



LEACHING KINETICS OF ULEXITE ORE IN AQUEOUS MEDIUM AT DIFFERENT CO₂ PARTIAL PRESSURES

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Abstract – This manuscript presents a study regarding the leaching kinetics of ulexite (Na₂O.2CaO.5B₂O₃.16H₂O) under different CO₂ partial pressures in aqueous media. The effects of the reaction temperature, particle size, CO₂ partial pressure, solid-liquid ratio, and agitation speed were investigated in the boron extraction from the ore. As a result of the experimental studies, it was found that the leaching rate increased with the rise in the reaction temperature and CO₂ partial pressure, and decreased with the increase in the particle size and solid-liquid ratio. The reaction temperature was found to be a significant parameter affecting the leaching rate, which varied from 13% to 97% between 303 and 393 K. Agitation speed appears to have no significant effect on the leaching rate. By using several empirical kinetic models to correlate the experimental data, it was found that the leaching rate fits to the Avrami Model. The activation energy of the process is found to be 21.1 kJ.mol⁻¹.

Keywords: Ulexite, leaching kinetics, CO₂ partial pressure, Avrami Model

INTRODUCTION

Throughout decades, possessing natural resources has been a critical driving force for global economic development. Among the other countries, Turkey possesses 72% of the world's reserves of boron minerals, and this gives her a superior advantage in boron mineral products (Ertuğrul, 2004; Kuşlu et al., 2010). Boron minerals are mainly compounds which consist of boron oxide with alkaline and/or alkaline earth metal oxides, and they exist in more than 230 forms in nature. Boron and its compounds are potentially valuable products for industry and have strategic importance (Elcicek et al., 2014; Guliyev et al., 2012). It is the most widely used element in engineering applications and in industry, such as nuclear engineering,

manufacturing of high-quality steel, ceramics, textiles; in the production of heat resistant polymers, cosmetics; processing of leather, rubber, paint; and in agriculture, or used as catalyst (Guliyev et al., 2012).

Since 1963, a number of studies have been published on the dissolution of boron minerals in various solutions, such as hydrochloric acid (Imamutdinova, 1963; Zdonovskii and Imamutdinova, 1963), phosphoric acid (Imamutdinova, 1967), perchloric acid (Imamutdinova and Vladykina, 1969), acetic acid (Imamutdinova and Abdrashitova, 1970) and oxalic acid (Kalacheva et al., 1980). The extraction of boric acid was investigated from colemanite ore (2CaO.3B₂O₃.5H₂O) by supercritical carbon dioxide. It has been reported that boric acid extraction efficiency was achieved between 71.7% and 96.9% from the CO₂-

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colemanite reaction at 60°C, for 2h of reaction time (Budak and Gönen, 2014). The extraction of boric acid was examined from tincal ($\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3\cdot 10\text{H}_2\text{O}$) mineral by supercritical ethanol. The maximum extraction efficiency of boric acid was 32.6%, at 250°C (Levent et al., 2016). One of the most important parameters affecting the dissolution kinetics of boron minerals is the choice of the solvent. Therefore, the results from this study have been compared with the results from previous studies in the literature in terms of solvents used, solubility of reaction products in water, and in terms of the obtained results, the reaction model and the activation energy in Table 1. The authors have not explained how their results are related to models. It is expected that the presence of strong acids increases the dissolution rate of ulexite. However, at the beginning of the reaction, H_3O^+ ions are furnished by the acid and boric acid is produced in a very fast reaction. So, a firm layer in which there are fine-grained boric acid crystals is produced around the ulexite particles. This layer resists the passage of H_3O^+ ions to the mineral surface, and affects the dissolution rate negatively. The dissolution kinetics of the ulexite under atmospheric conditions in carbonic acid solution was found to fit a first-order pseudo-homogeneous reaction model. The studies of the dissolution kinetics of ulexite in ammonia/ CO_2 and ammonium carbonate solution were described by a first-order pseudo-homogeneous

reaction model. In these systems, CaCO_3 crystals forming in the reactions do not form a firm film layer, and peel off.

In all the studies mentioned above, the experiments were conducted at low temperatures and low solid/liquid ratios under atmospheric pressure. The use of water, compared with other solvents in the industrial applications, provides economically feasible and safe operations. We believed that other solvents are only used during the laboratory tests to enhance solubility.

The study presented is about the leaching kinetics of ulexite ore in aqueous media under various CO_2 partial pressures. The results show that the leaching rate of ulexite increased with the increase in the pressure of CO_2 according to the studies conducted under atmospheric conditions (the other conditions are kept stable). Therefore, application of overpressures of CO_2 is more favoured. However, optimization study is required to make a decision (Elçiçek, 2012). The study conducted by Ata et al. (2000) was about optimization of boric acid extraction from colemanite in CO_2 -saturated water. Colemanite dissolution in CO_2 -saturated water is slower than that of ulexite. The dissolution kinetics of inderite [$\text{MgB}_3\text{O}_3(\text{OH})_5\cdot 5(\text{H}_2\text{O})$] and inyoite [$\text{Ca}_2\text{B}_6\text{O}_{10}(\text{OH})_{10}\cdot 8(\text{H}_2\text{O})$], which have no economic value, has less importance in CO_2 saturated water. Ulexite ore used in the present study contains nearly 75% ulexite, and is processed industrially (Alkan et al., 1991).

Table 1. Previous studies about leaching kinetics of ulexite.

No	Author	Solvent	Solubilities of reaction products	Reaction model	Activation Energy (kJ/mol)
1	Künkül et al. (1997)	Ammonia solution saturated with CO_2	Insoluble	First-order pseudo-homogeneous	55
2	Tunc et al. (2001)	Sulphuric acid solution	Insoluble	Avrami	NR*
3	Demirkıran and Künkül (2007)	Perchloric acid solution	Soluble	Avrami	19.12
4	Demirkıran (2008)	Ammonium acetate solution	Soluble	Chemical reaction	55.7
5	Ekmekyapar et al. (2008)	Acetic acid solution	Soluble	Chemical reaction	55.8
6	Demirkıran (2009)	Ammonium nitrate solution	Soluble	Chemical reaction	58.2
7	Doğan and Yartaşı (2009)	Phosphoric acid solution	Insoluble	Product plate (cinder) diffusion	26.17
8	Kuşlu et al. (2010)	Borax pentahydrate solution saturated with CO_2	Soluble	Chemical reaction	42.5
9	Abalı et al. (2011)	Oxalic acid solution	Insoluble	Product layer diffusion control	24
10	Demirkıran and Künkül (2011)	Ammonium carbonate solution	Insoluble	First order pseudo-homogeneous	53.06
11	Demirkıran et al. (2013)	Ammonium acetate solution	Soluble	Chemical reaction	41.5
12	Kavcı et al. (2014)	Sodium hydrogen sulphate solution	Insoluble	Shrinking core	36.4

* Not Reported

Dissolution of ulexite in water-saturated carbon dioxide was investigated by Kocakerim et al. (1993). In their study, the pure ulexite mineral was used; maximum temperature was 303 K, and all the experiments were carried out under atmospheric conditions. Activation energy in their study was found to be 51.7 kJ.mol⁻¹, which fits with first order kinetics.

Unlike the previous research mentioned above, this study aims to determine the leaching kinetics of ulexite in water at different CO₂ partial pressures. For this purpose, the effects of CO₂ partial pressure, reaction temperature, particle size, the solid-liquid ratio and the agitation speed on the leaching kinetics were investigated.

MATERIALS AND METHODS

Ulexite ore used in this study was obtained from Eti Mine Bigadic Boron Works. The sample was crushed by a jaw crusher and sieved using ASTM standard sieves to obtain the following size fractions: 355 to 600, 250 to

355, 180 to 250, and 150 to 180 μm. The chemical analysis of the fractions is given in Table 2. Gaseous CO₂ used in experiments was in a cylinder supplied from HABAŞ Corp. and was 99.5% pure. X-ray diffraction analysis of ulexite ore is shown in Fig. 1.

Experimental procedure

Experiments were conducted in a 1000 mL reactor (Model 4540, Parr Instrument Company) which provided the temperature, pressure, agitation speed and pH control. In each experiment, 200 mL of distilled water and suitable amounts of ulexite were loaded into the reactor according to the present solid-liquid ratios. The reactor was adjusted to the desired operating conditions, and it was heated to the desired temperature with an external heating jacket. Experiments were started after the CO₂ was pumped into the reactor to the desired pressure. The temperature and the pressure inside the reactor were monitored by the thermocouple and the pressure gauge. The samples were withdrawn from the reactor after 2.5, 7.5, 15, and 30 and

Table 2. Chemical composition of ulexite fractions.

Fractions (μm)	Components (%)				
	B ₂ O ₃	Na ₂ O	CaO	H ₂ O	Others
355 to 600	32.0	6.1	15.4	24.5	22.0
250 to 355	33.6	5.7	14.9	20.0	25.8
180 to 250	31.5	5.7	13.6	22.3	26.9
150 to 180	33.6	6.1	16.0	22.3	22.0

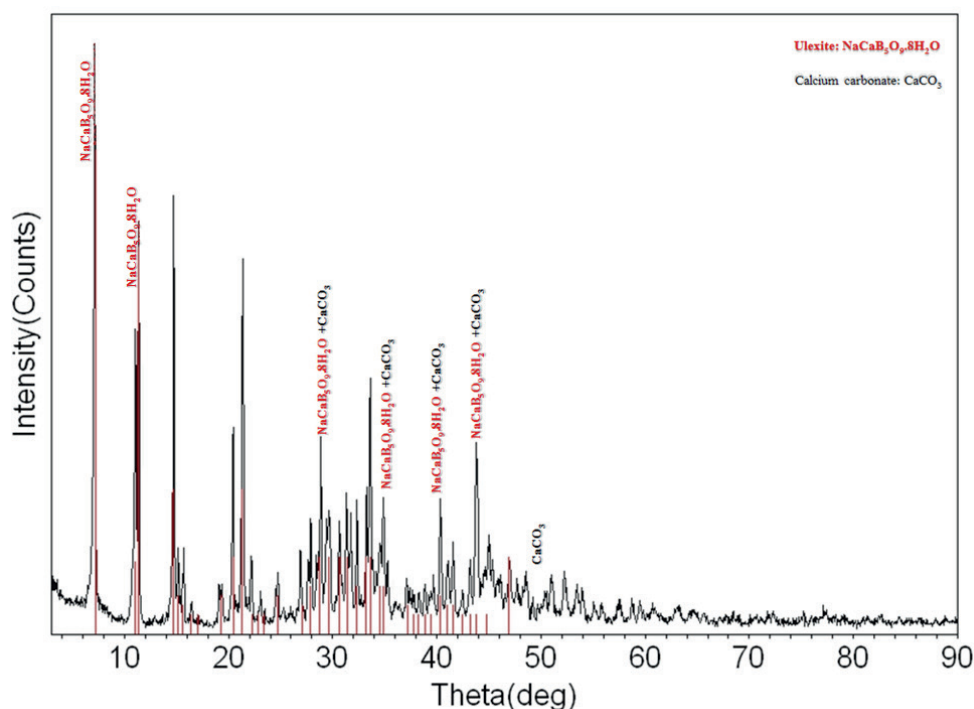


Figure 1. X-ray diffractogram of ulexite ore.

60 minutes of leaching. The schematic representation of the system used in the experiments is seen in Fig. 2. The chosen parameters and their ranges are presented in Table 3.

At the end of each experiment, the solutions were filtered using a blue band Whatman filter paper, and then the liquid phase was analysed for B_2O_3 by a volumetric method. Also, Na^+ and Ca^{2+} analyses were performed by a flame photometer with an uncertainty of $\pm 1\%$. The

flame photometer was calibrated before each analysis. The data obtained from each experiment were repeated two or three times, and the maximum standard deviation was approximately 5%. The accuracy values of the thermocouple and pressure gauge are $\pm 1^\circ C$ and 0.1%, respectively. The solution was stirred for the reaction duration with 0.1% rpm sensitivity. The errors in the parameters were measured. Total uncertainties are given in Table 4.

Table 3. The reaction parameters chosen and their ranges.

Parameters	Values
Total pressure, bar	5*, 10, 15, 20
Temperature, K	303*, 323, 343, 363, 393
Particle size μm	150 to 180, 180 to 250, 250 to 355, 355 to 600*
Solid-liquid ratio, g/mL	30/200, 40/200*, 50/200, 60/200
Stirring speed, rpm	300, 400, 500*, 730

*The values were kept constant when the effect of other parameters was investigated

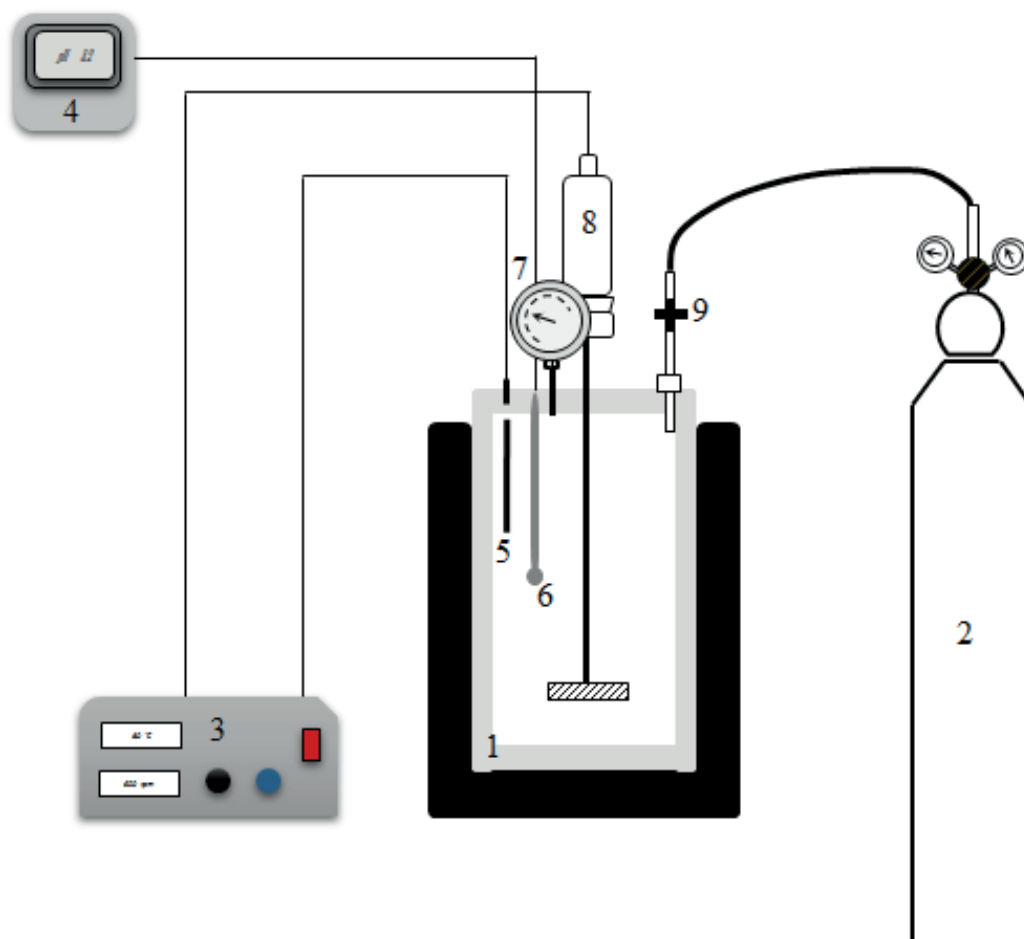


Figure 2. The schematic representation of the experimental setup (1-Reactor, 2- CO_2 tube, 3-Temperature and agitation speed control, 4- pH meter, 5- Thermocouple, 6- pH electrode, 7- Pressure gauge, 8- Agitator, 9-Tap).

Table 4. The errors in parameters and total uncertainties.

Parameters	Systematic errors
Temperatures	± 1 °C
Pressure	0.1% bar
Agitation speed	0.1% rpm
Time	±0.5%
Na ⁺	±1 ppm
Ca ²⁺	±1 ppm
B ₂ O ₃	±0.01% mL
Calculated results	Uncertainty

Leaching efficiency of B₂O₃ that passed from the ulexite ore into the solution was calculated by using the following Eq. 1:

$$\text{Leaching efficiency of } B_2O_3 = \frac{(\text{total amount of ulexite passing into the solution})}{(\text{total amount of ulexite in the original sample})} \times 100 \quad (1)$$

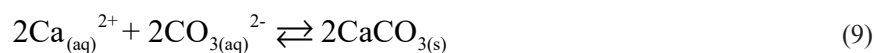
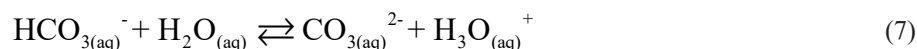
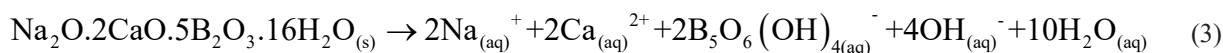
The amount of CO₂ captured was calculated from the change in CO₂ gas concentration according to the stoichiometry of the reaction. The calculation was carried out as follows:

$$g \text{ CO}_2 = \frac{(\text{amount of sample}) \times \left(\frac{\text{percent of ulexite in ore}}{100} \right)}{\text{molecular wt. of ulexite}} \left(\frac{\text{mole percent of } B_2O_3 \text{ leached}}{100} \right) (\text{stoichiometric constant}) (\text{molecular wt. of CO}_2) = \frac{(\beta)(\eta)(\chi)(2)(\alpha)}{10^4(\delta)} \quad (2)$$

RESULTS AND DISCUSSION

Dissolution Reactions

The important reactions occurring in the system are written below:



The total reaction is represented as follows:



According to reaction 3, ulexite completely dissociates to produce Ca^{2+} , Na^+ , $\text{B}_5\text{O}_6(\text{OH})_4^-$ and OH^- ions in water. The pH of the suspension rises up to 9.4. Also, according to reactions 5-8, the carbon dioxide gas dissolves in water and forms carbonic acid. The carbonic acid dissociates into a bicarbonate ion and a hydronium ion. Thus, the pH decreases with dissociation of the carbonic acid. A bicarbonate ion dissociates into a carbonate ion and a hydronium ion (Kocakerim et al., 1993). H_3O^+ ions react with OH^- ions according to reaction 8, and the pH drops approximately to 6.4 at the end of the experiments. As H_3O^+ ions have been consumed, dissociation of ulexite continues and also, sodium and pentaborate ions, $\text{B}_5\text{O}_6(\text{OH})_4^-$ pass continuously to the solution according to reaction 3. The solubility of ulexite depends on the pH value of the solution. On the other hand, sodium pentaborate has a strong buffer effect in the dissolution of ulexite in water at the pH value over the 6.4, whereby the buffer capacity of the solution increases as the partial pressure of CO_2 increases. Here, the sodium pentaborate solution with pH 6.4 contains some boric acid, sodium bicarbonate and dissolved carbon dioxide under CO_2 pressure. This suspension forms a buffer system.

When the CO_2 pressure is removed from the reactor, a portion of the CO_2 in the solution leaves the suspension and a suspension having about pH 6.4 remains. After leaching and filtering of the suspension and removing all of the CO_2 in it, the solution obtained was re-filtered. SEM and X-ray diffraction of the solid waste from filtration is seen in Figs. 3 and 4, respectively. SEM and XRD results confirm that

$\text{CaCO}_{3(s)}$ crystals are formed with the ulexite and in the aqueous media under CO_2 pressure. In addition, calcium carbonate crystals were observed in the solid products. They were randomly distributed, and were observed to be present in cubic structures.

Ca^{2+} ions are formed according to reaction 3 and $\text{CaCO}_{3(s)}$ is formed by reacting with CO_3^{2-} ions according to reaction 10. Ulexite converts CO_2 into a solid, stable carbonate form that contributes to the minimization of CO_2 emissions in the flue gas from the power plants. It is more important that the CO_2 does not require any cost for the dissolution of ulexite, and the product is sodium pentaborate. Also, its by-product, which is CaCO_3 , is not harmful for the environment.

The effect of the parameters

The effects of the parameters on the leaching rate are investigated using the values of each parameter given in Table 3. Constant parameters in the experiments are indicated by asterisks in Table 3. The data from the experimental results are plotted in the form of time against mole percent of B_2O_3 as illustrated in Figs. 5-6.

The effect of the CO_2 partial pressure on leaching rate of ulexite

The effect of CO_2 on the leaching rate of ulexite was studied by researchers to help determine how the change in the CO_2 amount affect the dissolution rate (Kocakerim et al., 1993; Künkül et al., 1997; Kuşlu et al., 2010). Also,

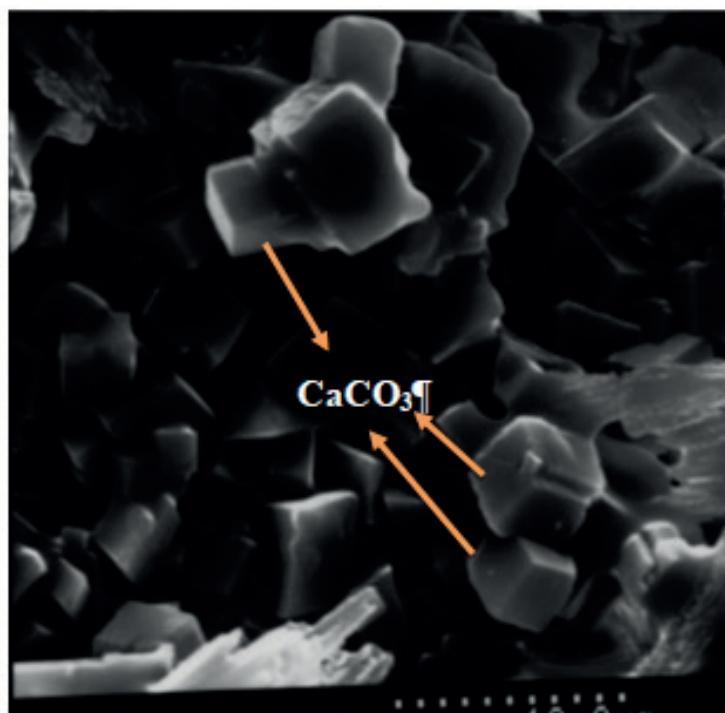


Figure 3. SEM photograph of reaction solid products.

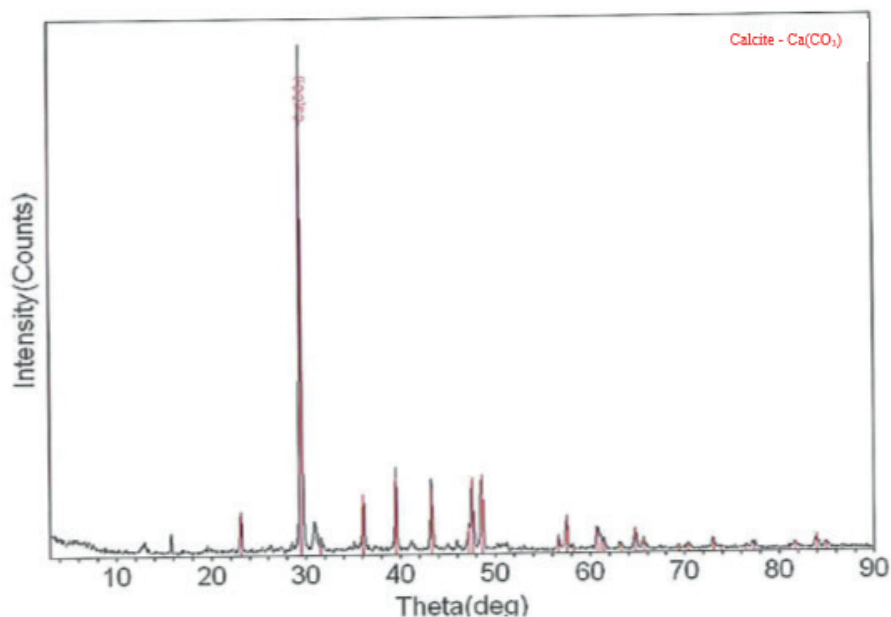


Figure 4. X-ray diffractogram of solid product.

dissolutions of various boron minerals, such as colemanite, inyoite and inderite minerals were investigated in CO₂ saturated water (Alkan et al., 1991; Ata et al., 2000). In these studies, all the experiments were carried out under atmospheric condition at low temperatures.

The solubility of CO₂ in water depends directly on the temperature and the partial pressure of CO₂ gas over the solution. In this study, CO₂ partial pressure is determined by calculating the difference between the total pressure value given in Table 3 and saturated vapour pressure value of water (Cengel and Boles, 2011) at the temperature given in Table 5. The leaching rate of ulexite ore has been investigated at the CO₂ partial pressures of 4.96, 9.96, 14.96 and 19.96 bar, as shown in Fig. 5a. As shown in Fig. 5a, the leaching rate increases with the increase in CO₂ partial pressure in at a certain time, and then the equilibrium is reached within 40–60 min.

The amount of CO₂ in the suspension increases with the increase of the CO₂ partial pressure, which increases the concentration of hydronium ion in the suspension. Hence, the dissolution rate of ulexite also increases with the increase in hydronium ion concentration (Kocakerim et al., 1993).

The effect of the reaction temperature on leaching rate of ulexite

The temperature is one of the most important parameters affecting the leaching rate. The increase in the reaction temperature will cause an increase in the number of collisions of particles; therefore, the reaction rate increases with increasing temperature.

In this study, the effect of reaction temperature was examined in the range of 303 to 393 K. Results of these experiments are shown in Fig. 5b. The leaching rate of the ulexite significantly increased with the increase in the reaction temperature. The maximum leaching efficiency (97.64%) was reached when the reaction temperature was 393 K for the time duration of 60 min. In these conditions, the amount of CO₂ captured stoichiometrically reached a maximum value as 3.30g, which was calculated using Eq. 2. The experimental results indicated that the reaction temperature was the most effective parameter for the leaching of ulexite.

The effect of the particle size on leaching rate of ulexite

The leaching rate is directly proportional to the interfacial surface area. A decrease in particle size causes an increase in the surface area per unit volume of solids. When ulexite ore and water react, increasing the surface area of ulexite ore increases the reaction rate. The experiments are carried out using the following different particle size fractions: 355 to 600, 250 to 355, 180 to 250, and 150 to 180 μ m. The results shown in Fig. 6a indicate that the particle size has a significant effect on the leaching of ulexite and the leaching rate increases with the decrease in particle size.

The effect of the reaction solid-liquid ratio on leaching rate of ulexite

The effect of the solid-liquid ratio on the leaching rate of ulexite ore was studied by using the following values:

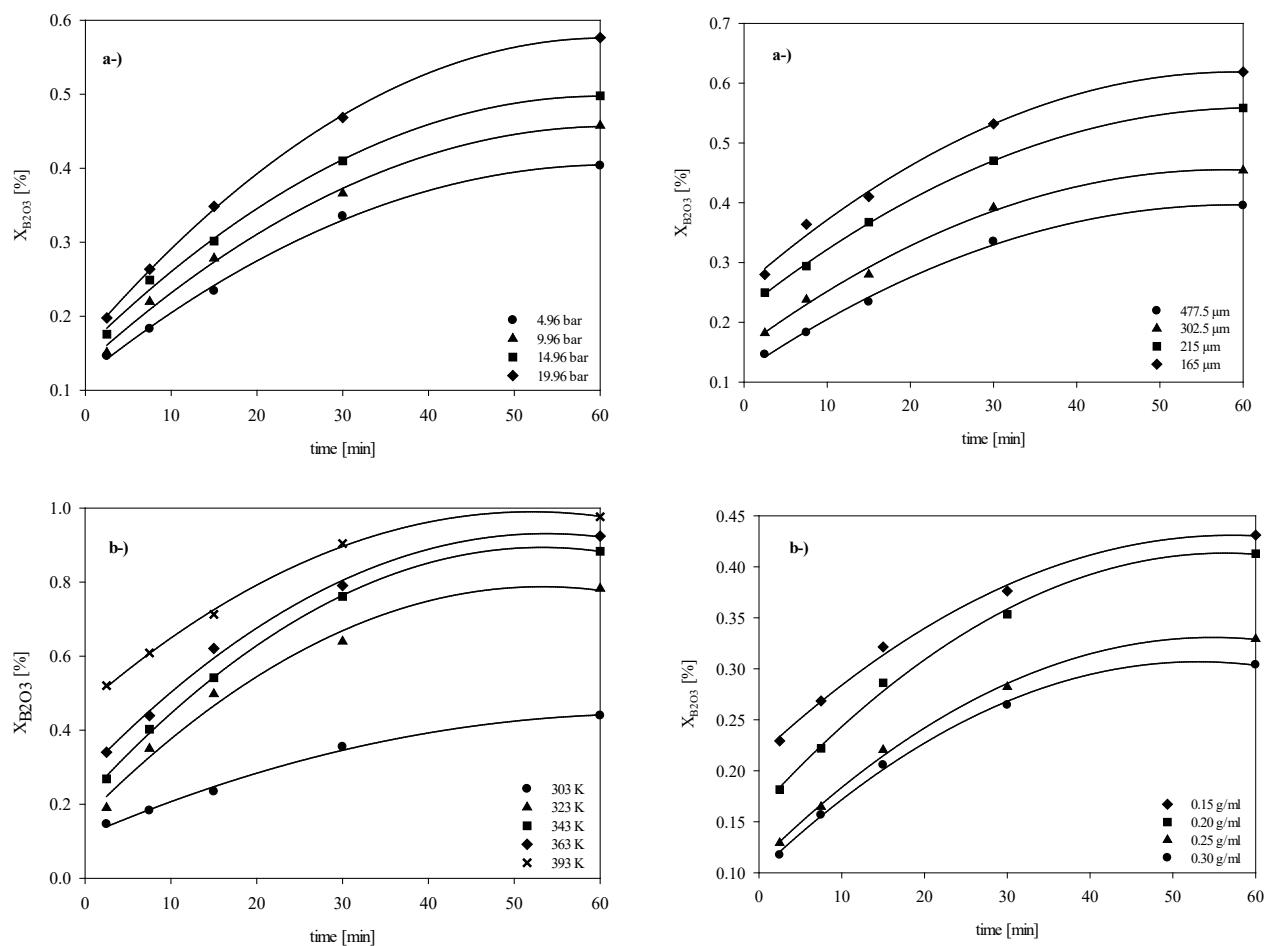


Figure 5. Effect of CO₂ partial pressure and temperature on leaching rate of ulexite.

Table 5. Vapour pressure of saturated water at different temperatures (Cengel and Boles 2011).

Temperature, K	Vapour pressure of saturated water, bar
303	0.04
323	0.12
343	0.31
363	0.69
393	1.96

30/200, 40/200, 50/200 and 60/200 g-ulexite/mL. Unlike the previous works (Künkül et al., 1997; Demirkıran, 2008; Doğan and Yartaşı, 2009; Kuşlu et al., 2010; Kavcı et al., 2014), a higher ratio of solid-liquid was selected for this study. The effect of the solid-liquid ratio is shown in Fig. 6b. As it can be seen in Fig. 6b, the leaching rate of ulexite decreases with increasing solid-liquid ratio. The maximum leaching rate at the solid-liquid ratio of 30/200 g-ulexite/mL at the 60th min was found to be about 48%. The leaching rate increases with the decrease in the solid-liquid ratio because of the reduction in the amount of ulexite in the solution. Depletion of the amounts of

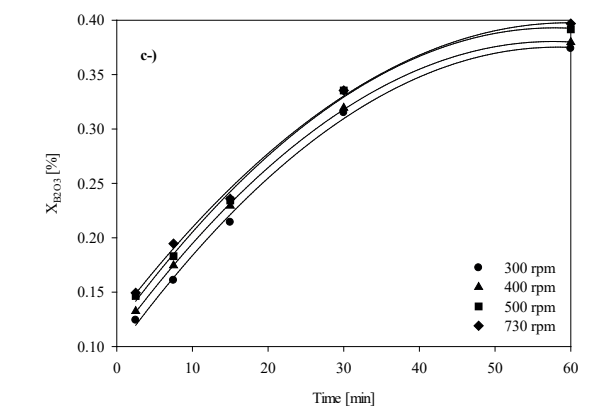


Figure 6. Effect of particle size solid-liquid ratio and agitation speed on leaching rate of ulexite.

ulexite in solution causes an easy diffusion of liquid to the surface of the ulexite particles.

The effect of the agitation speed on leaching rate of ulexite

The effect of the agitation speed on the leaching rate of ulexite was investigated at 300, 400, 500 and 730 rpm.

Maximum operating condition of the system was 730 rpm. The required homogeneity at lower speeds (<300 rpm) was not achieved during the reaction.

The variations of the agitation speed had no significant effect on the leaching rate (Fig.6c). It was observed that operation at 500 rpm provided the optimal condition, because further increase in the agitation speed did not increase leaching rate significantly. Therefore, the effect of the agitation speed was excluded from the overall correlation equations on the leaching rate and ignored according to experimental results. That agitation speed does not have an effect on the leaching rate of ulexite thus confirming that the rate is not controlled by fluid film diffusion.

Kinetic Analysis

In order to determine the kinetic parameters and the rate controlling step of the leaching of ulexite in the carbonic acid solution, non-catalytic heterogeneous reaction models were tested on the experimental data. For determining the kinetic model and the rate-determining step in the leaching of ulexite using the carbonic acid solution, the experimental data were analysed by plotting the model equations versus time and comparing the corresponding correlation coefficients (R²). The Avrami Model provided the best agreement with the obtained experimental data (Table 6). This result is also in agreement with the observation of calcium carbonate crystals on the ulexite particles (See Fig. 3).

Table 6. Model kinetic equations and correlation coefficients.

Model Kinetic Equations	R ²
$kt = 1 - 3(I-x)^{2/3} + 2(I-x)$	0.768
$kt = 1 - (I-x)^{1/3}$	0.589
$kt = 1 - (I-x)^{1/2}$	0.487
$kt = 1 - (I-x)^{2/3}$	0.337
$kt = -\ln(I-x)$	0.723
$kt = \sqrt[3]{(I-x)}$	0.865
$kt^n = -\ln(I-x)$	0.976
$kt = x^2$	0.695
$kt = x + (I-x)\ln(I-x)$	0.747

The general form of the Avrami model equation is given by Eq. 11.

$$-\ln(I-x) = kt^n \quad (11)$$

where x is the fraction of ulexite leached, k , the kinetic constant and t time. The logarithm of Eq. 11 is as follows:

$$\ln[-\ln(I-x)] = \ln k + n \ln t \quad (12)$$

$\ln(-\ln(I-x))$ is plotted versus $\ln t$ as can be seen in Fig. 7.

The slope (n) and the intercept ($\ln k$) of the line were determined from Fig. 7. The values of n and $\ln k$ at different reaction temperatures are given in Table 7. The average value of n and standard deviation are 0.55 and 0.04, respectively.

The factor n depends on the properties and geometry of the solid particles, but it is independent of operating conditions. The leaching reactions were classified into three main categories: for $n < 1$ the initial rate is infinite and the rate continually decreases with increasing time; for $n = 1$, the initial rate is finite; for $n > 1$, the reaction exhibits an initial rate approaching zero (Kabai, 1973; Zheng and Chen, 2014).

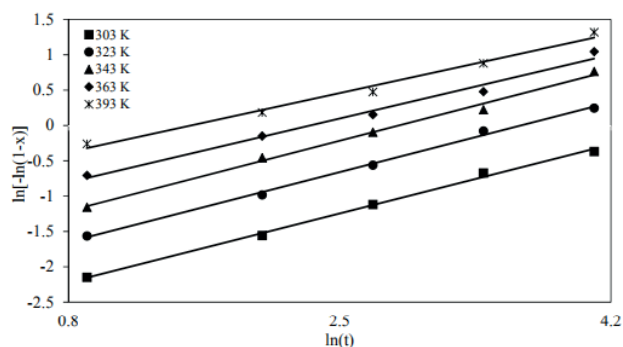


Figure 7. $\ln(-\ln(1-x))$ vs $\ln t$ at different reaction temperatures.

Table 7. Values of n and $\ln k$ at different reaction temperatures.

Temperature, K	$\ln k$	n	R ²
303	-2.681	0.574	0.9972
323	-2.118	0.583	0.9969
343	-1.680	0.585	0.9943
363	-1.229	0.531	0.9862
393	-0.773	0.493	0.9872
Average		0.553	
Standard deviation		0.040	

The kinetic equation of ulexite ore in carbonic acid solution can be written as follows:

$$-\ln(I-x) = kt^{0.55} \quad (13)$$

In order to determine the reaction rate constants, the variation of $-\ln(I-x)$ versus $t^{0.55}$ is plotted for the leaching conditions in Figs. 8–9. The empirical kinetic equation of leaching of ulexite ore related to these five variables can be expressed by the Arrhenius equation:

$$k = Ae^{\frac{-E_A}{RT}} \quad (14)$$

$$k = k_0 (D)^a (P_{CO_2})^b (S/L)^c e^{-\frac{E_A}{RT}} \quad (15)$$

where k_0 is the frequency factor, E_A is the activation energy of the process, A is the pre-exponential factor with the same units as the kinetic constant k , R is the universal gas constant ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$), T is the reaction temperature (K), D is the mean particle size (μm), P_{CO_2} is the CO_2 partial pressure (bar), S/L is the solid-liquid ratio (g/ml), a , b and c are constants.

The reaction rate constants were obtained from the slopes of the lines in Figs. 8–9. The $\ln k$ values were calculated from these k values. Unknown constants a , b and c were calculated using the linear regression analysis (using computer programs with non-linear estimation models, user-specified least squares regression, confidence value of 95%, and maximum number of iterations of 1000). The obtained results were in conformity with the results calculated by linear regression analysis. Thereby the unknown constant values were calculated as -0.55, 0.36 and -0.73, respectively. The logarithmic form of Eq. 14 is given as follows:

$$\ln k = -\frac{E_A}{RT} + \ln A \quad (16)$$

$$A = k_0 (D)^{-0.55} (P_{CO_2})^{0.36} (S/L)^{-0.73} \quad (17)$$

To determine the activation energy of the process, $\ln k$ was plotted against the inverse of the temperature. The activation energy of the process was calculated using the slope of the lines in Fig. 10. The activation energy and the pre-exponential factor (A) were determined to be 21.1 kJ.mol^{-1} and 304.3 , respectively. The value of k_0 was determined as 1277.4 using Eq. 17 and the pre-exponential factor (A). The base parameters are $D=477.5$, $P_{CO_2}=4.96$, $S/L=0.2$. The reaction rate constant was written as follows:

$$k = 1277.4 (D)^{-0.55} (P_{CO_2})^{0.36} (S/L)^{-0.73} \exp\left(-\frac{21092}{RT}\right) \quad (18)$$

Considering Eqs. 13 and 18, the empirical kinetic equation of leaching can be described as follows:

$$x = 1 - e^{-1277.4(D)^{-0.55} (P_{CO_2})^{0.36} (S/L)^{-0.73} \exp\left(-\frac{21092}{RT}\right) t^{0.55}} \quad (19)$$

The activation energy for dissolution of ulexite has been found to be lower than that of the one calculated by various authors for pure ulexite mineral (Demirkiran, 2009; Demirkiran, 2008; Ekmekyapar et al., 2008; Kocakerim et al., 1993; Künkül et al., 1997). The dissolution kinetics

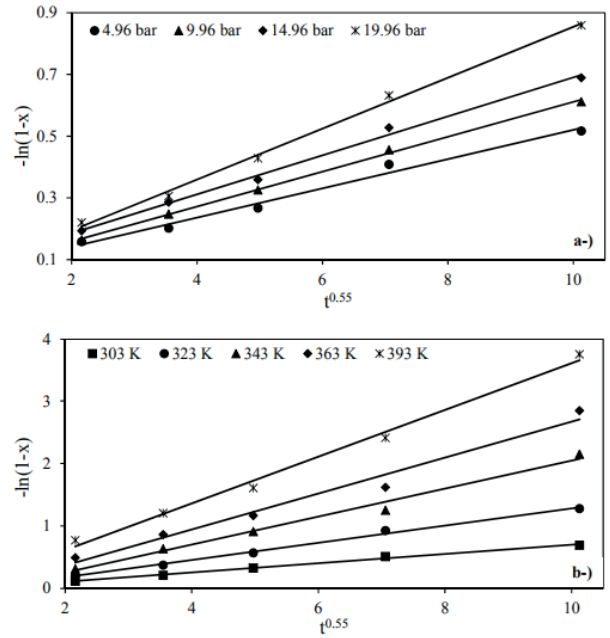


Figure 8. Variation of $-\ln(1-X)$ versus $t^{0.553}$ with different CO_2 partial pressures and temperatures.

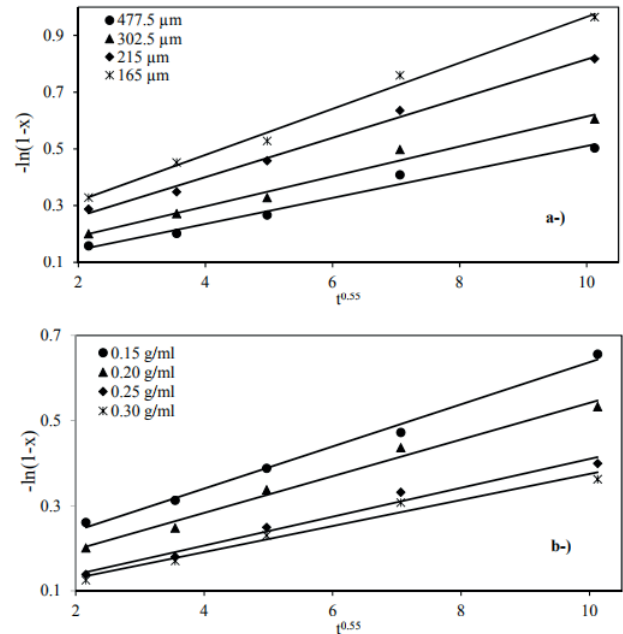


Figure 9. Variation of $-\ln(1-X)$ versus $t^{0.553}$ with different particle sizes and solid-liquid ratios.

of ulexite in H_2SO_4 solutions was investigated by Tunç et al. (2001). Massive fine-grained gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) forms around the ulexite particles with a slow reaction. Similar effects were observed in the present study and also formation of H_3O^+ ions increased with increasing CO_2 partial pressures in aqueous media; and formation of a firm layer which contained fine-grained CaCO_3 crystals occurred rapidly around ulexite particles. This firm layer affects the reaction rate negatively during the process.

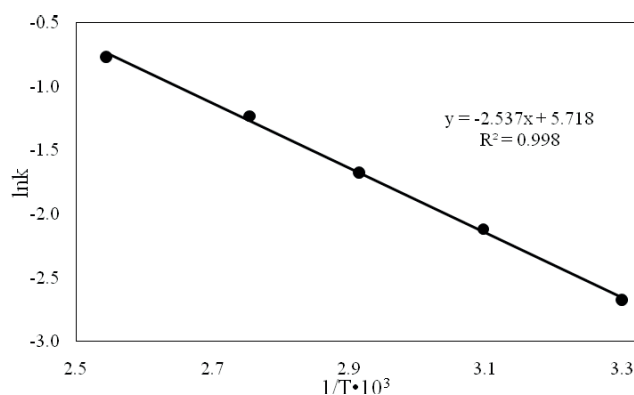


Figure 10. $\ln k$ against the inverse of the T .

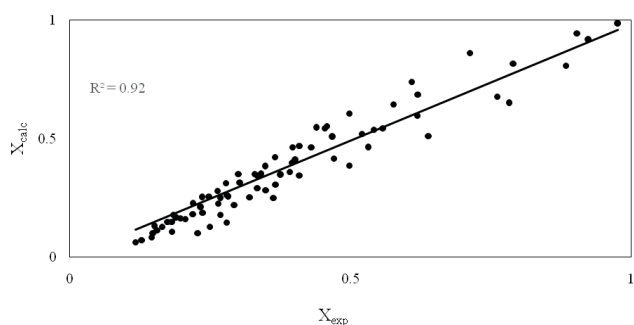


Figure 11. Parity plot of calculated and experimental conversion of ulexite in different experiments.

In the present study, calcium carbonate, which form as a shell around the ulexite mineral surface, caused a decrease in the dissolution rate of ulexite in aqueous medium because of the difficulty for the diffusion of H_3O^+ ions to the ulexite mineral surface. Therefore, the activation energy decreases, and the dissolution process fits to Avrami Model, which was developed for crystallization processes. Also, these components create difficulty for the diffusion of H_3O^+ to the surface and, due to the crystallisation, the Avrami Model can be used to describe the leaching process.

The dissolution rates obtained from the model equations and the experimental data are shown in Fig. 11. As can be seen in Fig. 11, the best correlation was observed between the model equation (Eq.19) and the experimental data.

CONCLUSIONS

In this study, the leaching kinetics of ulexite in solutions of carbonic acid was examined. The effects of the parameters such as CO₂ partial pressure, reaction temperature, particle size, solid/liquid ratio and stirring speed on leaching rate were investigated. As a result, it was found that the leaching rate increased with the increase in the reaction temperature and CO₂ partial pressure; and decreased with the increase in the particle size and the solid/liquid ratio. No effect of stirring speed was found on the leaching rate. To determine the effects of the

parameters and the model kinetic equations, homogeneous and heterogeneous reaction models were used. The Avrami Model was found to be the best model for expressing the process of leaching. The activation energy of this process was found to be about 21.1 kJ.mol⁻¹, and the expression connecting the parameters to the leaching fraction was determined as

$$x = 1 - e^{-1277.4(D)^{-0.55}(P_{CO_2})^{0.36}(S/L)^{-0.73} \exp\left(\frac{-21092}{RT}\right)t^{0.55}}$$

Finally, it was observed that CO₂, which does not require any cost for the dissolution of ulexite, can be captured. Besides, a valuable product sodium pentaborate can be produced.

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