

Dissolution Kinetics of Ulexite in Borax Pentahydrate Solutions Saturated with Carbon Dioxide

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Abstract: The aim of the study was to investigate the dissolution kinetics of ulexite in borax pentahydrate solutions saturated with carbon dioxide in a mechanical agitation system. The effects of reaction temperature, stirring speed, CO₂ flow rate, solid/liquid ratio and particle size on the rate of dissolution of ulexite were examined. It was observed that increase in the reaction temperature and decrease in the solid/liquid ratio causes an increase the dissolution rate of ulexite. The dissolution extent is not affected by the stirring speed rate in experimental conditions. The activation energy was found to be 58.7 kJ/mol. This value indicates the dissolution rate of ulexite is a chemically controlled reaction. The rate expression associated with the dissolution rate of ulexite depending on the parameters chosen may be summarized as: $1-(1-X)^{1/3} = 7.4 \times 10^5 \cdot D^{-0.8} \cdot (S/L)^{-0.6} \cdot W^{0.1} \cdot e^{(-58700/R T)} \cdot t$

Keywords: Ulexite, Borax Pentahydrate, Dissolution Kinetics, Heterogeneous reaction

Introduction

Boron is one of the most important mineral resources of Turkey (Davies et al., 1991). Turkey possesses 72 % of the world's boron reserves. Boron has both strategic and industrial importance. It is oxophilic, and occurs as borates (oxides) in nature (Kemp, 1956). The main boron minerals of different percentages of (B₂O₃) contents are Colemanite (Ca₂B₆O₁₁·5H₂O), Tincal (Na₂B₄O₇·10H₂O), Kernite (Na₂B₄O₇·4H₂O) Ulexite (Na₂O·2CaO·5B₂O₃·16H₂O), Datolite (Ca₂B₂O₅·Si₂O₅·H₂O) and Hydroboracid (CaMgB₆O₁₁·6H₂O) (Çetin et al., 2001). Although boron minerals can be employed as raw materials in some industries, the refined boron products and converted leading edge products are widely used in various industries (Garret, 1998; Özmetin et al., 1996). Borax is a natural mineral compound found in playa lakes. The basic structure of borax comprises chains of interlocking BO₂(OH) triangles and BO₃(OH) tetrahedrons bonded to chains of sodium- and water octahedrons. Borax can be mixed with other cleaning agents including chlorine bleach (Küçük et al., 2002). One of the most important minerals and derivatives of boron is ulexite, a hydrated calcium-sodium borate. It is a type of hydrated calcium borate with a monoclinic crystal structure and contains many clay minerals. It is used to produce boric acid (Küçük et al., 2002). Boric acid is the most commonly used boron compound, and is used as starting material in the preparation of many boron chemicals such as boron phosphate, boron tri halides, boron esters, boron carbide, organic boron salts and fluoroborates (Özmetin et al., 1996; Küçük et al., 2002; Temur et al., 2000). It is used as a source of B₂O₃ in many fused products (Kemp, 1956).

There are many studies in the literature connected with the dissolution kinetics of ulexite in various solutions. A summary of these studies is as follows: Alkan and Kocakerim (1987), studied it in water saturated by sulfur-dioxide and the activation energy was calculated as 58 kJ/mol. Kocakerim et al. (1993), investigated it in water saturated with CO₂ in low temperatures (17-35 °C) and the activation energy was found to be 51.7 kJ/mol. Künkül et al. (1997), studied it in ammonia solution saturated with CO₂ and described the dissolution rate

by a first-order pseudo-homogeneous reaction model and found the activation energy to be 55 kJ/mol. Tekin et al. (1998), carried out experiments with it in ammonium chloride solution and found the activation energy to be 80 kJ/mol. Tunç et al. (1999), investigated it in H_2SO_4 solution. They found that increasing H_3O^+ acid concentration increased the dissolution rate, but increasing SO_4^{2-} concentration reduced the dissolution rate due to the precipitation of a solid film of $CaSO_4$ and/or $CaSO_4 \cdot 2H_2O$. Alkan et al. (2000), reported it in aqueous EDTA solutions and its dissolution was expressed according to the un-reacted shrinking core model with changing fluid phase concentration and calculated the activation energy to be 35.95 kJ/mol. Künkül et al. (2003), studied it in ammonium sulfate solutions. They described dissolution process by heterogeneous diffusion control through the ash layer or product layer model and found the activation energy was 83,5 kJ/mol. Alkan et al. (2004), investigated it in oxalic acid solutions. The reaction rate was controlled by product-layer diffusion and calculated the activation energy as 59,8 kJ/mol. Demirkıran and Künkül (2007), studied it in perchloric acid solutions and found that the process was described by the Avrami model and found the activation energy was 19.2 kJ/mol. Ekmekyapar et al. (2008), studied it in acetic acid solutions. They found that the dissolution kinetics obeys a shrinking core model with the surface chemical reaction as the rate-controlling step. The activation energy was found to be 55.8 kJ/mol. Demirkıran (2008) investigated it in the ammonium acetate solutions. The dissolution rate fit the chemical reaction control model and the activation energy was found to be 55.7 kJ/mol. The aim of our study was to investigate the dissolution kinetics of ulexite in borax pentahydrate solutions saturated with CO_2 in a mechanical agitation system. There is no study reported in the literature about such a procedure. In our study, we choose reaction temperature, stirring speed, CO_2 flow rate, solid/liquid ratio and particle size of ulexite as parameters.

Materials and Methods

Ulexite samples used in the experiments were obtained from Bandırma Borax Corporation, TURKEY. The ulexite mineral samples were crushed, dried under vacuum and sieved with ASTM standard sieves to give fractions of average sizes 1840, 725, 275, 165 and 107.5 μm for dissolution experiments. The chemical analyses of original ulexite samples and the B_2O_3 content in the particle sizes used in the experiments are shown in Tables 1 and 2, respectively. Further, SEM photography of the original ulexite minerals is shown in Fig.1.

Leaching experiments were conducted under atmospheric pressure conditions. All reagents used in the experiments were prepared from analytical grade chemicals (Merck) and distilled water. A constant temperature water circulator was used in combination with the reactor to maintain the mixture in the reactor at a constant temperature. The experiments were carried out in a 500 mL spherical glass reactor. The reactor was equipped with a reflux condenser to prevent evaporation during heating and a mechanical stirrer to obtain a homogeneous suspension in the reactor. The mechanical agitation experimental system is fairly common, so no illustration of it appears in this paper. A typical experiment conducted was as follows: 400 mL of distilled water was poured into the flask. The solution was heated to the desired temperature, at which it was kept constant; to retain the ratio at [borax pentahydrate mol number / ulexite mol number] as $\frac{1}{4}$ in all experiments, a large quantity of borax pentahydrate was added to the distilled water.

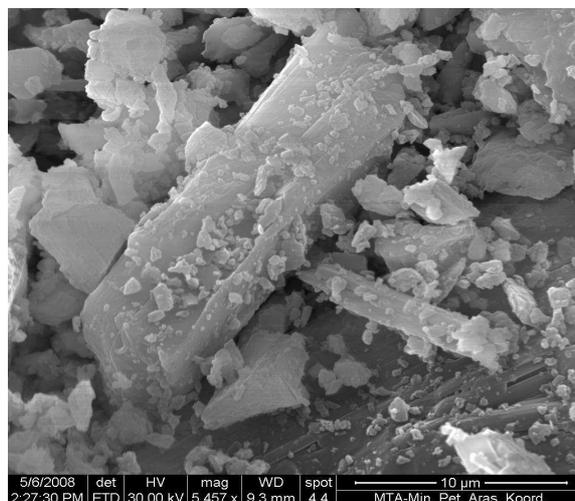


Fig.1- SEM photograph of ulexite minerals

Component	CaO	B ₂ O ₃	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	SrO	H ₂ O
%	14.69	41.12	7.48	1.78	< 0.01	4.13	< 0.01	1.43	29.35

Table 1. Chemical analyses of ulexite minerals

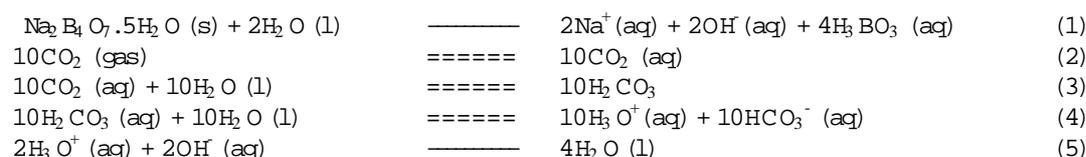
Part. size (μm)	1840	725	275	165	107.5
B ₂ O ₃ (%)	41.79	41.21	41.71	40.25	40.85

Table 2. Particle sizes of B₂O₃ utilized

All experiments were carried out using 725 μm size fractions, except in experiments where the effect of particle size on the reaction rate was investigated. The CO₂ gas (97 %) was supplied to the reactor from a CO₂ cylinder tank. CO₂ gas was continuously fed to the reactor during leaching studies to maintain saturation conditions. The flow rates of CO₂ were maintained at 514 mL/min. in all experiments. The gas was bubbled from the bottom of the reactor by means of a disk-type gas dispenser. CO₂ feed to the reactor for 20-25 min. was to obtain a saturated borax pentahydrate solution. After this, large quantities of solid ulexite and borax pentahydrate [depending on both the solid/liquid ratio in the reactor and the ratio between mol number of borax penta-hydrate and mol number of ulexite] were added to the solutions. Stirring of the solution was started immediately thereafter. The duration of the treatment depended on the experimental conditions. At definite time intervals, 1 mL samples of the reacted solution were taken for the assay of B₂O₃ and analyzed by potentiometric and titrimetric methods (Nemodruk et al., 1965; Sookg et al., 1996). Based on the B₂O₃ estimated, the degree of dissolution of ulexite was determined as a function of time.

Result and Discussion

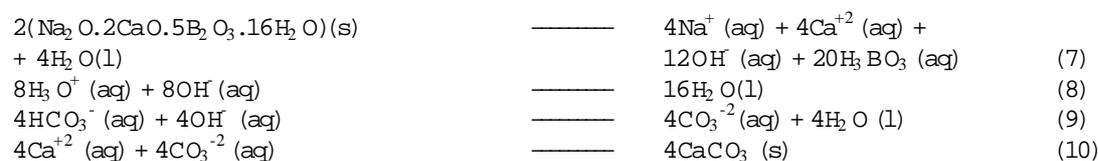
The following reactions occurred during the dissolution process:



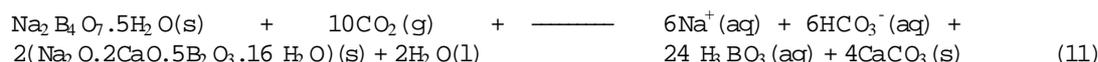
Hence, the overall reaction is follows:



When ulexite is added to the borax pentahydrate solutions, the reaction taking place in the solution can be written as follows:



The overall net reaction is:



Reaction temperature, stirring speed, CO₂ flow rate, solid/liquid ratio and particle size of ulexite is selected as process variables to investigate their effects on the dissolution level of ulexite. In the experiments, while the effect of one parameter was studied, the values of other parameters shown with asterisks in Table 3 were kept constant. The solubility of CO₂ in water under reaction conditions is shown in Table 4.

parameter	values
stirring speed (rpm)	0, 100, 150, 300, 600*, 700, 900
flow rate of CO ₂ (mL/min)	514*, 1594, 2696, 3804, 4978, 6101
reaction temperature (K)	313, 323*, 333, 343, 353, 358
solid/liquid ratio (g/mL)	1/50*, 1/25, 1/12, 1/6, 1/3
particle size (μm)	1840, 725*, 275, 165, 107.5

Table 3: Parameters chosen and their ranges

(* While the effect of one parameter was studied, the values of the other parameters were kept constant.)

Reaction Temperature (K)	313	323	333	343	353	358
Solubility of CO ₂ (g CO ₂ /100 cm ³ water)	0.0930	0.0761	0.0576	0.0553	0.0538	0.0529

Table 4: Solubility of CO₂ in water under reaction conditions

A quantity of 400 mL of borax pentahydrate solution saturated with CO₂ was used [borax pentahydrate mole number / ulexite mol number ratio was 1/4] and was kept constant in all experiments. Homogeneity of suspension in the reactor was obtained with a stirring speed of 600 rpm, kept constant in all experiments. The data obtained were plotted in the form of time versus fractional conversion as appearing in Fig. 2-10. In these figures, the fractional conversion X (%) is defined:

$$X(\%) = \frac{(\text{amount of dissolved } B_2O_3 \text{ in the solution})}{(\text{amount of } B_2O_3 \text{ in the original sample})} \times 100$$

The effect of reaction temperature was examined at 313, 323, 333, 343, 353 and 358 K. The dissolution curves obtained are shown in Fig. 2. Fig.2 also shows that the quantity of ulexite dissolved increases with increasing reaction temperature. The reaction rate constant is exponentially dependent on reaction temperature. The effect of the stirring speed on the dissolution rate of ulexite was investigated at 100, 150, 300, 600, 700 and 900 rpm. The dissolution curves are given in Fig. 3. It can be seen from the Fig. 3 that the dissolution level of the process increases with increase in the stirring speed rate until about 300 rpm. Although the stirring rate was increased from 400 rpm to higher speeds such as 600, 700 and 900 rpm, the dissolution level remained nearly steady. Homogeneity of the suspension was obtained at a stirring speed of 600 rpm. The stirring speed rate of 600 rpm was as constant value in all experiments. Although the stirring speed was increased from 300 to 600, 700 and 900 rpm, the increase of in dissolution rate was very small. It can, therefore, be assumed to have remained constant. Therefore, as all experiments were carried out at stirring speed of 600 rpm, it can be assumed that the dissolution level remained unaffected by the stirring speed in experimental conditions. In order to investigate the effect of flow rate of CO₂, experiments were carried out with varying CO₂ flow rates of 514, 1594, 2696, 3804, 4978 and 6101 mL/minute. It was observed that the flow rate of the gas has no significant effect on dissolution rate. This is probably because concentration of CO₂ is not dependent on its flow rate, and because its solubility in water at a given temperature is constant and excess gas leaves the solution.

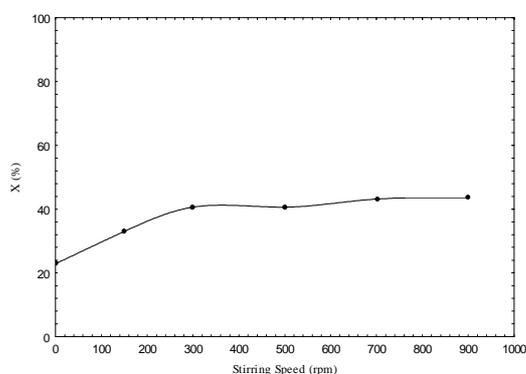


Fig. 3: Effect of stirring speed on dissolution rate of ulexite

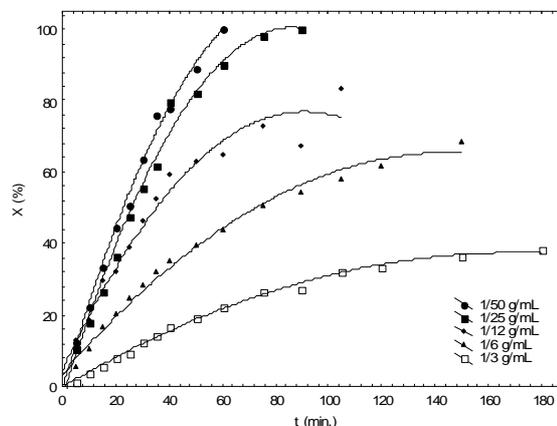


Fig. 4: Effect of solid/liquid ratio on dissolution rate of ulexite

The effect of solid/liquid ratio on the dissolution rate of ulexite was investigated by varying ratio to 1/50,

1/25, 1/12, 1/6 and 1/3 g/mL. The dissolution curves are given Fig. 4. It can be seen from the Fig.4 that, the dissolution rate decreases with increasing solid/liquid ratio. This situation can be explained by the decrease in the number of ulexite particles per amount of solutions. The effect of particle size was studied by treating five sizes of fractions of this mineral, namely 1840, 725, 275, 165 and 107.5 μm . The dissolution curves are presented in Fig. 5. As can be seen from Fig. 5, as the particle size decreases the dissolution rates increased because of increasing surface area.

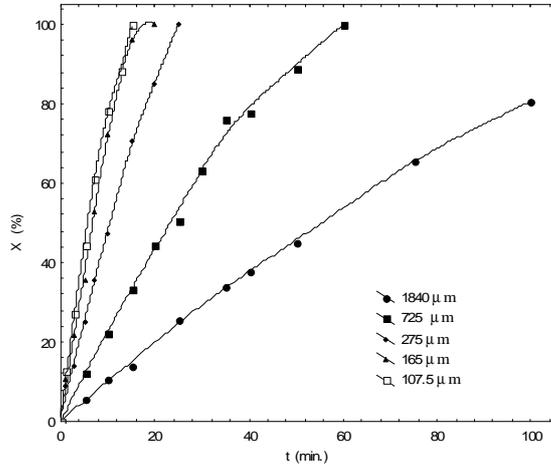


Fig. 5: Effect of particle size on dissolution rate

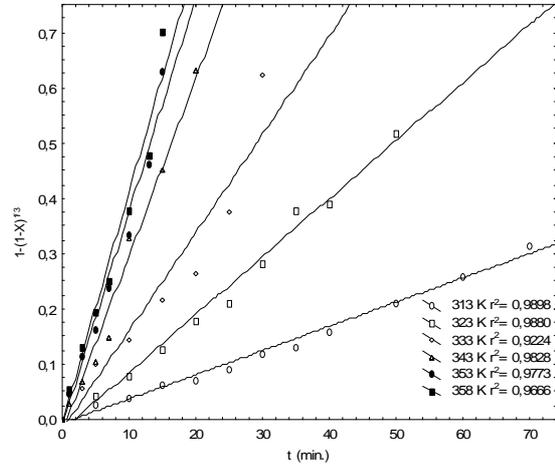


Fig.6: Variation of $1-(1-X)^{1/3}$ with time for various temperatures

The solid-fluid reaction rate can be obtained from the heterogeneous reaction model. To evaluate the rate-controlling step; the experimental data were analyzed based on the un-reacted shrinking core model (Levenspiel, 1972; Mazet, 1992). As ulexite particles are non-porous, the most appropriate reaction model appears to be that of shrinking non-porous particles. The rate of a reaction between a solid and a fluid can be expressed as heterogeneous and homogeneous reaction models. The heterogeneous reaction model gives rate equations for each control mechanisms. The kinetic data is analyzed based on the un-reacted shrinking core model to determine the rate-controlling step. The step with the highest resistance is the rate-controlling step. The model has been used for liquid-solid systems in both analytical and numerical methods. Integrated rate equations for the un-reacted shrinking-core model are shown in Table 5. According to the model, the kinetic data were treated by equations in Table 5.

rate-controlling step	rate equation		
surface chemical reaction	$t/t^* = [1 - (1 - X_B)^{1/3}]$	$t^* = \rho_B R / bksC_{Ag}$	(12)
the film diffusion control	$t/t^* = X_B$	$t^* = \rho_B R / 3bkgC_{Ag}$	(13)
diffusion control through the ash or product layer	$t/t^* = [1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)]$	$t^* = \rho_B R^2 / 6bDeC_{Ag}$	(14)

Table 5: Integrated rate equations for the un-reacted shrinking core model

The application of the above models to the experimental data will help in to determining the dissolution kinetics of the process. Experimental data that fits the rate determining step is the surface reaction chemical control. The evidence for this proposal is as follows: regression analysis has shown that experimental data correlate well with Equation 12, which means that the dissolution is chemically controlled surface reaction. During the reaction, calcium carbonate, CaCO_3 , precipitates. Therefore, it may appear that the reaction may be controlled by the ash film or a combination of ash film and chemically controlled surface reaction. The regression coefficients for ash film and chemically controlled surface reaction were found to be 0.9669 and 0.9993, respectively. The higher linearity between the two models obtained was 0.9993 for chemically controlled surface reaction. The variation of $1-(1-X)^{1/3}$ with time is plotted for reaction temperature, stirring speed, solid/liquid ratio and particle size in Figs. 6, 7, 8 and 9, respectively. Using the surface chemical reaction control model, the t^* values were plotted versus R. The high linearity between t^* and R is seen in Fig. 10. Fig. 10, also shows the regression coefficient (r^2) to be was found as 0.9993. Arrhenius plots of $\ln k_s$ versus $1/T$ are shown in Fig. 11. From the slopes of the straight lines, the activation energy of the reaction is found to be 58.7 kJ/mol. Further, this value indicates the dissolution rate of ulexite is a chemically controlled surface reaction. It

has been reported that, the activation energy of the chemically controlled surface reaction is in excess of 40 kJ/mol (Jackson, 1986). Similar results were found in the literature (Yartasi et al., 1987; Alkan and Dođan, 2004). Because all experiments was performed at a stirring speed of 600 rpm, it can be assumed that the dissolution level remained un affected by this parameter in experimental conditions. The fact that the dissolution rate of ulexite is independent of the stirring speed is shown by the fact that the control mechanism is the chemically controlled surface reactions. The values were found by non-linear regression analyses (Statistica 6.0, non linear estimation model, user- specified regression-least squares, security value of %95, comparison value of $1 \times \text{Exp}(-6)$, and maximum iteration values of 500) and the analyses gave the mathematical model as follows:
 $1-(1-X)^{1/3} = 7.4 \times 10^5 \cdot D^{0.8} \cdot (S/L)^{-0.6} \cdot W^{0.1} \cdot e^{(-58700/RT)} \cdot t$

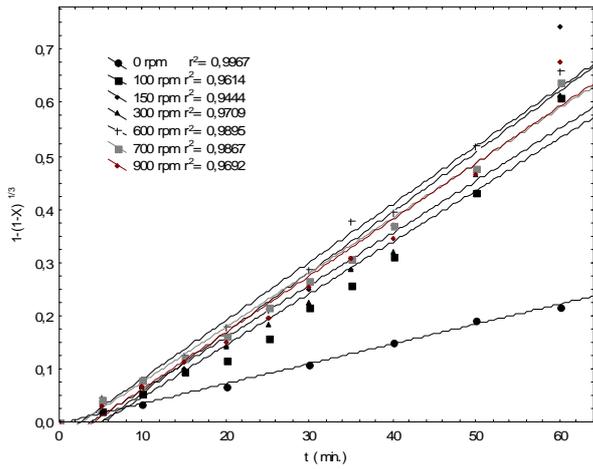


Fig. 7: Variation of $1-(1-X)^{1/3}$ with time for stirring speeds

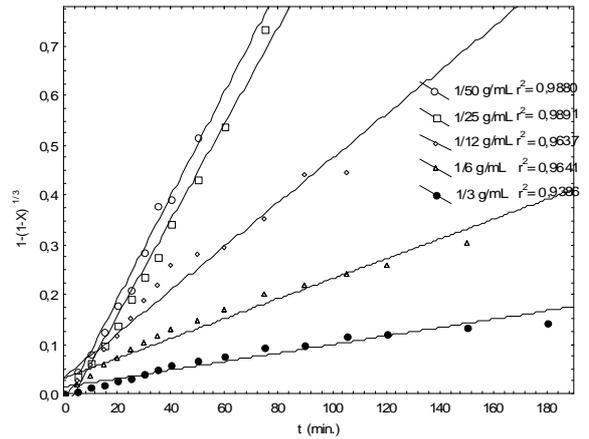


Fig. 8: Variation of $1-(1-X)^{1/3}$ with time for solid / liquid ratio

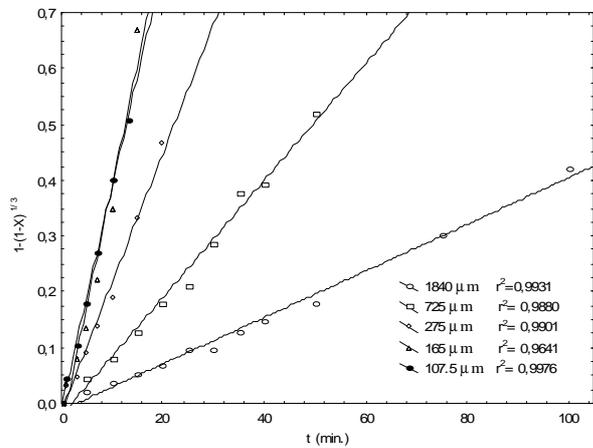


Fig. 9: Variation of $1-(1-X)^{1/3}$ with time for particle size of ulexite

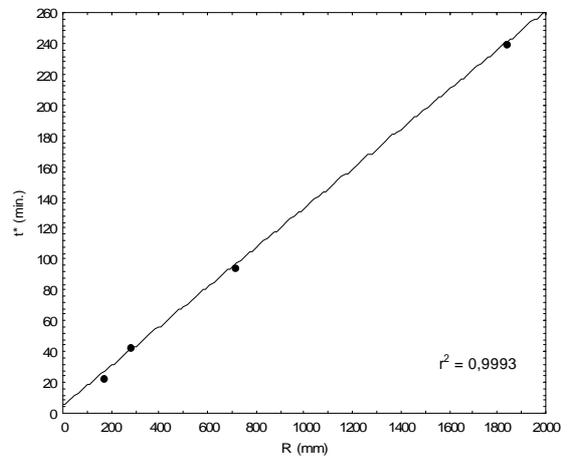


Fig. 10: Linearity between t^* and R

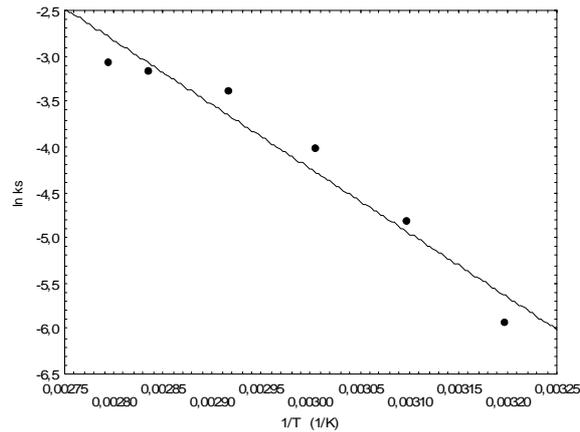


Fig. 11: Arrhenius plot of the dissolution process

Conclusion

The aim of the study was to investigate the dissolution kinetics of ulexite in borax pentahydrate solutions saturated with carbon dioxide in a mechanical agitation system. The solubility of ulexite can be increased by addition of CO₂. It was determined that the dissolution rate of ulexite increased with increase in reaction temperature and decrease in the solid/liquid ratio. The dissolution extent is not affected by the stirring speed rate in experimental conditions. The dissolution process was described by chemical control of the heterogeneous surface reaction. The activation energy was found to be 58.7 kJ/mol. The mathematical form of the model depended on the parameters chosen is as follows:

$$1-(1-X)^{1/3} = 7.4 \times 10^5 \cdot D^{-0.8} \cdot (S/L)^{-0.6} \cdot W^{0.1} \cdot e^{(-58700/RT)} \cdot t$$

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Nomenclature

b	stoichiometric coefficient (in eq. 7-9)
C	concentration of borax decahydrate solution (mol/m ³)
C _{Ag}	concentration of A in the bulk solution (mol/m ³)
D	mean particle size (m)
D _e	diffusion coefficient (m ² /min)
E _A	activation energy (kJ/kmol)
k _d	mass transfer coefficient (m/min)
k _s	reaction rate constant for surface reaction (mol/min)
k ₀	frequency or pre-exponential factor, min. ⁻¹
L	amount of liquid (mL)
n	mol number (mol)
r	correlation coefficient
R	universal gas constant (kJ/kmol)
R	initial radius of a solid particle (m)
S	amount of solid (g)
T	reaction temperature (K)
t	reaction time (min.)
t*	reaction time for complete conversion (min.)
X	fractional conversion of B ₂ O ₃
W	stirring speed (rpm)
ρ _B	molar density of solid reactant (mol/cm ³)

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