by



The rate of reaction between a solid and a fluid can be expressed by heterogeneous and homogeneous reaction models. According to the shrinking-core model, the reaction is considered to take place at the outer surface of the unreacted particle. When no ash forms, the reacting particle shrinks during reaction, and finally disappears. For a reaction of this kind, the following three steps are considered to occur in succession during reaction (Levenspiel, 1972).

- 1) Diffusion of the fluid reactant from the main body of the fluid film to the surface of the solid,
- 2) Reaction on the surface between the fluid reactant and the solid,
- 3) Diffusion of the products of reaction from the surface of the solid through the fluid film back into the main body of the fluid. Note that the ash layer is absent.

The integrated rate equations can be given as follows if the process is controlled by the resistance of the fluid film (Eq.8) or by the resistance of the surface chemical reaction (Eq.9).

$$x = \frac{3bk_g C_A}{\rho_B R} t \quad (\text{the film diffusion}) \quad (8)$$

$$1 - (1-x)^{1/3} = \frac{bk_s C_A}{\rho_B R} t \quad (\text{the surface chemical reaction}) \quad (9)$$

In addition to the heterogeneous models, pseudo-homogeneous models can also be used to derive the rate equations for the heterogeneous reactions. In pseudo-homogeneous models, the rate equations are written as,

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

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

In addition to these models, the Avrami model can also be used.

$$-\ln(1-x) = kt^m \quad (\text{for the Avrami model}) \quad (12)$$

The reaction kinetics between calcined ulexite and ammonium chloride solutions were analyzed statistically and graphically by using the shrinking-core model. When the experimental data obtained were plotted, straight lines passing through the origin were not obtained, and low regression coefficients were found. Therefore, it was determined that the heterogeneous models were inappropriate for this study. The data were then analyzed by using the pseudo-homogeneous models. The plots of the left side of Eq. 10 and 11 versus time must be a straight line if the dissolution follows these models. Similarly the plot of logarithm of the left side of Eq. 12 versus time would be a straight line if the dissolution follows Avrami Model. It was found that the data did not fit the first-order pseudo-homogeneous model and the Avrami model. Using the second-order pseudo-homogeneous reaction model, the left side of Eq. 11 was plotted against the reaction time. As can be seen from the plots given in Fig. 7-9, straight lines passing through the origin were obtained. Therefore, the dissolution process was found to follow the second-order pseudo-homogeneous model. In accordance with these results, the equation representing the kinetics of this process can be expressed as follows.

$$(1-x)^{-1} - 1 = kt \quad (13)$$

The dependence of the rate constant on the concentration, solid-to-liquid ratio and reaction temperature may be given by,

$$k = k_0 (C)^a (S/L)^b \exp(-E/RT) \quad (14)$$

The rate constant values obtained from Fig. 7-9 were used to calculate the values of the constants a and b, in Eq (14). Average calculated values of the constants a and b were 0.86 and -1.48, respectively. To determine the activation energy of the dissolution reaction, the plot of $\ln k$ versus $1/T$ was drawn. It is clear that Fig. 10 shows a straight line. The slope of this line 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 7740 and 1.46×10^8 , respectively.

Consequently, the following mathematical model can be written to represent the reaction kinetics of this leaching process

$$(1-x)^{-1} - 1 = 1.46 \times 10^8 (C)^{0.86} (S/L)^{-1.48} \exp(-7740/T)t \quad (15)$$

The activation energy of the dissolution reaction was

calculated to be 64.35 kJ/mol.

To test the agreement between the experimental conversion and the values calculated from the mathematical model, the graph of x_{exp} versus x_{cal} was plotted as shown in Fig. 11. It is observed that the agreement between the experimental and the calculated values is very good.

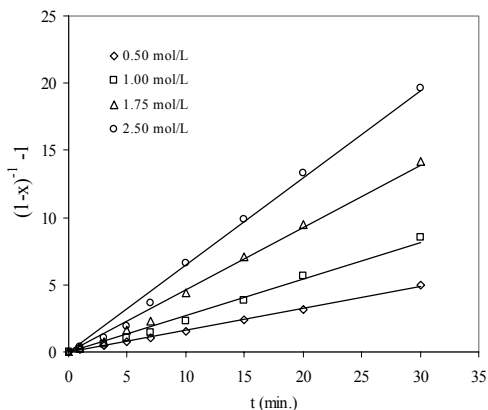


Figure 7: Variation of $(1-x)^{-1} - 1$ with time for different concentrations

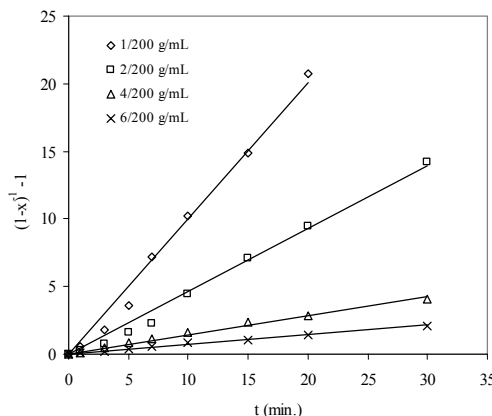


Figure 8: Variation of $(1-x)^{-1} - 1$ with time for different solid-to-liquid ratio

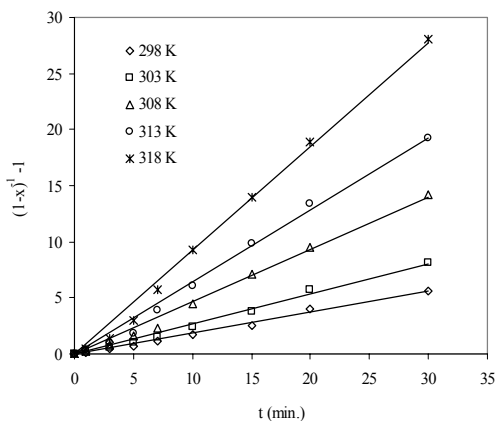


Figure 9: Variation of $(1-x)^{-1} - 1$ with time for different reaction temperatures

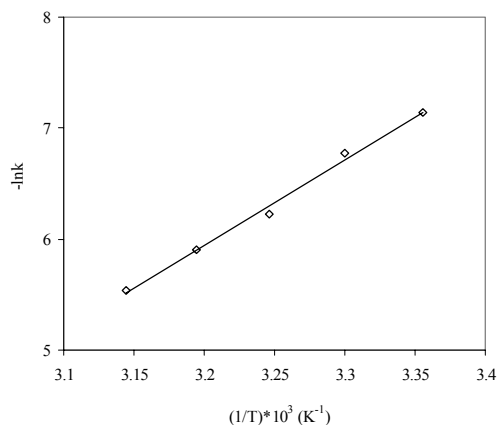


Figure 10: Arrhenius plot for the dissolution of calcined ulexite

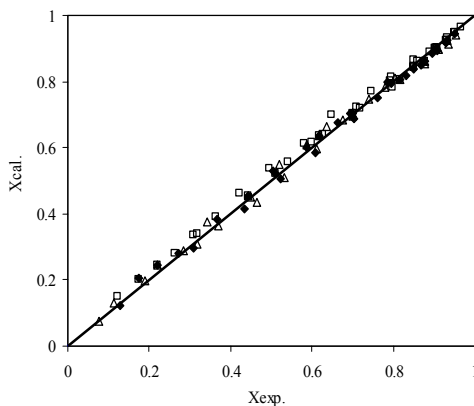


Figure 11: Agreement between experimental and calculated conversion values

CONCLUSION

In this work, the dissolution kinetics of calcined ulexite in ammonium chloride solutions was investigated. It was found that the dissolution rate increased with an increase in the dehydration temperature up to 413 K and decreased with an increase in the dehydration temperature above this temperature. It was determined that the conversion rate increased with an increase in the ammonium chloride concentration, an increase in the reaction temperature, and a decrease in the solid-to-liquid ratio. The dissolution process can be described by the second-order pseudo-homogeneous reaction model. The activation energy of the dissolution reaction was calculated to be 64.35 kJ/mol.

NOMENCLATURE

b	stoichiometric coefficient in Eq. 7	constant
C	concentration of ammonium chloride	mol/cm ³
C _A	bulk concentration of the fluid	mol/cm ³
E	activation energy	kJ/mol
S/L	solid-to-liquid ratio	g/mL
R	average radius of solid particle	cm
T	temperature	K
t	reaction time	s
x	converted fraction of the B ₂ O ₃	mass fraction, g/g
k	reaction rate constant	1/s
k _s	rate constant of surface reaction	cm/s
a, b, k ₀ , m	constants	
ρ _B	molar density of solid reactant	mol/cm ³

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