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Dissolution kinetics of calcined ulexite in ammonium carbonate solutions

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Abstract−The leaching kinetics of calcined ulexite in ammonium carbonate was studied in this work. The effect of parameters of ammonium carbonate concentration, solid/liquid ratio, stirring speed, calcination temperature and reaction temperature was determined in the experiments. It was found that the conversion rate increased with increasing ammonium carbonate concentration, reaction temperature and decreasing solid/liquid ratio. However, the effect of stirring speed on the conversion rate was insignificant. The experimental data practised the heterogeneous and homogeneous models, and an acceptable model for the conversion rates of ulexite was determined to be a first-order pseudo-homogeneous reaction model. The activation energy of dissolution process was determined to be 35.3 kJ/mol.

Key words: Ammonium Carbonate, Calcined Ulexite, Reaction Kinetics, Leaching

INTRODUCTION

Boron is found in nature in the form of metal borate, mostly as sodium, calcium and magnesium borates. Boron compounds are widely used in many industries such as cosmetic, leather, textile, rubber, paint and glass industries as well as medicine. Recently, the use of boron compounds has increased greatly because of its increasing demand in nuclear technology, in the glass and ceramic industries, as abrasives and refractors, in the production of heat-resistant polymer, as catalysts, etc. Among boron minerals, ulexite is one of the most common and is found in great amounts in Turkey. Ulexite is a sodium-calcium borate hydrate mineral $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$. Commercially, boric acid, boron oxides, and sodium perborate are the most utilized compounds of boron. Ulexite is one of the boron compounds used for the production of these compounds as a raw material [1-3].

When substances containing hydrated water are heated to given temperatures, they lose their weight, giving off their water content, a process known as dehydration. Dehydration processes can be applied due to technological and economical reasons, such as decreasing the weight of a material for reducing the transportation cost in the case where it includes hydrated water in large amounts, and also it may be a necessary step in a chemical process, or to obtain a porous solid for increasing the reaction rate of a solid-fluid reaction [4].

Most boron minerals, such as ulexite, tincal, colemanite and pandermite, include water. The dehydration of the hydrate boron minerals is an important stage of preparation before processes for the production of boron compounds [5]. The extra weight of water and other impurities in the raw materials increases transportation and energy costs for producing anhydrous borates. Therefore, the demand for raw hydrate borates has declined in recent years. This has forced producers to produce the dehydrated borates and boron products [6].

Hydrated boron minerals undergo a reduction in their initial weight after the heat treatment, due to loss of water molecules. Thermal treatment of boron minerals results in some structural modifications, due to formation of micropores and the resultant expansion of the crystal matrix upon development of uneven distribution of stresses [7]. When boron minerals are heated, internal thermal reactions occur. The mineral first loses its water of crystallization, followed by either the production of amorphous material or recrystallizes into a new phase. Therefore, the structure changes significantly. Colemanite decrepitates as a result of sudden release of confined water vapor within micropores during this thermal treatment, while ulexite does not decrepitate. Instead, it only exfoliates due to gradual removing of water vapor and the structure becomes amorphous with numerous microcracks and interstices [6].

During the thermal dehydration process, ulexite loses some part of its hydrate water content depending upon the dehydration temperature. The ulexite starts to lose its hydrate water content at about 50 °C and loses most of its water content between 100 and 250 °C; the mass loss continues gradually up to 650 °C. After 100 °C, structural changes take place in the ulexite [4]. Şener and Özbayoğlu [8] reported that the ulexite starts to lose its crystal water at around 60 °C and the amount of dehydration increases up to 190 °C. Low calcination temperatures and durations are not adequate for ulexite to lose an appreciable amount of crystal water from its structure. Some changes in the structure of ulexite can be observed by calcination. The ulexite structure changes within a wide range of temperature depending on calcination temperature and duration. Ulexite loses its crystal water gradually so that its structure is decomposed by forming a friable, porous structure below 240 °C but gains hardness and shows an amorphous structure at higher temperatures. Erşahan et al. [5] observed that the dehydration of ulexite begins at 100 °C and the dehydration rate is high up to 230 °C, above this temperature the dehydration continues at a quite low rate up to 530 °C, and above the temperature there is almost no weight loss. Şener et al. [6] reported that the decomposition of ulexite starts with two stage dehydration. The first stage of dehyroxylation reaction takes place within 180-260 °C, and the second stage of dehyroxylation occurs within a wide range of temperatures as 260-500 °C. During the dehydration of ulexite, amorphization was observed above 160 °C and

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the structure was found completely amorphous at 260 °C. Cheng et al. [9] investigated the dissolution and transformation ulexite in water.

The dissolution kinetics of boron minerals in different solutions was investigated by various investigators. The dissolution kinetics of ulexite in ammonia solutions saturated with carbon dioxide and ammonium sulfate [2,10], in aqueous EDTA and oxalic acid [11,12], in ammonium chloride [13] and in sulphuric acid [14] solutions has been examined. The dissolution kinetics of ulexite has been predicated to conform to first-order pseudo-homogeneous reaction model in ammonia solutions saturated with carbon dioxide, ash or product layer model in ammonium sulfate, the unreacted shrinking core model with changing fluid phase concentration in aqueous EDTA, product-layer diffusion in oxalic acid, second-order pseudo-homogeneous reaction model in ammonim chloride and the mineral surface through the product and product layer in sulphuric acid. The activation energy of ulexite by using these models was found to be 55 kJ/mol in ammonia solutions saturated with carbon dioxide, 83.5 kJ/mol in ammonium sulfate, 35.95 kJ/mol in aqueous EDTA, 59.86 kJ/mol in oxalic acid and 80 kJ/mol in ammonium chloride solutions. To determine the optimum dissolution conditions of ulexite in ammonium chloride solutions, the Taguchi method [15] has been used. Direct production of crystalline boric acid from borax and propionic acid was investigated by ZareNezhad [16].

As seen above, many investigations were carried out relating to the dissolution kinetics of ulexite in the literature. But, no work has been found in the literature relating to the dissolution kinetics of calcined ulexite in ammonium carbonate solution. In this study, the dissolution kinetics of calcined ulexite in ammonium carbonate solutions was examined. The effect of calcination temperature, concentration of solution, reaction temperature, solid/liquid ratio and stirring speed was investigated and kinetics parameters are reported here.

MATERIAL AND METHODS

The ulexite samples used in this study were obtained from Kırka, Eskisehir, Turkey. The material was first cleaned of visible various impurities. After cleaning, 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 dehydration of ulexite was performed isothermally, using a static method, in an oven made by Heraus. After 2 g of a sample having particle size fraction of −0.850+0.425 mm was put into a ceramic crucible, the ore was subjected to a given temperature for 3 hours. Following this procedure, the sample was cooled and weighed. Thus, the dehydration data of the samples at given temperatures were obtained. In various calcination temperatures, the B_2O_3 contents and the loss of weight in the calcined samples are given in Fig. 1. It is clear that the loss of weight is rather rapid up to 443 K and above this temperature, the dehydration rate decreases.

The parameters that were expected to affect the dissolution rate were chosen as the calcination temperature, acid concentration, reaction temperature, solid/liquid ratio and stirring speed. The ranges of parameters are presented in Fig. 1. The experiments were carried out in a 500 mL spherical glass reactor equipped with a mechanical stirrer, a reaction temperature control unit, and a cooler to avoid loss of solution by evaporation. The experimental procedure was as follows: a total 200 mL of an ammonium carbonate solution was 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 reaction the contents were filtered and the amount of B_2O_3 was determined in the solution [17]. Each experiment was repeated twice and the arithmetic average of the results was used in kinetic modelling.

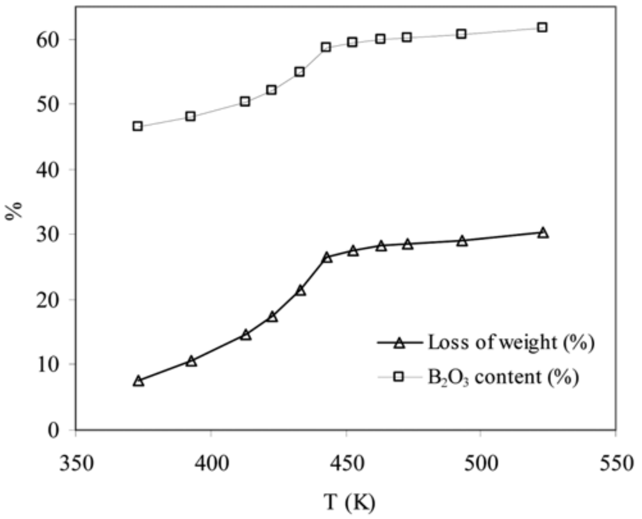

Fig. 1. The loss of weight and the B_2O_3 content at the calcined samples.

RESULTS AND DISCUSSION

1. Dehydration and Dissolution Processes

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

$$Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 16H_2O_{3(s)}$$
$$\text{-----}\ Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot nH_2O_{(s)}+(16-n)H_2O_{(g)}$$

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

The aim of the dissolution process performed was to observe the effect of the dehydration on the reaction rate. The effect of dehydration temperature on the dissolution rate was examined at 373, 393, 413, 423, 433, 443, 453, 463, 473, 493 and 523 K reaction temperatures, while concentration of solution 1 mol/L, solid to liquid ratio of 2 g/200 mL, particle diameter of −0.850+0.425 mm, stirring speed of 400 rpm and reaction temperature 303 K were kept constant. The results are given in Fig. 2. It can be seen that the dissolution rate increases with increasing dehydration temperature up to 433 K, and the rate of dissolution decreases with increasing dehydration temperature above this temperature. This behavior can be explained on the basis of the changes which occur during calcination. During the calcination process, ulexite loses its crystalline water depending mainly on the temperature. The changes to the crystal structure of ulexite allow the calcined mineral sample to react

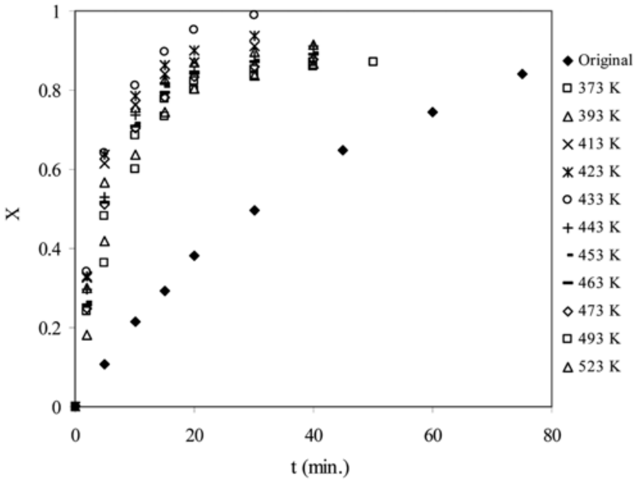

Fig. 2. Effect of dehydration temperature on the dissolution of calcined ulexite.

more easily and can be dissolved at a higher rate than the uncalcined sample. At higher temperartures than 433 K, the dissolution rate decreases. This situtiation may be attributed to the fact that unheated ulexite has a certain degree of porosity. This porosity may increase with heating up to 433 K, but may diminish at higher temperatures, since sintering can be expected after 433 K and the sintering rate of ulexite increases rapidly with increasing temperature. The decrease in porosity of ulexite particles as a result of sintering leads to the decrease in dissolution rate [2,11,13].

The effect of ammonium carbonate concentration on the dissolution rate was examined at a concentration of 0.25, 0.50, 1.00, 2.00 mol/L, while calcination temperature of 433 K, solid to liquid ratio of 2 g/200 mL, particle size of 0.850-0.425 mm, stirring speed of 400 rpm and reaction temperature of 303 K were kept constant. The results are presented in Fig. 3. This figure shows that conversion rate increases as the concentration of solution increases.

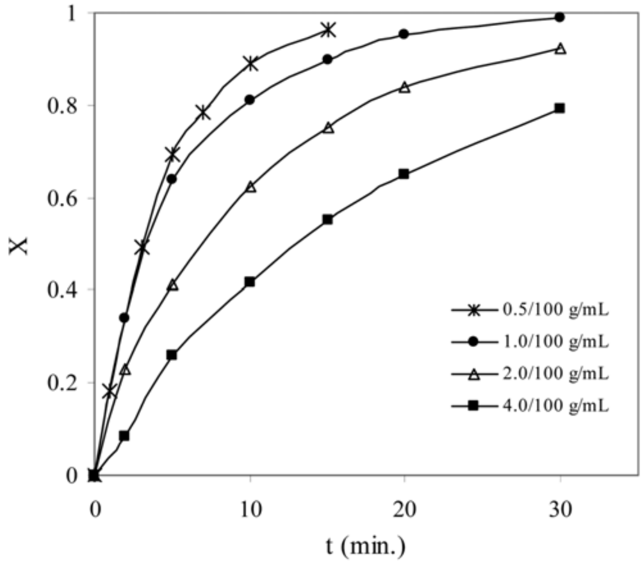

Fig. 4. Effect of solid/liquid ratio the dissolution of calcined ulexite.

To observe the effect of the solid to liquid ratio on dissolution rate, experiments were carried out 0.5/100, 1/100, 2/100, 4/100 g/mL. During experiments, the calcination temperature, concentration, stirring speed and reaction temperature were kept constant at 433 K, 1.00 mol/L, 400 rpm, 303 K, respectively. The results plotted Fig. 4 show that the dissolution rate increases with decreased solid to liquid ratio.

The effect of the stirring speed on the conversion rate was identified by using stirring speeds of 300, 400 and 500 rpm. During experiments, the calcination temperature, concentration, solid to liquid ratio and reaction temperature were kept constant at 433 K, 1.00 mol/L, 2 g/200 mL, 303 K, respectively. As seen from the results plotted in Fig. 5, the change in stirring speed has no effect on conversion rate. Even the lowest stirring speed (300 rpm) seems to be enough for mass transfer.

To observe the effect of the reaction temperature on dissolution

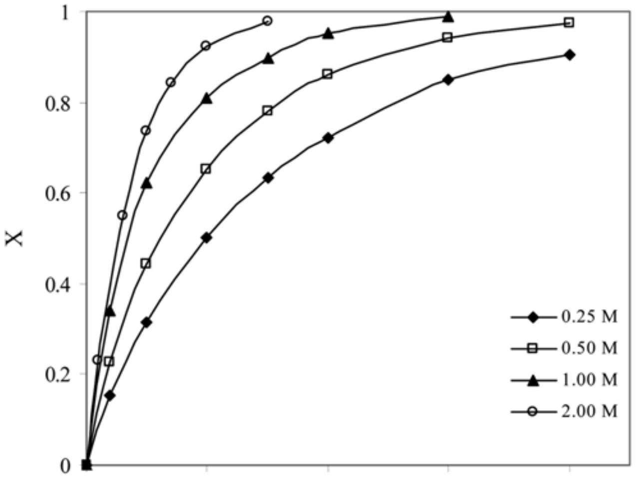

Fig. 3. Effect of concentration on the dissolution of calcined ulexite.

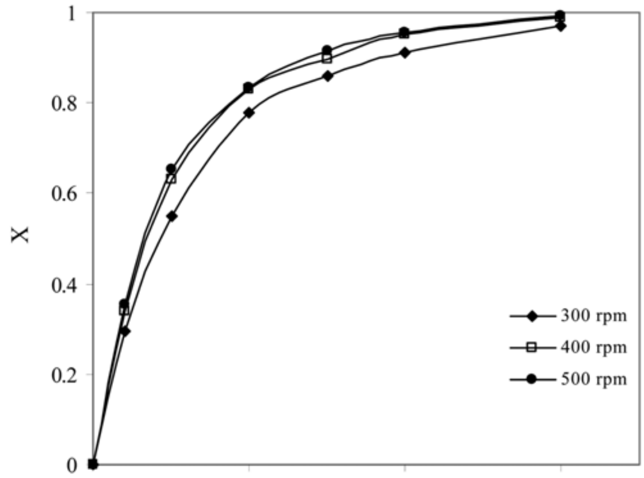

Fig. 5. Effect of stirring speed on the dissolution of calcined ulexite.

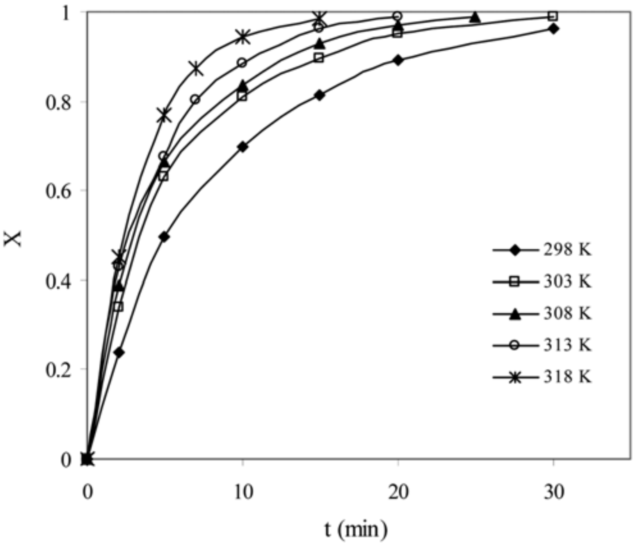

Fig. 6. Effect of reaction temperature on the dissolution of calcined ulexite.

rate, the experiments were carried out at the temperature of 298, 303, 308, 313 and 318 K, while calcination temperature of 433 K, concentration of solution 1.00 mol/L, solid to liquid ratio of 2 g/200 mL, stirring speed of 400 rpm were kept constant. It was found that conversion rate increases with increasing in the reaction temperature as can be seen in Fig. 6.

2. Kinetics Analysis

In a noncatalytic reaction between a solid particle B and a fluid A, given as

A (fluid)+bB (solid)=products (fluid and/or solid),

all or some of the following steps occur.

(1) Diffusion of a fluid reactant through a fluid film on a solid product

(2) Diffusion of a fluid reactant through a solid product on the surface of a solid reactant

(3) Reaction between a fluid reactant and a solid reactant

(4) Diffusion of fluid products through a solid product film to a fluid film

(5) Diffusion of fluid product through a fluid film to a bulk fluid.

The resistance of each step described above is different than another. It is stated that steps 4 and 5 do not generally contribute to the reaction resistance [18]. The step with the highest resistance is considered to be the rate-controlling step. The rate of a reaction between a solid and a fluid such as the system considered here can be expressed by homogeneous and heterogeneous models [18]. The heterogeneous model assumes that the rate may be controlled by diffusion through a fluid film, by diffusion through the ash or product layer, or by a surface chemical reaction. There is a different integrated rate equation for each control and particle geometry. For spherical particles, the fractional conversion, x, as a function of the reaction time, t, is given by,

$$t/t^{*}=X \qquad \text{(for film diffusion control)} \qquad (5)$$

$$t/t^{*}=1-(1-X)^{1/3} \qquad \text{(for surface chemical reaction control)} \qquad (6)$$

$$t/t^{*}=1-3(1-X)^{2/3}+2(1-X)$$
$$\text{(for film diffusion control through the ash or product layer)} \qquad (7)$$

In order to determine the rate equation in such systems, for pseudo-homogeneous models it may be written as,

$$-\ln(1-X)=kt \text{ (for the first-order pseudo-homogeneous model)} \qquad (8)$$

$$(1-X)^{-1}-1=kt \text{ (for the second-order pseudo-homogeneous model)} \qquad (9)$$

As mentioned previously, the kinetics of the reaction between ulexite and ammonium carbonate was statistically and graphically determined by using heterogeneous and homogeneous reaction models. Experimental data did not fit to any heterogeneous rate models. Low regression coefficients and ineffectiveness of stirring speed failed the existing heterogeneous reaction models. The data obtained

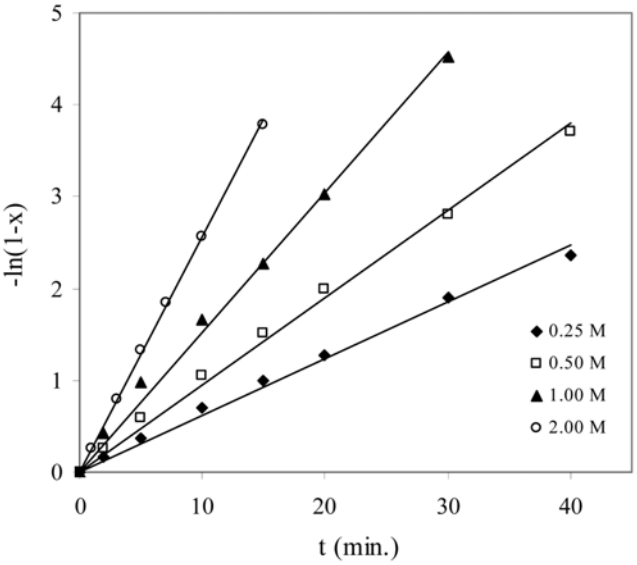

Fig. 7. −ln(1−x) vs time plot for various concentration.

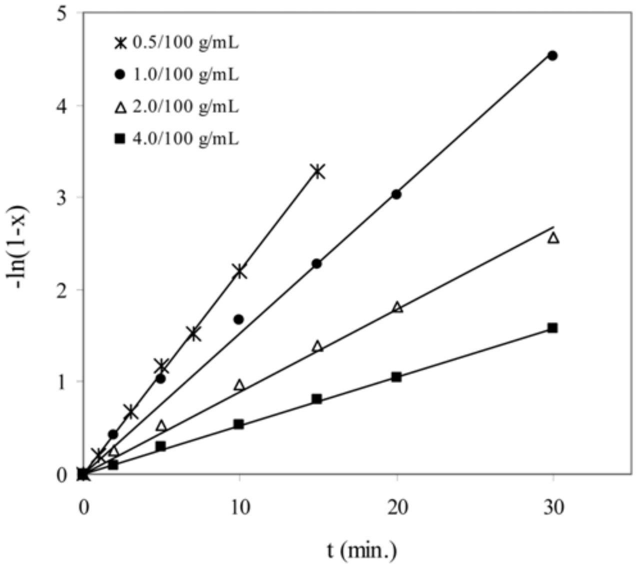

Fig. 8. −ln(1−x) vs time plot for various solid/liquid ratio.

in this study were analyzed for first-order pseudo-homogeneous and second-order pseudo-homogeneous reaction models. But the second-order pseudo-homogeneous reaction model was found inappropriate. Using the first-order pseudo-homogeneous reaction model, the left side of −ln(1−x) value is plotted against the reaction time. As can be seen, the plots given in Fig. 7-9 are in linear form and pass through the origin. Therefore, the dissolution process is found to be a first-order pseudo-homogeneous reaction model. The dependence of the rate constant on the concentration, solid to liquid and reaction temperature may be given by

$$k=k_o\cdot(C)^a\cdot(S/L)^b\cdot\exp(-E/RT) \qquad (10)$$

Rate constant values obtained from Figs. 7-9 were used to calculate constants a and b in Eq (10). Average calculated values of a and b were 0.68 and −0.70, respectively. To determine the activation energy of the dissolution reaction, a plot of lnk 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 is k_o. The values of E/R and k_o were found to be 4,250 and 8.2×10^2, respectively. Mathematical form of the model is

$$-\ln(1-x)=(C)^{0.68}\cdot(S/L)^{-0.70}\cdot\exp(4{,}250/T)\cdot t \qquad (11)$$

The activation energy of the dissolution reaction was calculated to be about 35 kJ/mol. To determine the compatibility of the model with the experimental data, a plot of theoretical conversion versus experimental conversion is given in Fig. 11.

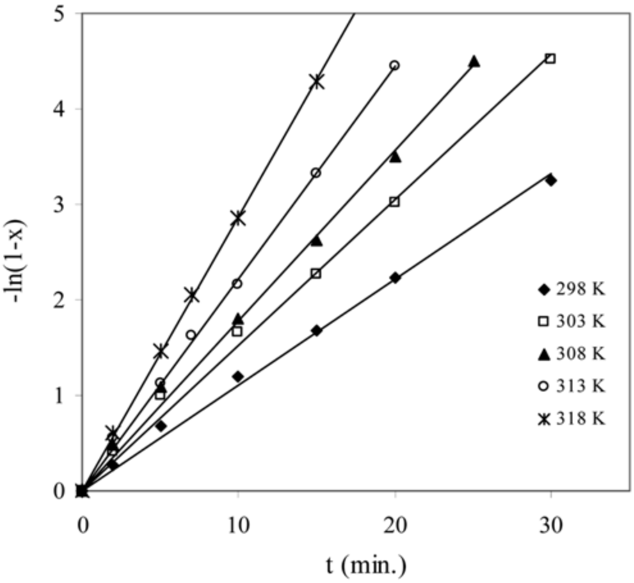

Fig. 9. −ln(1−x) vs time plot for reaction temperature.

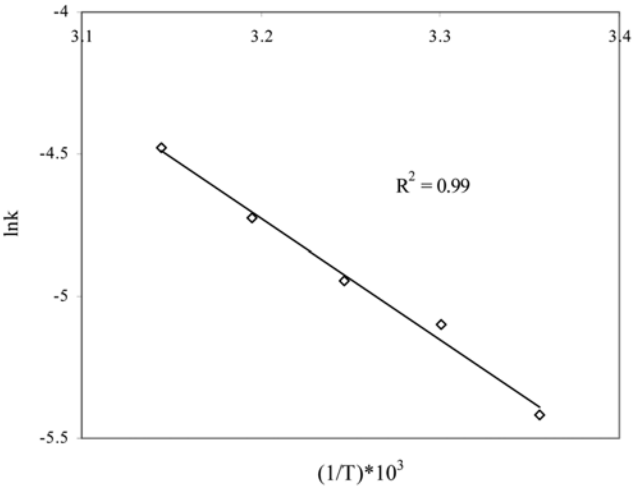

Fig. 10. Arrhenius plot for dissolution of calcined ulexite.

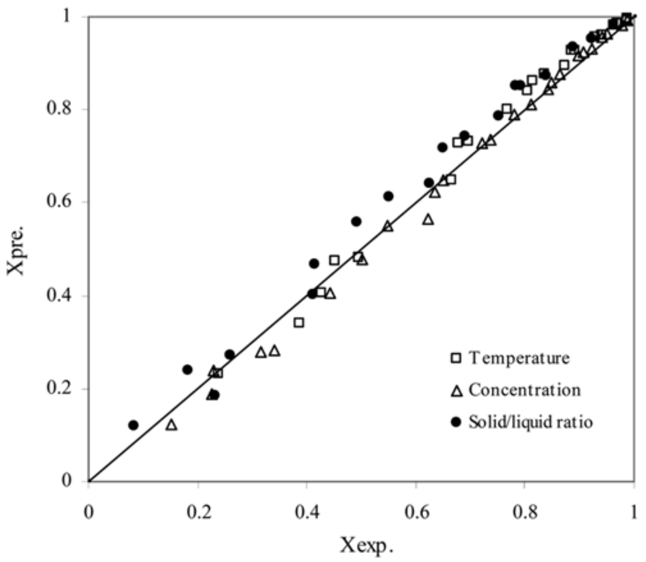

Fig. 11. Plot of predicted conversion rates against experimental values.

CONCLUSION

In this work, the dissolution kinetics of calcined ulexite in ammonium carbonate solutions was investigated. It was determined that the conversion rate increased with increasing ammonium carbonate concentration, reaction temperature, and with decreasing solid to liquid ratio, but it was not affected by stirring speed. The dissolution process was described by a first-order pseudo-homogeneous reaction model.

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