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A study on dissolution of ulexite in ammonium acetate solutions

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Abstract

Ulexite, sodium–calcium–borate hydrate, has a chemical formula of $Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$, and is found in great amounts in Turkey. In this study, the dissolution of ulexite in ammonium acetate solutions was investigated in a batch reactor. The effects of the concentration of solution, particle size, solid-to-liquid ratio, stirring speed and reaction temperature on the dissolution rate were determined. It was found that the dissolution rate increased with an increase in concentration and reaction temperature, and with a decrease in particle size and solid-to-liquid ratio. No effect of stirring speed was observed on the conversion. It was determined that the dissolution rate fit the chemical reaction control model. The activation energy of this dissolution process was found to be 55.7 kJ/mol.

Keywords: Ulexite; Dissolution; Ammonium acetate

1. 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, including nuclear technology, production of heat resistant materials (such as refractors and ceramics), heat-resistant polymers, catalysts, and in the medical, pharmaceutical and electronic sectors, among others. 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, borate esters, boron carbide and metal alloys such as ferroboron. Ulexite and colemanite are used as raw materials in the production of boric acid. Ulexite, sodium–calcium–borate hydrate, has a chemical formula of $Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$, is a commercially important boron mineral [1–3].

The dissolution of minerals in aqueous solutions is the basis of an important operation in hydrometallurgy known as leaching [4]. Many studies on the dissolution of boron minerals in various media have been found in literature. Some researchers investigated the dissolution kinetics of boron minerals in diverse acid solutions [5–11]. In acid solutions, it was determined that the decomposition rates of boron minerals decreased in order of $HClO_4$, HNO_3, HCl, H_3PO_4, CH_3COOH, H_2SO_4[8]. Kocakerim et al. [12] studied the kinetics of dissolution of ulexite in CO_2-saturated water. Künkül et al. [13] 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. [14], and the activation energy of the process was found to be approximately 55 kJ/mol. The dissolution kinetics of ulexite in sulphuric acid solutions was studied by Tunç et al. [15].

Since the acidity of many of the inorganic acids used as leaching reagents is generally high, it is expected that they have a low selectivity, while simultaneously having a high corrosive effect, making pH control more difficult [16]. When inorganic acids are used, some undesired impurities can pass into the leaching media. Additionally, basic ores cause excess acid consumption in the leaching process. Therefore, less acidic lixiviants than inorganic acids may be more attractive in the leaching processes. Some studies on the use of ammonium salts of inorganic acids in the leaching of ores were per-

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Nomenclature

a, b, c	constants in Eq. (12)
b	stoichiometric coefficient in Eq. (7)
C	concentration of ammonium acetate (mol/cm^3)
C_A	bulk concentration of the fluid (mol/cm^3)
D	particle diameter (cm)
D_e	effective diffusion coefficient (cm^2/s)
E_a	activation energy (J/mol)
k_d	apparent rate constant for diffusion through the product layer (s^{-1})
k_g	mass-transfer coefficient for the fluid film (cm^3/cm^2 s = cm/s)
k_r	apparent rate constant for the surface chemical reaction (s^{-1})
k_s	rate constant of surface reaction (cm/s)
k_0	frequency or pre-exponential factor (s^{-1})
k_l	apparent rate constant for diffusion through the fluid film (s^{-1})
S/L	solid-to-liquid ratio (g/mL)
R	universal gas constant (J/mol K)
R_0	average radius of solid particle (cm)
t	reaction time (s)
T	temperature (K)
x	converted fraction

Greek letter

ρ_B	molar density of solid reactant (mol/cm^3)

formed. Ammonium carbonate [17], ammonium chloride [18], and ammonia/ammonium carbonate solutions [19] were used as an extracting agent in the leaching of malachite ore. The leaching of magnesite ore was investigated in ammonium chloride solutions [20,21]. The dissolution kinetics of ulexite was examined in ammonium chloride [22] and ammonium sulphate [2] solutions.

Organic reagents are usually more selective than inorganic reagents [23]. Organic acids have high selectivity although their dissolving abilities are weak. They may be an attractive extracting agent, though, because the extraction can be performed under mildly acidic conditions [24]. Therefore, various organic acids such as acetic acid [25–28], citric acid [23], gluconic acid [29], and lactic acid [30] have been used in the leaching studies of ores in recent years. The dissolution kinetics of colemanite was studied in acetic acid [31] and oxalic acid [32] solutions. The dissolution kinetics of ulexite was investigated by Alkan et al. [33] in aqueous EDTA solutions. Alkan et al. [34] examined the dissolution kinetics and mechanism of ulexite in oxalic acid solutions, and determined that the reaction rate was controlled by product-layer diffusion.

In the literature, there was no study found that ammonium acetate was used as a leaching reagent. Thus, the aims of this study were to investigate the dissolution of ulexite using ammonium acetate solutions, and to determine the effects of the experimental parameters, including solution concentration, solid-to-liquid ratio, particle size, stirring speed and reaction temperature. A kinetic analysis was performed using the shrinking core model.

2. Experimental

The ulexite samples used in this study were obtained from Kırka, Eskisehir, Turkey. The material was first cleaned of visible impurities, crushed and ground. The samples were sieved to obtain different particle size fractions. The original mineral sample was analyzed, and it was determined that the mineral contained 42.08% B_2O_3, 13.94% CaO, 7.85% Na_2O, 35.96% H_2O and 0.17% insoluble matter.

Parameters that were expected to affect the dissolution rate were chosen including the concentration of solution, reaction temperature, solid-to-liquid ratio, particle size and stirring speed. The ranges of parameters are given Table 1. The leaching experiments were carried out in a 500 mL cylindrical glass batch reactor equipped with a mechanical stirrer, a reaction temperature control unit, and a cooler to avoid loss of solution by evaporation. In each experiment, a volume of 200 mL ammonium acetate solution at a definite concentration was placed in the glass reactor. The reactor jacket was heated to the desired temperature and the stirring speed was set. The sketch of the apparatus used in the dissolution process of ulexite is shown in Fig. 1. A given amount of solid sample was added to the solution. The dissolution process was performed for various reaction times. At the end of each reaction, the contents of the reactor were filtered, and the amount of calcium in the leach solution was determined complexometrically by EDTA in the medium of buffered solution (about pH 10) [35]. Each experiment was repeated twice and the arithmetic average of the results was used in kinetic modelling. These experiments could be repeated with a maximum deviation of approximately ±2.2% in terms of the conversion fraction.

Table 1
The ranges of parameters used on the experiments

Parameter	Value				
Concentration (mol/L)	0.25	0.50	1.00[a]	1.75	
Particle size (mm)	−0.840 + 0.420	−0.420 + 0.250[a]	−0.250 + 0.180	−0.180 + 0.150	
Solid/liquid ratio (g/mL)	0.5/200	1.0/200[a]	1.5/200	2.0/100	2.5/200
Stirring speed (rpm)	300	400[a]	500		
Temperature (K)	298	303	308[a]	313	318

[a] The constant values used when the effect of the parameters was investigated.

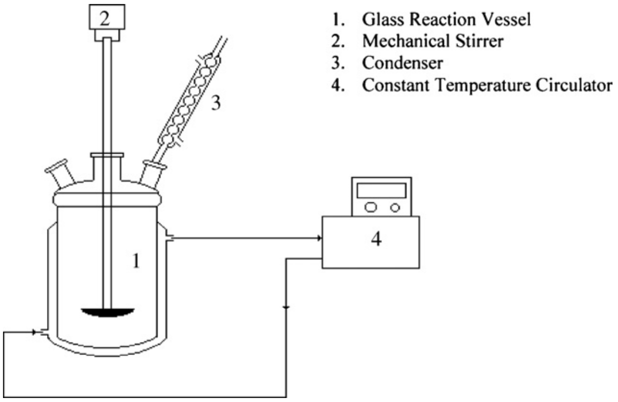

Fig. 1. Schematic view of experimental setup.

3. Results and discussion

The dissolution rate of ulexite was determined as a function of time by changing the ammonium acetate concentration, particle size, solid to liquid ratio, stirring speed and reaction temperature. In the experiments, while the effect of one parameter was examined, the values of the other parameters shown with “a” in Table 1 were kept constant. The data obtained were plotted as a function of conversion, described as x = amount of dissolved calcium in the solution/amount of calcium in the original sample, versus time.

3.1. Dissolution reactions

Ammonium acetate is the salt of a weak acid and a weak base. According to the following reaction, ammonium acetate ionizes in aqueous medium:

$$NH_4CH_3COO \rightarrow NH_4{}^+ + CH_3COO^- \tag{1}$$

Ammonium and acetate ions become hydrolysis:

$$NH_4{}^+ + H_2O \leftrightarrow NH_3 + H_3O^+ \tag{2}$$

$$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^- \tag{3}$$

When ulexite is added into ammonium acetate solution, the reactions occuring during the dissolution process are probably as follows:

$$\begin{aligned} &Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O_{(s)} + 2H_2O_{(l)} \\ &\quad \rightarrow 2Na_{(aq)}{}^+ + 2Ca_{(aq)}{}^{2+} + 4H_3BO_{3(aq)} + 6B(OH)_{4(aq)}{}^- \end{aligned} \tag{4}$$

$$B(OH)_{4(aq)}{}^- + H_3O_{(aq)}{}^+ \leftrightarrow H_3BO_{3(aq)} + 2H_2O_{(l)} \tag{5}$$

The overall reaction can be written as follows:

$$\begin{aligned} &Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O_{(s)} + 6NH_4CH_3COO_{(aq)} + 4H_2O_{(l)} \\ &\quad \rightarrow 2NaCH_3COO_{(aq)} + 2Ca(CH_3COO)_{2(aq)} + 6NH_{3(aq)} \\ &\qquad + 10H_3BO_{3(aq)} + 8H_2O_{(l)} \end{aligned} \tag{6}$$

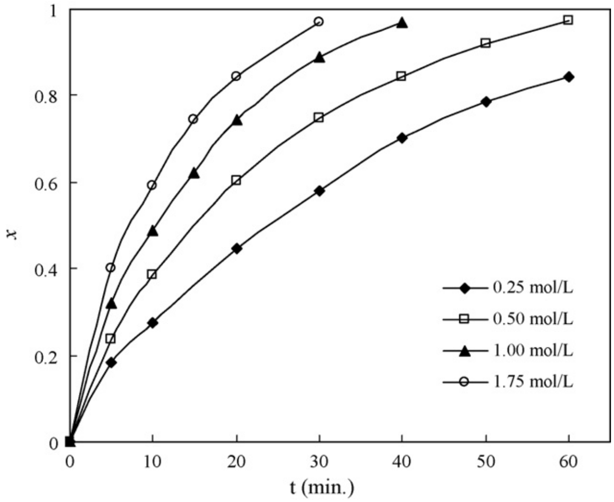

Fig. 2. Effect of concentration on the dissolution of ulexite.

Ammonium acetate is a neutral salt. pH of 1 mol/L ammonium acetate solution was measured as 6.65. The pH values at the end of the leaching experiments were measured about 7.5–7.7. Ammonia/ammonium and acetic acid/acetate buffered systems form in the reaction medium. No precipitation was detected at the end of the dissolution. The products of the reaction are soluble in the reaction medium.

3.2. Effects of parameters

3.2.1. Effect of concentration

To investigate the effect of the ammonium acetate concentration on the dissolution rate, the experiments were carried out in the 0.25–1.75 mol/L concentration range while the temperature, particle size, stirring speed and solid-to-liquid ratio were kept constant at 308 K, −0.420 + 0.250 mm, 400 rpm, and 1.00/200 g/mL, respectively. The results plotted in Fig. 2 show that the dissolution rate increases with an increase in solution concentration.

3.2.2. Effect of particle size

The effect of the particle size on the dissolution rate was studied using the following size fractions: −0.840 + 0.420, −0.420 + 0.250, −0.250 + 0.180, −0.180 + 0.150 mm. The concentration of ammonium acetate, solid-to-liquid ratio, stirring speed, and reaction temperature were kept constant at 1.00 mol/L, 1.00/200 g/mL, 400 rpm, and 308 K, respectively. Fig. 3 shows the experimental results concerning the effect of the particle size. As can be seen in Fig. 3, as the particle size decreases, the dissolution rate increases.

3.2.3. Effect of solid-to-liquid ratio

The effect of the solid-to-liquid ratio on the dissolution rate was determined by performing all experiments in the range of 0.50/200−2.5/200 g/mL. In these experiments, solution concentration, particle size, stirring speed, and reaction temperature were kept constant at 1.00 mol/L, −0.420 + 0.250 mm, 400 rpm, and 308 K, respectively. The variation of the dissolution rate for

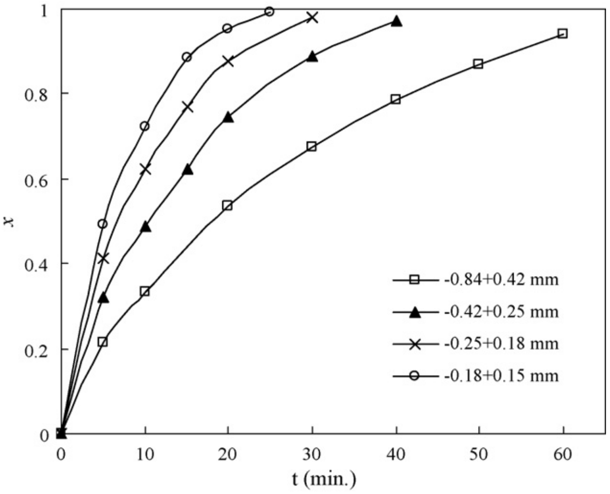

Fig. 3. Effect of particle size on the dissolution of ulexite.

various solid-to-liquid ratios is given in Fig. 4. Fig. 4 shows that the dissolution rate decreases as the solid-to-liquid ratio increases.

3.2.4. *Effect of stirring speed*

Tests were carried out at stirring speeds of 300, 400 and 500 rpm to observe the effect of the stirring speed on the dissolution rate. In these experiments, ammonium acetate concentration, particle size, solid-to-liquid ratio, and reaction temperature were fixed at 1.00 mol/L, −0.420 + 0.250 mm, 1.00/200 g/mL, and 308 K, respectively. The experimental results for the effect of stirring speed on the dissolution process showed that the dissolution rate was practically independent of the stirring speed.

3.2.5. *Effect of reaction temperature*

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 concentration of solution, particle size, solid-to-liquid ratio, and stirring speed were kept constant at 1.00 mol/L, −0.420 + 0.250 mm, 1.00/200 g/mL, and 400 rpm, respectively. The experimental results were plotted in Fig. 5. From this figure, it is seen that the dissolution rate increases as the reaction temperature increases.

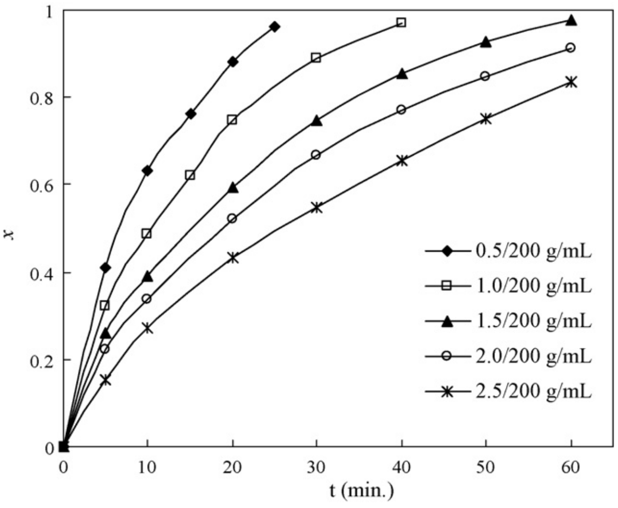

Fig. 4. Effect of solid-to-liquid ratio on the dissolution of ulexite.

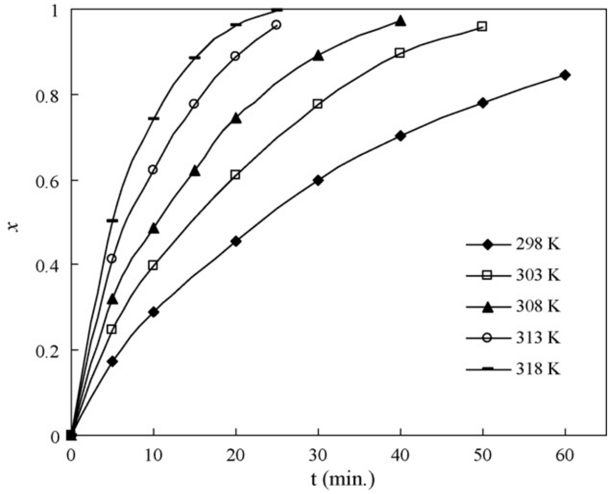

Fig. 5. Effect of reaction temperature on the dissolution of ulexite.

3.3. *Kinetic analysis*

Fluid–solid heterogeneous reaction systems have many applications in chemical and hydrometallurgical processes. This kind of reaction is found in various fields such as mineral leaching or precipitation The reaction between a solid and a fluid may be represented by

$$\mathrm{A\,(fluid)} + b\mathrm{B\,(solid)} \rightarrow \mathrm{products} \qquad (7)$$

The rate of reaction between a solid and a fluid can be expressed by heterogeneous reaction model. 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 the reaction, finally disappering. For a reaction of this kind, the following three steps are considered to occur in succession during the reaction [36].

1. Diffusion of the fluid reactant from the main body of the fluid film to the surface of the solid.
2. Diffusion of the fluid reactant through the ash layer to the surface of the unreacted core.
3. Reaction on the surface between the fluid reactant and the solid.

According to above steps, the rate of a non-catalytic heterogeneous reaction is generally controlled by one of the following steps: diffusion through the fluid film, diffusion through the product layer, or the chemical reaction at the surface of the core of the unreacted particle [36]. The integrated rate equations of these steps can be written as follows:

$$x = \frac{3bk_{\mathrm{g}}C_{\mathrm{A}}}{\rho_{\mathrm{B}}R_0}t = k_1 t \quad \text{(the film diffusion control)} \qquad (8)$$

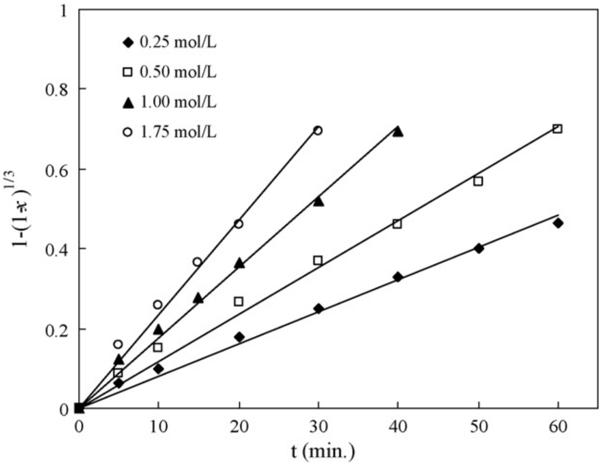

Fig. 6. Variation of $1-(1-x)^{1/3}$ with time for different concentrations.

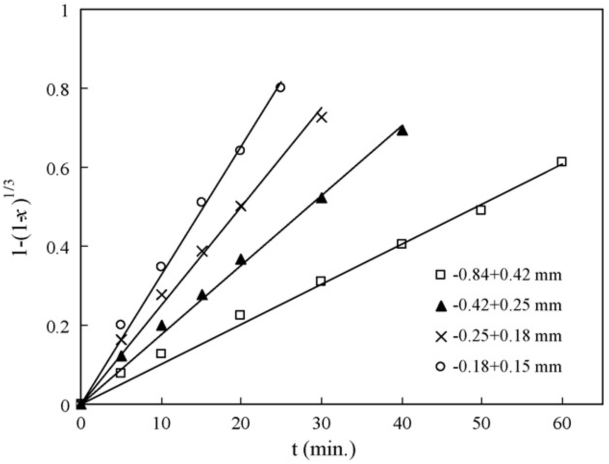

Fig. 7. Variation of $1-(1-x)^{1/3}$ with time for different particle sizes.

$$1-3(1-x)^{2/3}+2(1-x)=\frac{6bD_\mathrm{e}C_\mathrm{A}}{\rho_\mathrm{B}R_0^2}t=k_\mathrm{d}t$$

(the product layer diffusion control) (9)

$$1-(1-x)^{1/3}=\frac{bk_\mathrm{s}C_\mathrm{A}}{\rho_\mathrm{B}R_0}t=k_\mathrm{r}t$$

(the chemical reaction control) (10)

To determine the kinetic parameters and the rate-controlling step of the dissolution of ulexite in ammonium acetate solutions, the experimental data were analyzed on the basis of shrinking core model. The validity of the experimental data into the integrated rate equations was tested by statistical and graphical methods. The stirring speed does not show a significant effect on the dissolution rate (as mentioned in Section 3.2.4), which indicates that the diffusion through the fluid film does not act as a rate-controlling step. Therefore, the experimental data were analyzed according to Eqs. (9) and (10). By applying these equations to the experimental data obtained, the apparent rate constants were calculated. The left side of Eqs. (9) and (10) versus the reaction times were plotted for diffusion through the product layer and the chemical reaction model, respectively. The apparent rate constant values calculated from these equations and their correlation coefficients for each parameter are given in Table 2. According to the data in Table 2, the biggest regression coefficients were obtained for the chemical reaction model. The linear relation between $1-(1-x)^{1/3}$ and the reaction time can be seen in Figs. 6–8. In accordance with these results, the equation representing the kinetic of this process was determined to obey the chemical reaction model. Therefore, the integral rate expression can be written as follows:

$$1-(1-x)^{1/3}=k_\mathrm{r}t \quad (11)$$

Moreover, if the surface chemical reaction controls the reaction rate, the relation between the apparent rate constant and the inverse of the particle radius must be linear. This relationship is given in Fig. 9. This figure confirms that the chemical reaction model can be the rate-controlling step for this process. To include the effects of the reaction parameters on the rate constant of reaction, a semi empirical model can be written as follows:

$$k_\mathrm{r}=k_0C^aD^b\left(\frac{S}{L}\right)^c\mathrm{e}^{-E_\mathrm{a}/RT} \quad (12)$$

Combining Eqs. (11) and (12), the following equation is obtained:

$$1-(1-x)^{1/3}=k_0C^aD^b\left(\frac{S}{L}\right)^c\mathrm{e}^{-E_\mathrm{a}/RT}t \quad (13)$$

The constants a, b and c were estimated from the apparent rate constants given in Table 2. Using the rate constant values given

Table 2
The k_r, k_d and correlation coefficients values

	Surface chemical reaction $1-(1-x)^{1/3}$		Diffusion through the product layer $1-3(1-x)^{2/3}+2(1-x)$	
	k_r (min^{-1})	R^2	k_d (min^{-1})	R^2
Concentration (M)				
0.25	0.0081	0.9903	0.0067	0.9562
0.50	0.0117	0.9917	0.0119	0.9699
1.00	0.0177	0.9936	0.0176	0.9576
1.75	0.0235	0.9916	0.0234	0.9612
Temperature (K)				
298	0.0081	0.9862	0.0068	0.9652
303	0.0132	0.9964	0.0131	0.9555
308	0.0177	0.9936	0.0176	0.9576
313	0.0264	0.9953	0.0263	0.9543
318	0.0336	0.9943	0.0356	0.9855
Particle size (mm)				
0.84–0.42	0.0102	0.9931	0.0097	0.9527
0.42–0.25	0.0177	0.9936	0.0176	0.9576
0.25–0.18	0.0251	0.9915	0.0254	0.9727
0.18–0.15	0.0327	0.9936	0.0346	0.9832
Solid-to-liquid ratio (g/mL)				
0.5/200	0.0263	0.9930	0.0261	0.9477
1.0/200	0.0177	0.9936	0.0176	0.9576
1.5/200	0.0120	0.9928	0.0122	0.9668
2.0/200	0.0096	0.9860	0.0088	0.9685
2.5/200	0.0076	0.9920	0.0061	0.9400

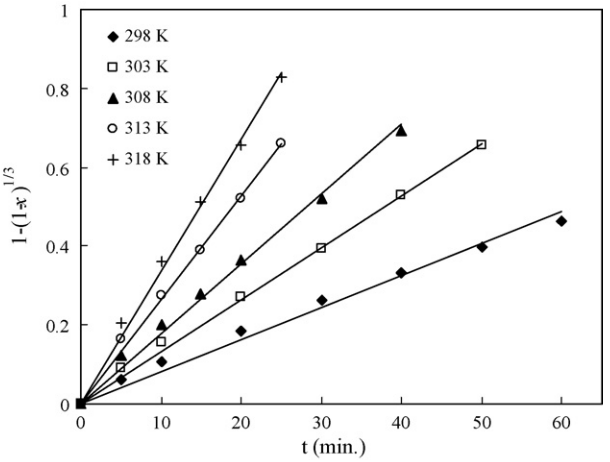

Fig. 8. Variation of $1-(1-x)^{1/3}$ with time for different temperatures.

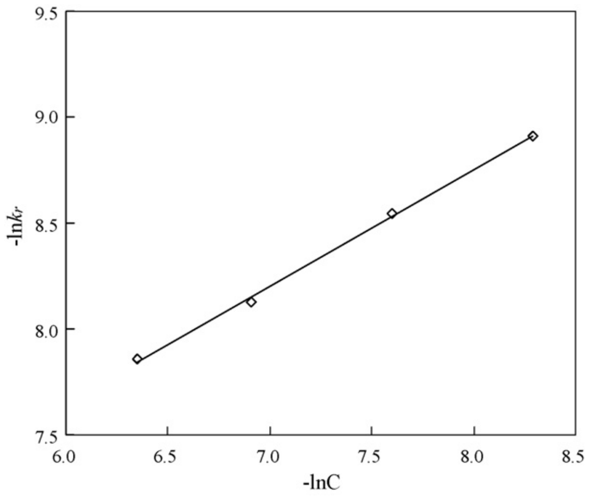

Fig. 10. Plot of $\ln k_r$ vs. $\ln C$.

in Table 2 for the concentration, a plot of $\ln k_r$ versus $\ln C$ was drawn in Fig. 10. The slope of the straight line in Fig. 10 is the reaction order with respect to concentration. The reaction order is proportional to 0.55 power of concentration with a correlation coefficient of 0.998. In order to determine the orders of reaction with respect to particle size and solid-to-liquid ratio were also used the data in Table 2. According to the results found, the reaction order is proportional to −0.84 power of particle size and −0.77 power of solid-to-liquid ratio. The correlation coefficients of these parameters are 0.999 and 0.987, respectively.

The activation energy of this process was determined from the Arrhenius equation. The Arrhenius plot of the process is shown in Fig. 11. From the slope of the straight line in Fig. 11, the activation energy was calculated to be 55.7 kJ/mol. The intercept was determined to be 3.9×10^4. The value of the activation energy indicates that the dissolution of ulexite in ammonium acetate solutions is controlled by chemical reaction. The activation energy of chemically controlled reactions is usually above 40 kJ/mol. As a result, a kinetic expression including the parameters used in this dissolution process can be written as follows:

$$1-(1-x_{C_a})^{1/3}=3.910^4 C^{0.55} D^{-0.84} \left(\frac{S}{L}\right)^{-0.77} e^{-55700/RT} t \qquad (14)$$

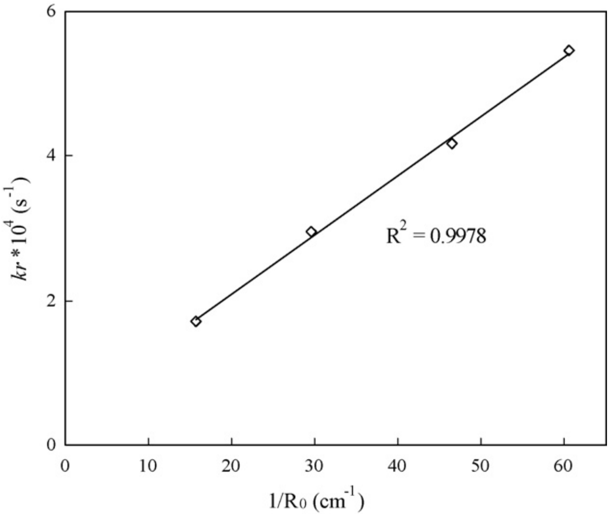

Fig. 9. Plot of k_r vs. $1/R_0$ for particle size.

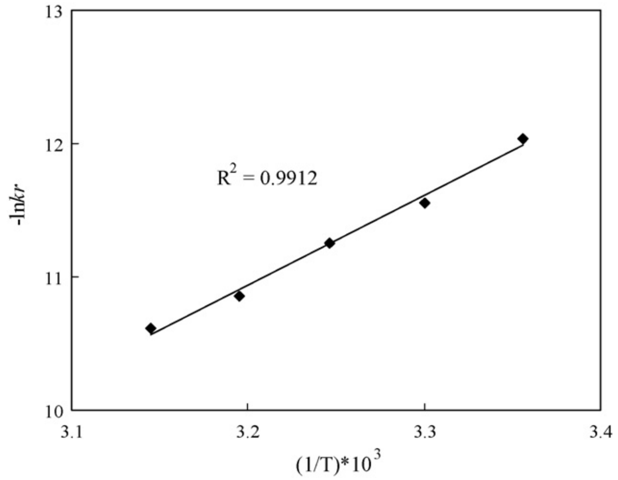

Fig. 11. Arrhenius plot for the dissolution of ulexite.

4. Conclusions

In this study, the dissolution rate of ulexite in ammonium acetate solutions was investigated. The effects of the chosen parameters on the dissolution rate were examined and evaluated. It was determined that the conversion rate increased with an increase ammonium acetate concentration and reaction temperature, and with a decrease solid-to-liquid ratio and particle size. The dissolution rate was not affected by stirring speed. It was observed that the reaction rate was sensitive to both particle size and reaction temperature. The dissolution kinetics follows a shrinking-core model with the chemical reaction control as the rate-controlling step. The activation energy of the dissolution process was found to be about 55.7 kJ/mol.

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