

Dissolution Leaching Kinetics of Ulexite in Disodium Hydrogen Phosphate Solutions

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Abstract—Ulexite ($\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 16\text{H}_2\text{O}$) is boron mineral that is found in large quantities in the Turkey and world. In this study, the dissolution of this mineral in the disodium hydrogen phosphate solutions has been studied. Temperature, concentration, stirring speed, solid liquid ratio and particle size were selected as parameters. The experimental results were successfully correlated by linear regression using Statistica program. Dissolution curves were evaluated 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 the dissolution rate of ulexite. The activation energy was found to be 63.4 kJ/mol. The leaching of ulexite was controlled by chemical reaction.

Keywords—Disodium hydrogen phosphate, Leaching kinetics, Ulexite.

I. INTRODUCTION

BORON is a hard, brittle semi-metallic element. Its atomic number is 5, its atomic weight is 10.81 g/mol. Boron does not occur in nature as a free element. The boron element can be found in nature in over 150 naturally occurring boron [1]. Ores with concentrations of calcium, sodium and magnesium elements as well as hydrate compounds are economically more viable to mine. Boron mineral beds are concentrated in Turkey, the USA, Argentina, Russia, Kazakhstan, China, Bolivia, Peru and Chile. Turkey holds approximately 67% of global boron reserves with 883 million tons B_2O_3 . Boron does not occur in nature as a free element, but crude borax exists as a mineral associated with clay and other impurities [2], [3]. Boron products are used in close to 500 different areas including space and aeronautics, nuclear applications, military vehicles, fuels, electronics and communications, agriculture, glass industry, chemical and detergents ceramics and polymeric materials, nanotechnology, automotive and energy sectors, metallurgy and construction [4], [5].

Boron compounds are used in the cement production; in the pharmaceuticals and cosmetics, in the leather and textile industries, and in the glass industry. And also used to production of cameras, lenses and binoculars to increase durability so that you record your unforgettable moments as close to real life as possible. And also boron compounds have properties that keep food fresh for longer and preserve

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nutrients, and they are widely used in the food and beverage industry [5].

There are over 200 naturally occurring boron containing minerals but the most important minerals (salts, known as borates) are tincal, colemanite, ulexite and kernite. These ores are refined into chemical compounds. Ulexite's 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 [4], [5].

It has been known that the investigation of the dissolution of ulexite ore in various solutions have been studied for 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 is as follows: [6] investigated it in water saturated by sulfur-dioxide and the activation energy was calculated as 58 kJ/mol. Reference [7] studied it in water saturated with CO_2 in low temperatures (17-35 °C) and the activation energy was found to be 51.7 kJ/mol. Reference [8] carried out it in ammonia solution saturated with CO_2 and described the dissolution rate by a first-order pseudo-homogeneous reaction model and found the activation energy to be 55 kJ/mol. Reference [9] studied experiments with it in ammonium chloride solution and found the activation energy to be 80 kJ/mol. Reference [10] reported 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 $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$. Reference [11] investigated 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 kJ/mol. Reference [12] investigated 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. Reference [13] studied it in oxalic acid solutions. The reaction rate was controlled by product-layer diffusion and calculated the activation energy as 59.8 kJ/mol. Reference [14] 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. Reference [15] 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 as 55.8 kJ/mol. Reference [16] investigated it in the ammonium acetate solutions. The

dissolution rate fit the chemical reaction control model and the activation energy was found as 55.7 kJ/mol. Reference [17] studied the dissolution kinetics of ulexite in ammonium nitrate solutions in a batch reactor. It was determined that the dissolution rate fit to the chemical reaction control model. Activation energy was found to be 58 kJ/mol. Reference [18] investigated dissolution kinetics of ulexite prepared under different calcination temperatures in ammonium chloride solutions. They found that the rate fit to the second-order pseudo-homogeneous model and activation energy was found as 64.3 kJ/mol. Reference [19] studied the dissolution kinetics of calcine ulexite in ammonium chloride solutions at high solid-to-liquid ratios. Activation energy was found to be 84 kJ/mol and the rate fit homogeneous reaction model. Reference [20] investigated leaching kinetics of ulexite in sodium hydrogen sulphate solutions in a mechanical agitation system.

The aim of our study is to investigate the dissolution kinetics of ulexite in disodium hydrogen sulphate solutions in a mechanical agitation system and also to declare an alternative reactant to produce the boric acid. Investigation on the dissolution conditions and the dissolution kinetics of ulexite in disodium hydrogen phosphate solutions will be beneficial to the solution of some problems. The kinetic data for the reaction of ulexite with disodium hydrogen phosphate are important for industrial application. The dissolution kinetics of ulexite in disodium hydrogen phosphate solutions were examined according to the heterogeneous reaction models.

II. EXPERIMENTAL DESIGN

A. Dissolution Tests

The sample used in this research was hand-picked from the ulexite mine at Bigadiç-Boron Works located in the Bigadiç country of Balıkesir, Turkey. The raw ore mined from the plant's own mines has been enriched into concentrated colemanite and concentrated ulexite in the 650000 tons/year capacity concentrator facilities since 1980 and grinded into ground colemanite and ground ulexite in the 90000 tons/year capacity grinding facility since 1998.

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: 300 mL of disodium hydrogen phosphate solutions was poured into the reactor. The solution was heated to the desired temperature, at which it was kept constant. The ulexite samples were crushed,

dried and sieved with ASTM standard sieves to give fractions of average sizes 1550, 780, 231 and 137.5 μm for dissolution experiments. All experiments were carried out using 231 μm size fractions, except in experiments where the effect of particle size on the reaction rate was investigated. The chemical analysis of ulexite samples used in the experiments can be shown in Table I.

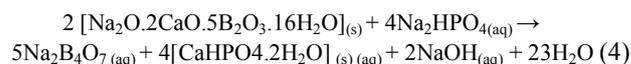
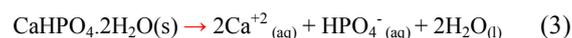
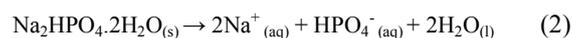
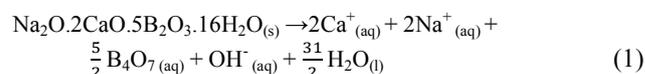
TABLE I
CHEMICAL ANALYSIS OF ULEXITE

| Component | CaO | B ₂ O ₃ | Na ₂ O | H ₂ O | SiO ₂ and others |
|-----------|-------|-------------------------------|-------------------|------------------|-----------------------------|
| % | 18.85 | 36.37 | 6.6 | 35.47 | 2.71 |

After this, large quantities of solid ulexite were added to the solutions in the reactor. 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 [20], [21]. Based on the B₂O₃ estimated, the degree of dissolution of ulexite was determined as a function of time. 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 630 rpm. Because of this, the stirring speed rate of 630 rpm was as constant value in all experiments to get guaranteed to obtain homogeneity in the batch reactor.

B. Dissolution Reactions

The reaction in the solution can be written as [20]:



Parameters chosen and their ranges can be seen in Table II. In the experiments, while the effect of one parameter was studied, the values of other parameters shown with asterisks in Table II were kept constant. A quantity of 300 mL of sodium hydrogen sulphate solutions was used and kept constant in all experiments.

Homogeneity of suspension in the reactor was obtained with a stirring speed of 700 rpm, kept constant in all experiments. The data obtained were plotted in the form of time versus fractional conversion as appearing in Figs. 1-5. In these figures, the fractional conversion X is defined:

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

TABLE II
PARAMETERS CHOSEN AND RANGES

| Parameter | Values |
|--------------------------------------|---|
| Reaction Temperature | 20, 25, 30, 35, 40, 45, 50*, 55, 60, 65, 70, 75, 80 |
| Concentration (mol L ⁻¹) | 0.0, 0.15, 0.25, 0.35, 0.50*, 1.0 |
| stirring speed (rpm) | 75, 150, 300, 450, 630*, 900, 1200 |
| solid/liquid ratio (g/mL) | 1/50*, 1/25, 1/12, 1/6 |
| particle size (μm) | 1550, 780, 231*, 137.5 |
| reaction time (h) | 1, 2, 3, 4, 5, 6 |

*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, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80°C. The fact that the activation energies are different can probably be attributed to the differences of the chemical reaction mechanism. The effect of reaction temperature was investigated for the temperature range 20-55°C and 60-80°C. The dissolution curves obtained for 20-55°C are shown in Fig. 1 and 60-80°C are shown in Fig. 2. It can be shown from Figs. 1 and 2 that, the quantity of ulexite dissolved increases with increasing reaction temperature.

In general, the leaching rate increases with increased concentration of reagent, but only up to a certain maximum level. The effect of concentration of disodium hydrogen phosphate solutions was studied by varying to 0.0, 0.15, 0.25, 0.35, 0.50 and 1.0 M. The dissolution curves are given in Fig. 3. It can be seen from Fig. 3 that the dissolution level of the process increases with increase in the concentration of disodium hydrogen phosphate solutions.

The effect of the stirring speed on the dissolution rate of ulexite was investigated at 0, 75, 150, 300, 450, 630, 900 and 1200 rpm. The change between stirring speed and conversion can be seen in Fig. 4. It can be seen from Fig. 4 that the dissolution level of the process increases with increase in the stirring speed rate.

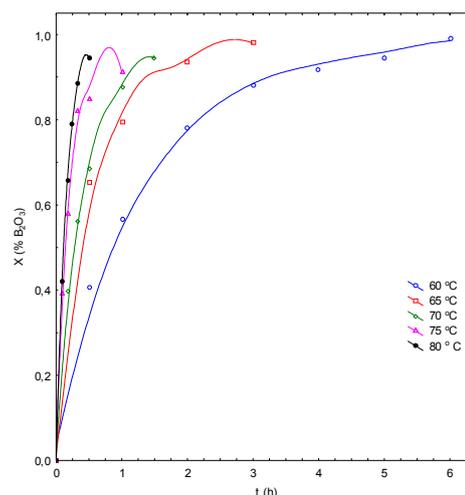


Fig. 2 Effect of reaction temperature (between 60 and 80°C) on dissolution rate of ulexite

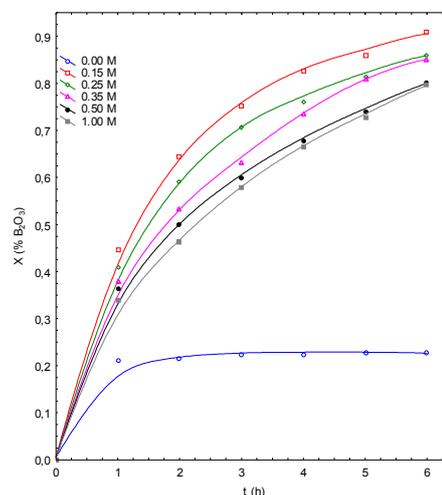


Fig. 3 Effect of concentration of disodium hydrogen phosphate on dissolution rate of ulexite

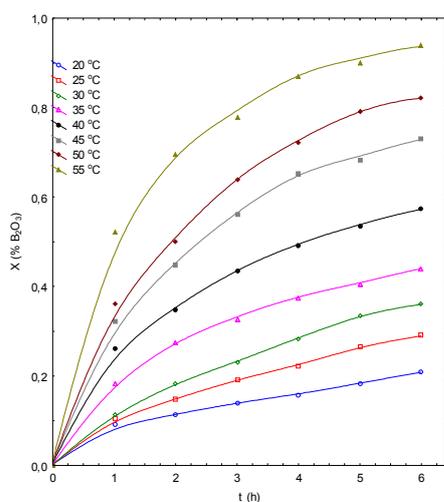


Fig. 1 Effect of reaction temperature (between 20 and 55°C) on dissolution rate of ulexite

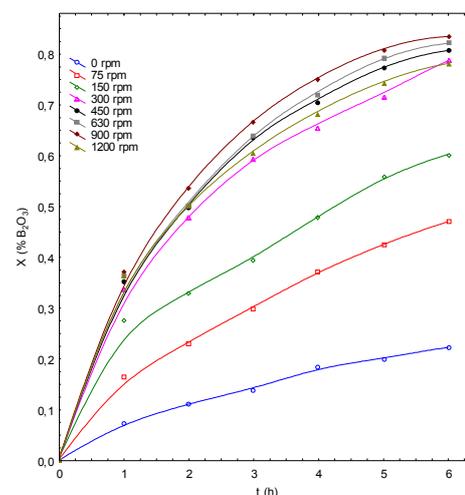


Fig. 4 Effect of stirring speed on dissolution rate of ulexite

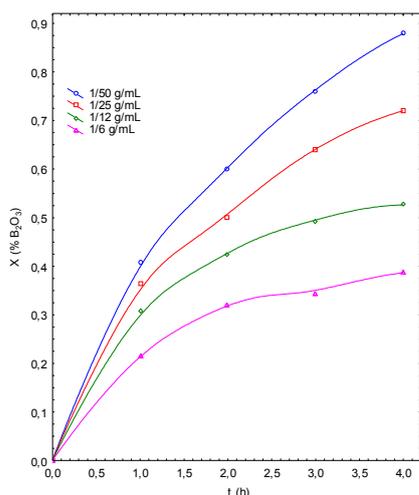


Fig. 5 Effect of solid/liquid ratio on dissolution rate of ulexite

The effect of solid/liquid ratio on the dissolution rate of ulexite was investigated by varying ratio to 1/50, 1/25, 1/12 and 1/6 g/mL. The dissolution curves are given Fig. 5. It can be seen from Fig. 5 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 1550, 780, 231 and 137.5 μm . The dissolution curves are presented in Fig. 6. As can be seen from Fig. 6, as the particle size decreases the dissolution rates increased because of increasing surface area.

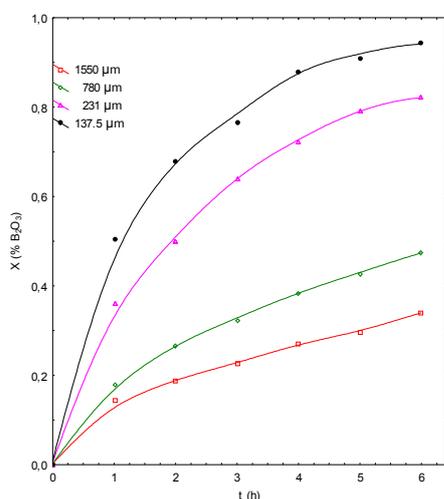
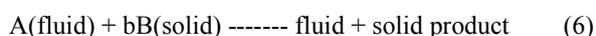


Fig. 6 Effect of particle size on dissolution rate of ulexite

IV. KINETIC ANALYSIS

The solid-fluid heterogeneous reaction rate can be obtained from the heterogeneous reaction model. The leaching reaction of ore particles by a reagent may be represented as:



The reaction between solid and fluid reactants takes place on the surface of the solid. The solid reactant is surrounded by a fluid film. Mass transfer occurs between the solid and the bulk fluid. The experimental data were analyzed based on the un-reacted shrinking core model to evaluate the rate-controlling step [23]-[25].

The heterogeneous reaction model gives rate equations for each control mechanisms. The step with the highest resistance is the rate-controlling step. The model has been used for solid-liquid heterogeneous systems in both analytical and numerical methods. Integrated rate equations for the un-reacted shrinking-core model and the other models are shown in Table III. According to the model, the kinetic data were treated by equations in Table III.

The data were analyzed based on the shrinking core model using the rate expression given in Table III for determining rate-controlling step of the leaching of ulexite in disodium hydrogen phosphate solutions. The apparent rate constants, k_r , k_f and k_d for kinetic models and correlations coefficients values for reaction temperatures are shown in Table IV.

The high regression coefficients were obtained for the chemical reaction. The leaching mechanism often becomes diffusion controlled when, during the leaching, a porous product layer forms on the surface of the particle to be leached. The mechanism of diffusion controlled leaching of spherical particle is often called the shrinking core model [23]-[25]. The application of the above models to the experimental data will help in to determining the dissolution kinetics of the process. In the cases in which the chemical reaction is much Experimental data fits the heterogeneous chemical reaction controlled in the form of $t/t^* = 1 - (1-X)^{1/3}$.

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_o , 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.

The evidence for this proposal is as follows: Apparent reaction rate constant with all reaction temperatures can be shown in Fig. 9. Regression analysis has shown that experimental data correlate well with (7) in Table III, which means that the dissolution is chemical reaction controlled. The regression coefficient was found to be 0.9874 as higher linearity. The variation of $1 - (1-X)^{1/3}$ with time (t) is plotted for reaction temperature, in Fig. 6. Equation (7) in Table III is the expression for chemical reaction controlled leaching according to the shrinking core model.

As is evident from the equation, the reaction time for complete conversion is proportional to the particle radius. For chemical reaction controlled leaching, the reaction time for complete conversion is proportional to R. Using the heterogeneous chemical reaction controlled the t^* values were plotted versus R.

TABLE IV
 THE APPARENT RATE CONSTANTS

| T(°C) | Diffusion through the Liquid Film | | Surface Chemical Reaction | | Diffusion through the Product Layer | |
|-------|-----------------------------------|--------|---------------------------|---------------|-------------------------------------|--------|
| | X | k_i | r^2 | k_r | r^2 | k_d |
| 20 | 0.9154 | 0.0306 | 0.9833 | 0.0111 | 0.9282 | 0.0025 |
| 25 | 0.9501 | 0.0451 | 0.9837 | 0.0169 | 0.9639 | 0.0055 |
| 30 | 0.9609 | 0.0579 | 0.9789 | 0.0225 | 0.9756 | 0.0091 |
| 35 | 0.8847 | 0.0664 | 0.9976 | 0.0270 | 0.9188 | 0.0137 |
| 40 | 0.8782 | 0.0861 | 0.9987 | 0.0382 | 0.9286 | 0.0258 |
| 45 | 0.8761 | 0.1113 | 0.9926 | 0.0561 | 0.9447 | 0.0494 |
| 50 | 0.8791 | 0.1264 | 0.9934 | 0.0708 | 0.9630 | 0.0714 |
| 55 | 0.7750 | 0.1341 | 0.9930 | 0.0937 | 0.9403 | 0.1100 |
| 60 | 0.7554 | 0.1362 | 0.9847 | 0.1156 | 0.9520 | 0.1420 |
| 65 | 0.6651 | 0.2690 | 0.9763 | 0.2232 | 0.9116 | 0.2693 |
| 70 | 0.7832 | 0.5433 | 0.9936 | 0.3921 | 0.9515 | 0.4677 |
| 75 | 0.6734 | 0.8378 | 0.9422 | 0.7204 | 0.9041 | 0.8803 |
| 80 | 0.8107 | 1.7755 | 0.9836 | 1.2366 | 0.9556 | 1.4376 |

Where; k_i , apparent rate constants for diffusion through the liquid film; k_r , apparent rate constants for surface chemical reaction; k_d , apparent rate constants for diffusion through the product layer; X, fractional conversion of B_2O_3 ; r, correlation coefficient.

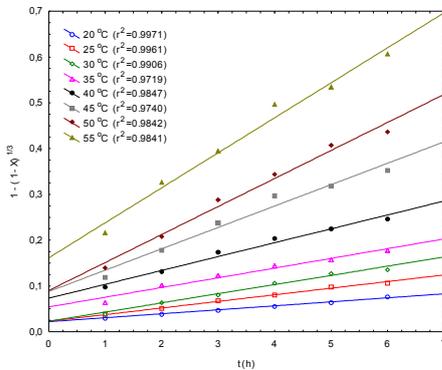


Fig. 7 Variation of $1 - (1-X)^{1/3}$ with time for reaction temperatures (between 20 and 55 °C)

The high linearity between t^* and R is seen in Fig. 10. The regression coefficient (r^2) was found to be 0.9981. Otherwise, the regression coefficient (r^2) between t^* and R^2 was found to be 0.9199. The Arrhenius plots of $\ln k_s$ versus $1/T$ were drawn for to found the activation energy of the reaction [23]-[26]. Arrhenius plot of the dissolution process for reaction temperatures are shown in Fig. 11. From the slopes of the straight lines of Fig. 11, the activation energy of the reaction is found to be 63.4 kJ/mol. It has been reported that the activation energy of chemical reaction controlled are higher 40 kJ/mol [25]-[31]. Similar results were found in the literature [10]-[14]. Further, this value indicates the dissolution rate of ulexite is a chemical reaction controlled.

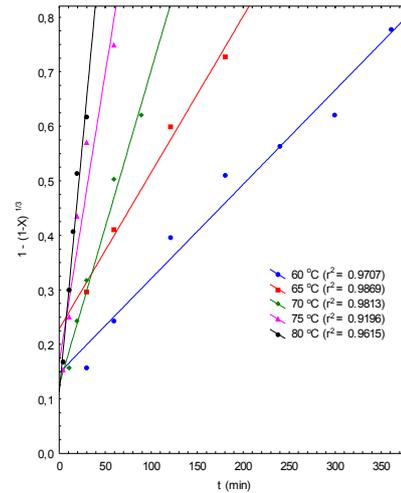


Fig. 8 Variation of $1 - (1-X)^{1/3}$ with time for reaction temperatures (between 60 and 80 °C)

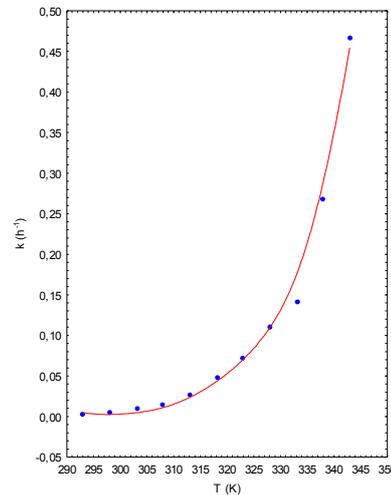


Fig. 9 Variation of apparent reaction rate constant with reaction temperatures

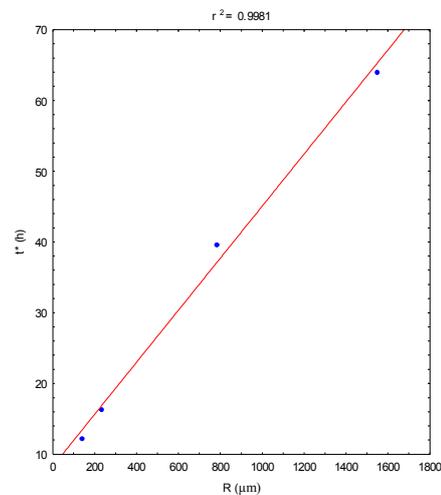


Fig. 10 Linearity between t^* and R

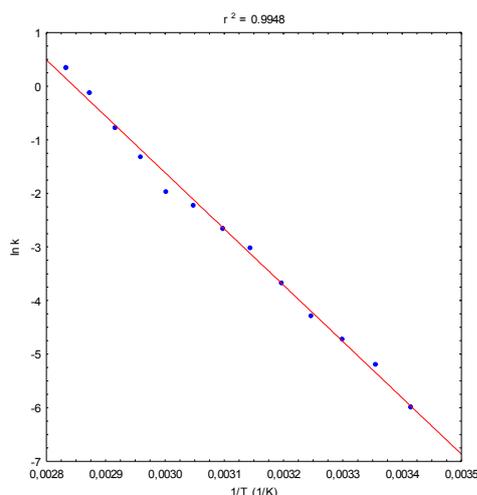


Fig. 11. Arrhenius plot of dissolution process

V. CONCLUSIONS

Based on the results obtained in this research, the following conclusion may be drawn:

- The dissolution rate of ulexite increased with increase in reaction temperature and decrease in the solid/liquid ratio.
- The dissolution extent is highly increased with increase the stirring speed rate between 100-700 rpm.
- The dissolution process follows a shrinking core model with the heterogeneous chemical reaction as the rate controlling step.
- The activation energy of the reaction is found to be 63.4 kJ/mol.

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