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INVESTIGATION OF KINETICS AND MECHANISM OF PRICEITE LEACHING IN SULPHURIC ACID SOLUTIONS

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Abstract: The leaching kinetics and mechanism of priceite having the formula of $4\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ was investigated in sulphuric acid solutions. For the dissolution process, the effects of reaction temperature, sulphuric acid solution concentration, solid/liquid ratio, particle size, and stirring speed were investigated as effective parameters for the experiments. The experimental data indicated that the dissolution rate increased with the increasing reaction temperature, the decreasing particle size, and the solid/liquid ratio. The conversion rate increased up to 1.0 mol/dm^3 with the increasing acid concentration, and then decreased with the increasing acid concentration over concentrations of 1 mol/dm^3 . It was also determined that the stirring speed had no significant effect on the dissolution rate. The dissolution process of priceite in sulphuric acid solution was tested with regard to heterogeneous and homogeneous reaction models, and it was found that the dissolution rate was controlled by first order pseudo-homogeneous reaction model. The activation energy of the dissolution process was determined as $26.07 \text{ kJ}\cdot\text{mol}^{-1}$. The results were evaluated graphically and statistically. The experimental data were found to fit well with the mathematical model.

Keywords: boron minerals, priceite, sulphuric acid, leaching kinetics, boric acid

Introduction

Boron and its compounds today are used in many different applications and processes. Boron salt production has significantly increased due to demand by the nuclear industry for heat-resistant materials, ceramics, high quality steel, polymers, etc. (Nemodruk and Karalova, 1965). There have been many studies examining the kinetics of boron ores leaching including leaching kinetics of inderite and inyoite in water saturated with CO_2 (Alkan et al., 1991), colemanite in ammonium nitrate (Gur, 2008), in perchloric acid solutions (Gur, 2008), in potassium hydrogen sulphate solutions (Guliyev et al., 2012), in citric acid solution assisted by mechanic agitation and microwaves (Cavus and Kuslu, 2005), and ulexite in borax pentahydrate solutions

saturated with CO₂ (Kuslu et al., 2010). Gur (2006) studied the leaching kinetics of calcined ulexite in ammonium chloride solutions at a high solid/liquid ratio revealing that the dissolution rate increased with the increase of the calcination temperature, solution concentration, and reaction temperature. However, it was not affected by pre-hydration. Additionally, graphical and statistical methods were employed in the leaching process. The results showed that the dissolution based on a homogeneous reaction model can be shown as $[1-X(B_2O_3)]^{-1} = k(c(NH_4Cl))^{1.982} \cdot t$ where X is the conversion factor (X =amount of dissolved B₂O₃ in the solution/amount of B₂O₃ in the original sample), k is the rate constant, and c is the solution concentration.

Gulensoy and Kocakerim (1978) investigated the solubility of ulexite mineral in water saturated with CO₂ in natural and calcined samples at different temperatures. They found that the calcination process and the solution pH had a positive effect on the leaching rate. Davies et al. (1991) performed the thermally decomposed powdered colemanite as enlarging the extraction ratio of boric acid in acid solutions for calcined mineral samples, and they found the optimal calcination temperature was 600 °C. At higher temperature, flash calcinations produced vitrified cenospheres becoming highly resistant to acidic dissolution. The 600 °C flash calcinations could make calcined samples dissolving as efficiently as the calcined produced by ordinary soak calcinations for a longer time. Alkan et al. (1991) investigated the leaching kinetics of colemanite samples in water saturated with CO₂ changing particle size, pre-heating temperature of mineral, and reaction temperature. They determined that the leaching process was controlled chemically. In another work by Ozmetin et al. (1996) examining the leaching kinetics of colemanite in acetic acid solutions, the conversion factor was found to be increasing with the increasing temperatures and decreasing particle sizes. It was also observed that the dissolution rate was unaffected by the stirring speed to any significant extent. Meanwhile, some researchers carried out the leaching of boron minerals in nitric acid (Imamutdinova and Bickhurova, 1967), in hydrochloric acid (Zdanovskii and Imamutdinova, 1963), and in ammonium chloride (Gur and Kandilcik, 2009). Kunkul et al. (1997) studied the leaching kinetics of ulexite in ammonia solutions saturated with CO₂ and determined that the leaching rate increased with the increasing the ammonia solution concentrations, reaction temperatures and calcination temperatures. It was also detected that the leaching process can be showed by a first-order pseudo homogeneous kinetic reaction model. Kunkul et al. (2003) carried out ulexite leaching in an ammonium sulfate solution and found that the dissolution rate rose with increasing ammonium sulfate concentrations, mixing speed and reaction temperatures. They also indicated that the diffusion controlled ash or product layer defined and fitted the process.

Priceite is first in rank boron mineral mined in Turkey and is an important source for boric acid production. There are few studies into the leaching of priceite in literature, and there has to date been no study analyzing the kinetics of priceite in sulphuric acid solutions. Filling this gap in literature is the objective of this work, in which it is aimed both to contribute to literature, and to emphasize the importance of

the leaching kinetics of priceite. In this regard, the goal of this study is to clarify the dissolution mechanism of priceite in sulphuric acid solutions, and to indicate the effects of the designed experimental parameters in regards to acid concentration, solid/liquid ratio, particle size, stirring speed, and reaction temperature on the dissolution rate.

Experimental

Preparation of materials

The priceite samples used in this study originated from the Sultancayiri region in Balikesir, Turkey. First, the visible impurities were separated manually from the mineral, then ground, crushed, and sieved using ASTM standard sieves to obtain particle sizes in the range of $-1.4+1$ mm, $-1+0.6$ mm, $-0.6+0.4$ mm, and $-0.4+0.225$ mm. The sample used in the experimental section was analyzed, and the mineral content was 47.72% B_2O_3 , 31.54% CaO, 17.74% H_2O , and 3% insoluble matter.

Apparatus and procedure

In the experimental section, the leaching rate of the priceite sample was determined as a function of time by changing the sulphuric acid solution concentration, particle size, solid/liquid ratio, stirring speed, and reaction temperature. The dissolution experiments were performed in a 250 cm^3 glass reactor at atmospheric pressure. A mechanic mixer was employed for mixing reaction medium, and a thermostat was used to maintain a constant reaction temperature. Then, 50 cm^3 of a sulphuric acid solution was added the reactor. When the desire reaction temperature was reached, a given quantity of priceite was put into the solution, and stirring was started at a constant speed. As soon as the reaction time was finished at a certain time period, the solution content was filtered. The quantity of B_2O_3 in the filtrate was measured using a volumetric method (Scott, 1963), and the results were plotted as a function of conversion factor, and defined as: X =amount of dissolved B_2O_3 in the solution/amount of B_2O_3 in the original sample, versus time. The variables thought to affect the dissolution rate were selected as particle size, acid concentration, solid/liquid ratio, reaction temperature and stirring speed. The experimental design for the dissolution process is presented in Table 1.

Table 1. Parameters used in the experiments

Particle size (mm)	-1.4+1	-1+0.6 *	-0.6+0.4	-0.4+0.25
Acid concentration (mol/dm ³):	0.5	1*	1.5	2
Solid/ liquid ratio (g/cm ³):	0.01*	0.02	0.04	0.06
Reaction temperature (K):	293	303	313*	323
Stirring speed (rpm):	400*		500	600

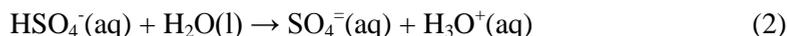
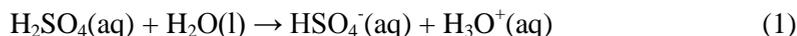
*values shown with asterisks were used when one of the parameters was studied

Results and discussion

Firstly, the effect of stirring speed on dissolution rate was investigated. The experiments were carried out at stirring speeds of 400, 500, and 600 rpm. In these experiments, the sulphuric acid solution concentration, particle size, solid/liquid ratio, and reaction temperature were kept at 1 mol/dm³, -1+0.6 mm, 1/50 g/cm³, and 313 K, respectively. It was determined from the experimental results that 64.85% of XB₂O₃ at 400 rpm, 65.32% of XB₂O₃ at 500 rpm, and 65.48% of XB₂O₃ at 600 rpm were obtained for a 10 min leaching time. It can be understood from these results that the reagent amounts of grains were completely suspended in the medium, and further, it can be inferred that stirring speed had no significant impact on the leaching, according to which, stirring speed was omitted from the analysis (Gur and Kandilcik, 2009).

Reaction occurring during dissolution

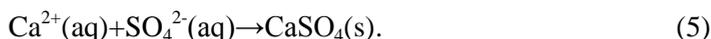
In aqueous medium sulphuric acid dissociates according to the following reactions:



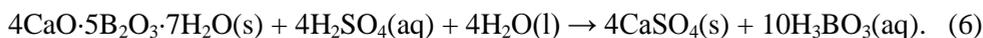
and the equilibrium constant of reaction (2) is $K_a = 0.012$. When priceite is placed in a sulfuric acid solution, the following reaction occurs:



When Ca²⁺ concentration reaches a limiting value in the sulfuric acid solution, Ca²⁺ and SO₄²⁻ ions form a solid CaSO₄(s) that restricts the dissolution of priceite according to Eqs. (4) and (5):



Thus, the leaching reaction of priceite in sulfuric acid solutions can be defined with the following reaction:



Effects of parameters

The parameters affecting the dissolution rate of priceite in sulfuric acid solutions were carried out for each parameter using the values indicated in Table 1. While the effect of one parameter was done, the other parameters value indicated with asterisks in Table 1 were kept constant.

Effect of particle size

The experiments focusing on the particle size were carried out with 1.4+1 mm, -1+0.6 mm, -0.6+0.4 mm, and -0.4+0.25 mm size fractions. The experimental data showed in Fig. 1 indicate that particle size had a reasonable effect on the leaching of priceite in sulphuric acid solutions. According to Fig. 1, the conversion factor increased as the particle size decreased. The increasing dissolution rate with the decreasing particle size resulted in the growth of the contact surface of the mineral with volume (in cm^3) of the acid solution (Gur and Kandilcik, 2009).

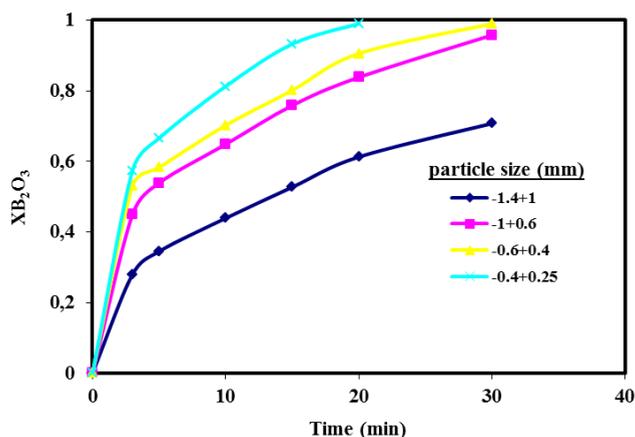


Fig. 1. Effect of particle size on dissolution rate (T 313 K; C 1 mol/dm^3 ; S/L 0.5/50 g/cm^3 , SS 400 rpm)

Effect of sulphuric acid concentration

The effect of H_2SO_4 concentration on the dissolution rate was studied at different H_2SO_4 concentrations of 0.50, 1, 1.50, and 2.0 mol/dm^3 . In the experiments, the dissolved amount of mineral was measured at reaction temperature of 40 °C, solid/liquid ratio of 1/50 (g/cm^3), and the stirring speed of 400 rpm. The experimental data seen in Fig. 2 indicate that leaching degree decreased with the increasing H_2SO_4 concentrations. This evidence can be elucidated the increasing SO_4^{2-} ion per unit volume by the increasing H_2SO_4 concentration. This caused the appearance of reaction (5), being the precipitation of solid CaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on the mineral surfaces. This solid by-product layer generates obstacle for H_3O^+ ion to diffuse to the mineral, and causes a decrease in the dissolution rate on the mineral surface (Tunc et al., 1999).

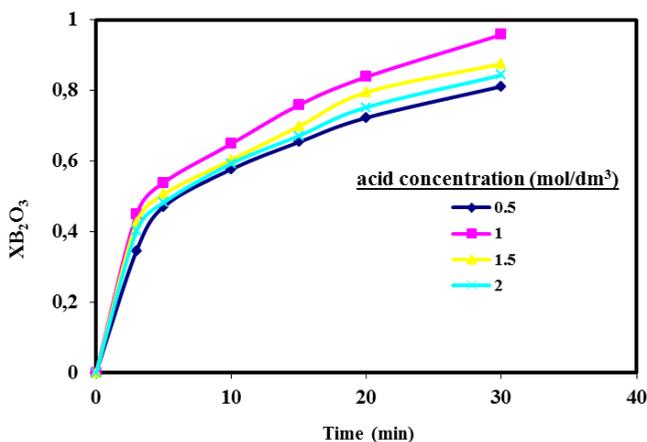


Fig. 2. Effect of H_2SO_4 concentration on dissolution rate (T 313 K, PS -1+0.6 mm, S/L 0.5/50 g/cm^3 , SS 400 rpm)

Effect of solid/liquid ratio

In order to determine the effect of the solid/liquid ratio on the dissolution of priceite, the experiments were carried out with different solid/liquid ratios in the range of 0.5/50 to 3/50 g/cm^3 . The results presented in Fig. 3 show the effect of this parameter, and indicating that the conversion factor of priceite decreased as the solid/liquid ratio increased, which can be expressed in terms of the decreasing ratio of solids per quantity of the reagent in the suspension media (Gur and Kandilcik, 2009).

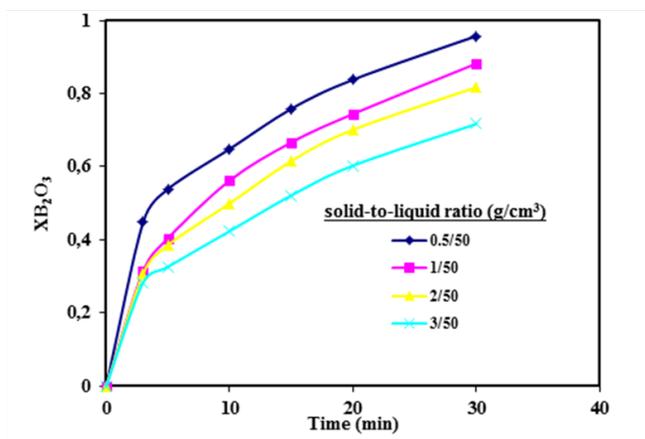


Fig. 3. Effect of solid/liquid ratio on dissolution rate (T 313 K, PS -1+0.6 mm, C 1 mol/dm^3 , SS 400 rpm)

Effect of reaction temperature

The effect of temperature on the dissolution rate was investigated at the temperatures of 293, 303, 313, and 323 K, and the results are presented in Fig. 4. According to the experimental data presented in Fig. 4, increasing reaction temperatures resulted in an increased dissolution of priceite owing to the exponential dependency of the rate constant in the Arrhenius equation.

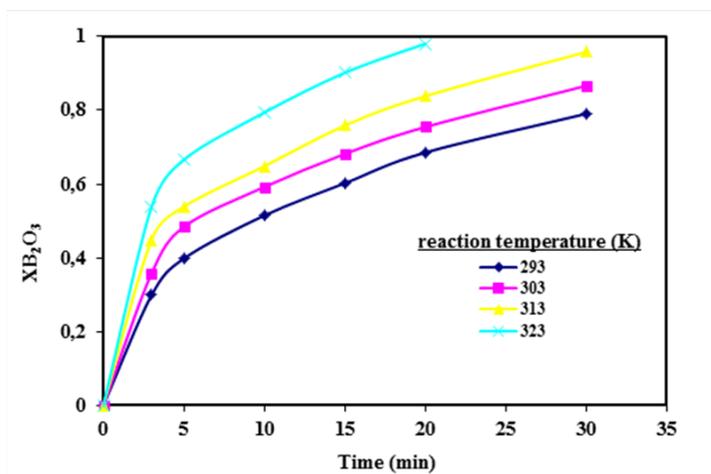


Fig. 4. Effect of reaction temperature on dissolution rate ($PS -1+0.6$ mm, C 1 mol/dm³. S/L 0.5 g/50 cm³, SS 400 rpm)

Kinetic analysis

The reaction between a solid and liquid can be represented using heterogeneous and homogeneous control models. A diffusion film control, surface chemical reactions control and product layer control models were used as heterogeneous reaction control models in this study. A first-order pseudo reaction control and a second-order pseudo reaction control model were used as homogenous models in this study.

Heterogeneous reaction models

Fluid solid heterogeneous reactions have important applications in chemical and metallurgical processes. A prosperous reactor plan for these processes relies chiefly upon kinetic results. The reactions taking place between a fluid and spherical solid particle are:



The following models are proposed.

Diffusion film control model

The kinetics of a diffusion film control model are indicated through Eq. 8 (Levenspiel, 1972):

$$k_1 \cdot t = X \quad (8)$$

where k_1 is the reaction rate constant (min^{-1}), t reaction time (min), X conversion factor, and Eq. 9:

$$k_a = k_1 \rho R / 3bC \quad (9)$$

where k_a is the mass transfer coefficient between fluid and solid particle ($\text{cm} \cdot \text{min}^{-1}$), C is the concentration of sulphuric acid (mol/cm^3), R is the radius of particle (cm), ρ is the density of mineral (mol/cm^3), and b is the stoichiometric coefficient of the solid.

Surface chemical reactions control model

The kinetics of the chemical reaction control model are shown through Eq. 10 (Levenspiel, 1972):

$$k_2 \cdot t = 1 - (1 - X)^{1/3} \quad (10)$$

where k_2 is the reaction rate constant (min^{-1}), t time (min), X conversion factor, and Eq. 11:

$$k_b = k_2 \rho R_o / bC \quad (11)$$

where k_b is the rate constant ($\text{cm} \cdot \text{min}^{-1}$), C is the concentration of sulphuric acid (mol/cm^3), R_o is the radius of the particle (cm), ρ is the density of mineral (mol/cm^3), and b is the stoichiometric coefficient of the solid.

Product layer diffusion control model

The kinetics of the product layer diffusion control model are shown through Eq. 12 (Levenspiel, 1972)

$$k_3 \cdot t = [1 - 3(1 - X)^{2/3} - 2(1 - X)] \quad (12)$$

where k_3 is reaction rate constant (min^{-1}), t time (min), X conversion factor, and Eq. 13

$$k_c = k_3 \rho R_o^2 / 6bC \quad (13)$$

where k_c is the determinant diffusion factor of gaseous reactant in the ash layer ($\text{cm} \cdot \text{min}^{-1}$), C is the concentration of sulphuric acid (mol/cm^3), R_o is the radius of the particle (cm), ρ is the density of the mineral (mol/cm^3), and b is the stoichiometric coefficient of the solid.

Homogeneous reaction models

In homogeneous reactions all reacting materials are found in a single phase of either gas, liquid, or solid. Though there are several of ways explaining the rate of reaction, the potent estimate, dependent on the unit volume of reacting fluid, is used almost for homogeneous system.

First order pseudo homogenous reaction control

The kinetics of the product layer diffusion control model are indicated through Eq. 14 (Levenspiel, 1972).

$$k_4.t = -\ln(1-X) \quad (14)$$

where k_4 is the reaction rate constant (min^{-1}), t is the time (min), and X is the conversion factor.

Second order pseudo homogenous reaction control

The kinetics of the product layer diffusion control model are indicated through Eq. 15 (Levenspiel, 1972):

$$k_5.t = [X(1-X)-1] \quad (15)$$

where k_5 is the reaction rate constant (min^{-1}), t is the time (min), and X is the conversion factor.

The experimental data in this investigation were analyzed according to both heterogeneous and homogeneous reaction models using graphical and statistical methods. When the results were analyzed graphically and statistically using the non-catalytic heterogeneous reaction models, it was determined that the results fitted well with none of the heterogeneous reaction kinetic models. The results were then tested with the homogeneous models, and it was determined that the process could be stated by a first-order pseudo homogeneous reaction kinetics model (Gur and Kandilcik, 2009).

As can be seen graphically in Fig. 5, fine linear agreements exist between the formula of the first-order pseudo homogeneous reaction kinetic model and time for various reaction temperatures. Imamutdinova and Bikchurova (1967) revealed the salting out of particles from the solution. The dissolving is a very complex structure containing gradual dissolution of likely boric acid film and diffusion of the reacting reagent via this film besides the other steps. The process can be indicated by a first-order pseudo homogeneous reaction model. The concentrations of reagent types do not lower in the film. It can be taken to be constant in every part. The reaction occurring in the reaction area is rapid enough, while the total system may be shown by a pseudo homogeneous first-order reaction model (Gur and Kandilcik, 2009; Tunc et al., 1999).

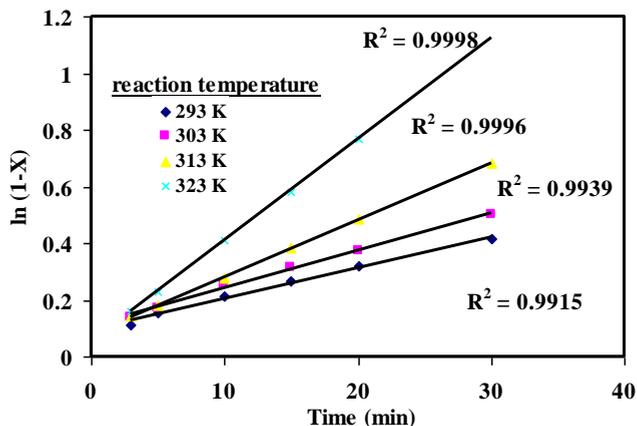


Fig. 5. Conformity of experimental results with $\ln(1-X)$ versus time for reaction temperature

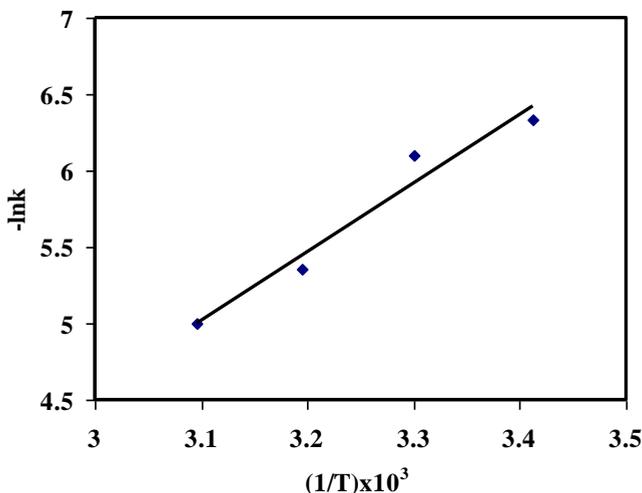


Fig. 6. Arrhenius plot for dissolution process

For this process, the rate expression can be written as follows:

$$\ln(1-X)=kt. \tag{16}$$

To contain the effect of the parameters on the rate constant, the reaction model can be shown as follows:

$$k=k_o(D)a(C)b(S/L)c \exp(-E_a/RT). \tag{17}$$

Combining Eqs. (16) and (17), Eq. 18 gives

$$\ln(1-X) = k_o (D) a (C) b (S/L) c \exp (-E_a/RT) t. \tag{18}$$

The constant values of a , b , c (in Eqs. (17) and (18)) were calculated as -0.8822, 0.7090, and -0.3436, respectively. The Arrhenius equation was used to calculate the leaching activation energy. The dependency of the reaction temperature on the chemical reactions is described by the Arrhenius equation. For this process, the Arrhenius plot is shown in Fig. 6, and the activation energy of the dissolution process can be calculated from this equation. From the slope of this line, the activation energy of process was found to be 26.07 kJ.mol⁻¹, and the intercept was calculated as 1.04.102.

In conclusion, the kinetic statement containing the parameters used in this leaching process can be described as follows:

$$\ln(1-X)=1.04 \times 102(D)-0.8822(C)0.7090 (S/L)-0.3436 \exp(-3130/T)t. \quad (19)$$

Conclusions

The leaching kinetics of priceite was investigated in sulphuric acid solutions. The dissolution rate increased with the sulphuric acid concentrations up to 1 mol/dm³, and then decreased with the increasing sulphuric acid concentrations over 1 mol/dm³. The increase in the reaction temperature, decrease in the particle size and solid/liquid ratio increased the dissolution rate. The present study has also explained the dissolution process of priceite in H₂SO₄ solutions. According to the data obtained from the experiments, increasing H₃O⁺ ion concentrations increased the dissolution, while increasing SO₄²⁻ ion concentrations decreased the dissolution due to the formation of CaSO₄ and/or CaSO₄.2H₂O which substantially restricted the diffusion of H₃O⁺ ions the mineral surface. The graphical and statistical methods employed in the kinetic models provided leaching kinetics of priceite in sulphuric acid solutions which was described by the first-order pseudo homogenous reaction control model. The activation energy for leaching process of priceite in sulphuric acid solutions was established to be 26.07 kJ/mol. A semi empirical mathematical model was constructed.

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