

Dissolution Leaching Kinetics of Ulexite in Sodium Dihydrogen Phosphate Solutions

Emine Teke, Soner Kuşlu, Sabri Çolak, Turan Çalban

Abstract—The aim of the present study was to investigate the dissolution kinetics of ulexite in sodium dihydrogen phosphate in a mechanical agitation system and also to declare an alternative reactant to produce the boric acid. Reaction temperature, concentration of sodium dihydrogen phosphate, stirring speed, solid-liquid ratio, and ulexite particle size were selected as parameters. The experimental results were successfully correlated by using linear regression and a statistical program. Dissolution curves were evaluated in order to test the shrinking core models for solid-fluid systems. It was observed that increase in the reaction temperature and decrease in the solid/liquid ratio causes an increase in the dissolution rate of ulexite. The activation energy was found to be 36.4 kJ/mol. The leaching of ulexite was controlled by diffusion through the ash (or product) layer.

Keywords—Sodium dihydrogen phosphate, leaching kinetics, ulexite.

I. INTRODUCTION

TURKEY has approximately 60% of the boron ores of the world. Boron is one of the most important elements [1]. Boron is oxophilic and occurs as borates (oxides) in nature. It has both strategic and industrial significances. Boron and its derivatives have a comparative advantage in foreign markets: they are used in a wide range of applications for almost all manufacturing areas in a variety of ways. Boron compounds are used in the detergent industry, in nuclear reactors, in rocket engines, in agriculture, in fire deterrents, in the ceramics and glass industry, in the production of heat resistant polymers, in textiles, and so on [2]. One of the most important minerals and derivatives of boron is ulexite. Its chemical formula is $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$. Boric acid is used as a source of B_2O_3 in many fused products and 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 [3]-[8]. It has been known that the investigation of the dissolution of ulexite ore in various solutions has been studied for the production of boron compounds. There are many studies in the literature connected with the dissolution kinetics of ulexite in various solutions. A summary of these studies can be seen in Table I.

Investigation on the dissolution conditions and the dissolution kinetics of ulexite in sodium dihydrogen phosphate

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solutions will be beneficial to the solution of some problems. The kinetic data for the reaction of ulexite with sodium dihydrogen phosphate are important for the industrial applications. The dissolution kinetics of ulexite in sodium dihydrogen phosphate solutions were examined according to the heterogeneous reaction models.

TABLE I
A SUMMARY OF STUDIES

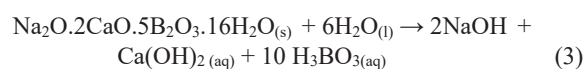
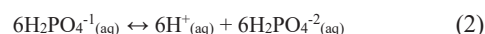
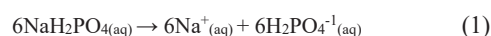
Solution	A.E. (kJ/mol)	Control	Reference
ammonium chloride	80	Chemical reaction	[9]
H_2SO_4	-	Chemical reaction	[10]
aqueous EDTA	35	diffusion control through the ash layer	[11]
ammonium sulfate	83.5	diffusion control through the ash layer	[12]
oxalic acid	59.8	by product- layer diffusion	[13]
perchloric acid	19.2	-	[14]
acetic acid	55.8	chemical reaction	[15]
ammonium acetate	55.7	chemical reaction	[16]
ammonium nitrate	58	chemical reaction	[17]
ammonium chloride	64.3	chemical reaction	[18]
ammonium chloride	84	chemical reaction	[19]
sodium hydrogen sulphate	-	chemical reaction	[20]

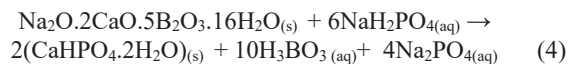
II. EXPERIMENTAL DESIGN

Ulexite samples used in the experiments were obtained from Bandırma Borax Corporation, Turkey. The ulexite ore samples were crushed and sieved with ASTM standard sieves to give fractions of average sizes 3.075, 1.550, 0.725, and 0.390 mm for dissolution experiments. The chemical analysis showed that the ore contained: 18.85% CaO, 36.37% B_2O_3 , 6.6% Na_2O , 35.47% H_2O , and 2.71% SiO_2 , and others. Each experiment was repeated twice, and the arithmetic average of the results of the two experiments was used in the kinetic analysis. Homogeneity of the suspension was exactly obtained at a stirring speed of 450 rpm. Because of this, the stirring speed rate of 450 rpm was a constant value in all experiments to securely obtain homogeneity in the batch reactor. The reactant concentrations during the leaching are constant.

A. Dissolution Reactions

The reaction in the solution can be written as:





Parameters and their ranges can be seen in Table II. The data were plotted in the form of time versus fractional conversion as appearing in Figs. 1-5. In these figures, the fractional conversion X :

$$X = \frac{(\text{amount of dissolved } \text{B}_2\text{O}_3 \text{ in the solution})}{(\text{amount of } \text{B}_2\text{O}_3 \text{ in the original sample})} \quad (5)$$

TABLE II
PARAMETERS AND RANGES

Parameter	Values
Temperature (°C)	20, 30, 40, 50*
Concentration (mol L ⁻¹)	0.15, 0.30, 0.50*, 0.75, 1.0, 1.25, 1.50
Stirring speed (rpm)	0, 75, 150, 300, 450, 600*
Solid/liquid ratio (g/mL)	1/50*, 1/25, 1/12, 1/6
Particle size (mm)	3.075, 1.550*, 0.725, 0.390
Reaction time (min.)	10, 20, 40, 60, 90

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

III. RESULT AND DISCUSSION

The temperature is a factor of great importance for the leaching kinetics. The effect of reaction temperature was examined at 20, 30, 40, and 50 °C. The dissolution curves obtained for 20-50 °C are illustrated in Fig. 1. It can be shown from Fig. 1 that, the quantity of ulexite dissolved increases with increasing the reaction temperature.

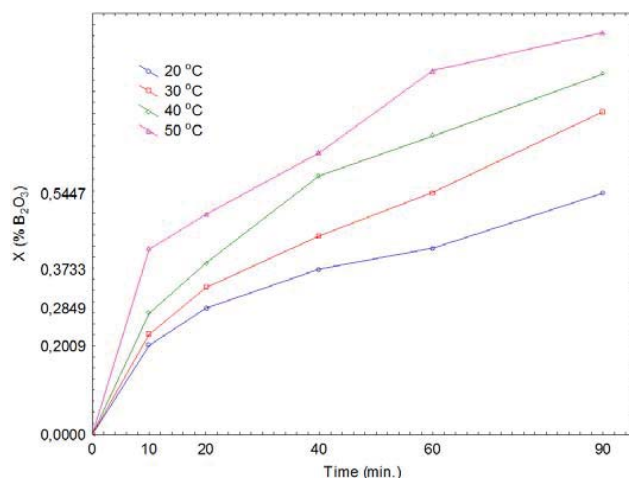


Fig. 1 Effect of temperature on dissolution rate of ulexite

In general, the leaching rate increases with increased concentration of reagent, but only up to a certain maximum level. The effect of concentration of sodium dihydrogen phosphate solutions was studied by varying to 0.0, 0.15, 0.30, 0.50, 0.75, 1.0, 1.25, and 1.50 M. The dissolution curves are given in Fig. 2. It can be seen from Fig. 2 that the dissolution level of the process increases with the increase in the concentration of disodium hydrogen phosphate solutions.

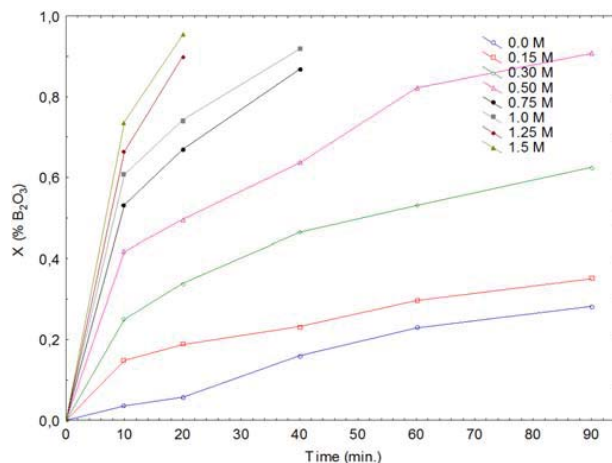


Fig. 2 Effect of concentration of sodium dihydrogen phosphate on dissolution rate of ulexite

The effect of the stirring speed on the dissolution rate of ulexite was investigated at 0, 75, 150, 300, 450, and 600 rpm. The change can be remarked in Fig. 3. It can be seen from Fig. 3 that the dissolution level of the process increases with the increase in the stirring speed rate.

The effect of solid/liquid ratio was investigated by varying ratio to 1/50, 1/25, 1/12, and 1/6 g/mL. The dissolution curves are given in Fig. 4. It can be seen from 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.

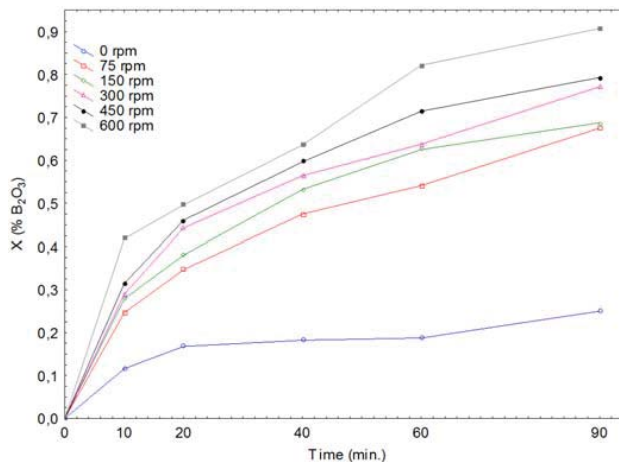


Fig. 3 Effect of stirring speed on dissolution rate of ulexite

The effect of particle size was studied by treating four sizes of fractions of this mineral, namely 3.075, 1.550, 0.725, and 0.390 mm. The dissolution curves are presented in Fig. 5. As can be seen from Fig. 5, while the particle size decreases, the dissolution rates increase because of increasing surface area.

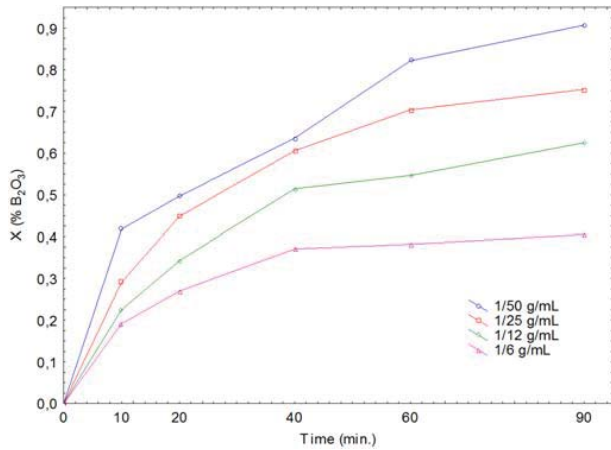


Fig. 4 Effect of solid/liquid ratio on dissolution rate of ulexite

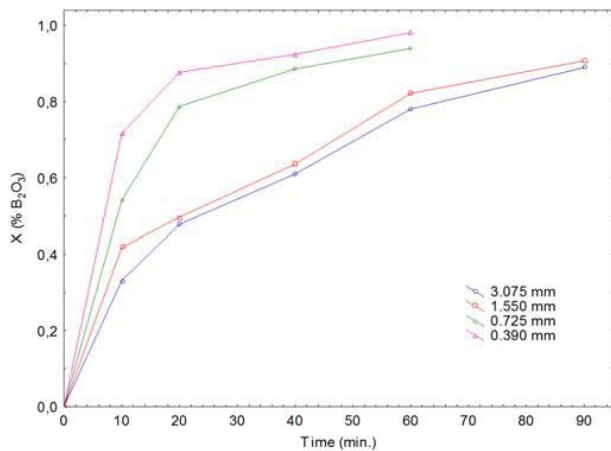
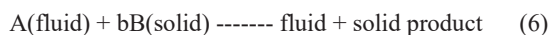


Fig. 5 Effect of particle size on dissolution rate of ulexite

IV. KINETIC ANALYSIS

The reaction rate can be obtained from the heterogeneous reaction model. The leaching reaction by a reagent may be represented as:



The heterogeneous reaction model gives the rate equations for each control mechanisms. The step with the highest resistance is the rate-controlling step. Integrated equations and the other models are shown in Table III. The kinetic data were treated by equations in Table III.

In the cases where the chemical reaction is excessive, experimental data fit the heterogeneous chemical reaction controlled in the form of $t/t^* = 1 - 3(1-X)^{2/3} + 2(1-X)$.

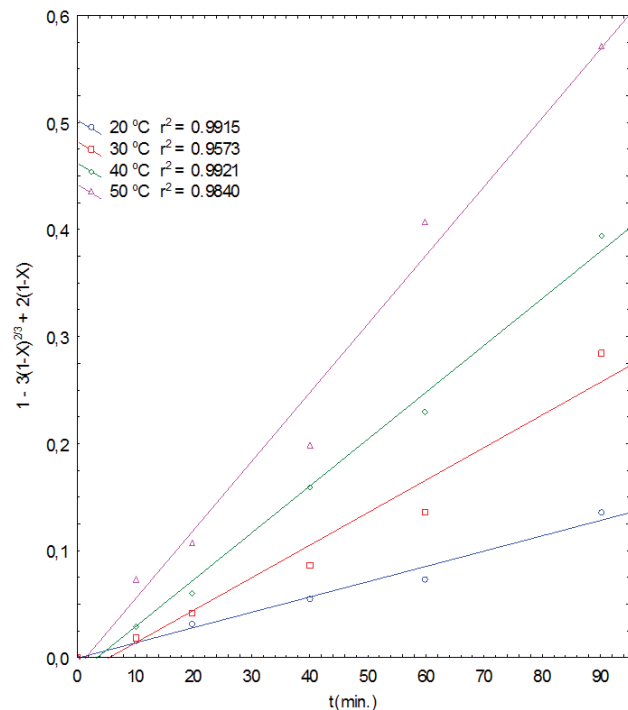
Experimental data correlate well with (9) in Table III, which means that the dissolution is diffusion (through the ash or product layer) controlled. The regression coefficient was found to be 0.9967 as higher linearity. The variation of $1 - 3(1-X)^{2/3} + 2(1-X)$ with time (t) is plotted for reaction temperature, in Fig. 6. Equation (9) in Table III is the expression for

diffusion (through the ash or product layer) controlled leaching according to the shrinking core model.

TABLE III
INTEGRATED RATE EQUATIONS

rate-controlling step	rate equation
surface chemical reaction	$t^* = \rho_B R / bksC_{Ag}$ (7)
the film diffusion control	$t^* = \rho_B R / 3bkgC_{Ag}$ (8)
diffusion control through the ash or product layer	$t^* = \rho_B R^2 / 6bDeC_{Ag}$ (9)
First-order pseudo-homogeneous model	$-\ln(1-X) = kt$ (10)
Second-order pseudo-homogeneous model	$(1-X)^{-1} = kt$ (11)
Avrami model	$-\ln(1-X) = kt^m$ (12)

C_{Ag} , A concentration in the bulk solution (mol m^{-3}); D_e , diffusion coefficient ($\text{m}^2 \text{min}^{-1}$); R , initial radius of a solid particle (m); t^* , reaction time for complete conversion (min.); X , fractional conversion of B_2O_3 ; ρ , molar density of solid reactant (kmol m^{-3}); k , reaction rate constant.

Fig. 6 $1 - 3(1-X)^{2/3} + 2(1-X) - t$ for reaction temperatures

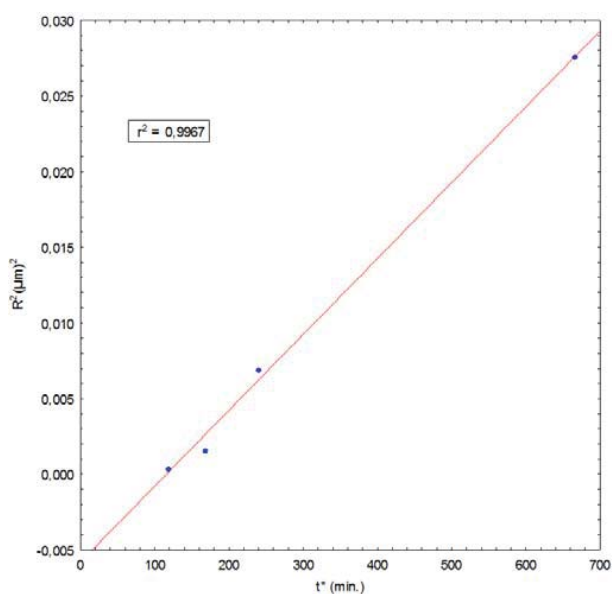
The reaction time for complete conversion is proportional to the particle radius. For diffusion control through the ash or product layer leaching, the reaction time for complete conversion is proportional to R^2 . Linearity between t^* and R^2 can be seen from Fig. 7.

Time for complete conversion (t^*) and the diffusion coefficients (D_e) obtained in the experimental system can be seen in Table IV.

The high linearity between t^* and R^2 is shown in Fig. 7. The regression coefficient (r^2) was found to be 0.9966. The regression coefficient (r^2) between t^* and R was found to be 0.9296.

TABLE IV
VALUES OF t^* AND De OBTAINED

T °C	C mol/L	W rpm	S/L g/mL	D mm	t^* min.	De m/s ²
20	0.5	450	1/50	1.550	714	2.22×10^{-9}
30	0.5	450	1/50	1.550	333	4.93×10^{-9}
40	0.5	450	1/50	1.550	227	7.47×10^{-9}
50	0.5	450	1/50	1.550	156	1.12×10^{-8}
50	0.15	450	1/50	1.550	2000	2.92×10^{-8}
50	0.30	450	1/50	1.550	476	6.13×10^{-8}
50	0.50	450	1/50	1.550	156	1.12×10^{-8}
50	0.75	450	1/50	1.550	83	1.41×10^{-8}
50	1.0	450	1/50	1.550	68	1.29×10^{-8}
50	1.25	450	1/50	1.550	36	1.94×10^{-8}
50	1.50	450	1/50	1.550	28	2.08×10^{-8}
50	0.5	75	1/50	1.550	400	4.37×10^{-8}
50	0.5	150	1/50	1.550	357	4.90×10^{-9}
50	0.5	300	1/50	1.550	277	6.32×10^{-9}
50	0.5	450	1/50	1.550	244	7.17×10^{-9}
50	0.5	600	1/50	1.550	156	1.12×10^{-9}
50	0.5	450	1/25	1.550	270	6.48×10^{-9}
50	0.5	450	1/12	1.550	454	3.85×10^{-9}
50	0.5	450	1/6	1.550	1250	1.40×10^{-9}
50	0.5	450	1/50	3.075	167	1.05×10^{-9}
50	0.5	450	1/50	1.550	156	1.12×10^{-8}
50	0.5	450	1/50	0.725	91	1.92×10^{-8}
50	0.5	450	1/50	0.390	79	2.21×10^{-8}

Fig. 7 Linearity between t^* and R^2

The Arrhenius plot of $\ln k_s$ versus $1/T$ were drawn to find the activation energy of the reaction [21]-[26]. Arrhenius plot of the dissolution process is shown in Fig. 8. From the slope of the straight line in Fig. 8, the activation energy of the reaction is found to be 36.4 kJ/mol. It has been reported that the activation energy of chemical reaction is higher than 40 kJ/mol [25]-[31]. Similar results were found in literature [10]-[14].

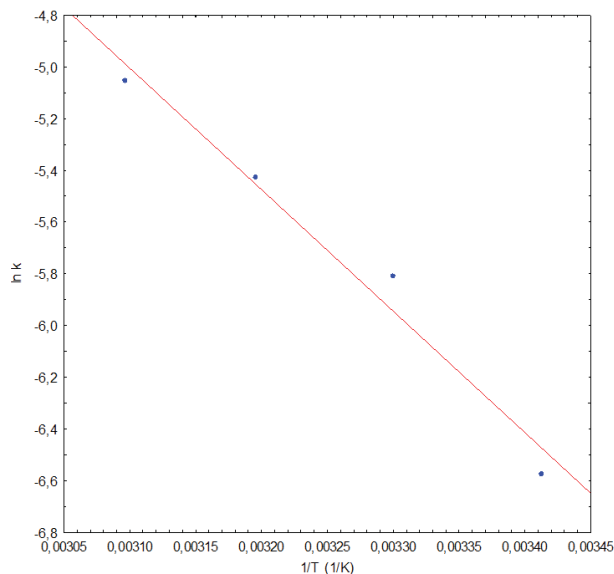


Fig. 8 Arrhenius plot of dissolution process

V. CONCLUSIONS

Based on the results, the following conclusion may be drawn:

- The dissolution rate of ulexite increased with the increase in the reaction temperature and with the decrease in the solid/liquid ratio.
- The dissolution extent is highly increased with the increase of the stirring speed rate in the interval of 75-600 rpm.
- The dissolution process follows a shrinking core model with the controlled heterogeneous diffusion through the ash (or product) layer as the rate controlling step.
- The activation energy of the reaction is found to be 36.4 kJ/mol.

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