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Dissolution Kinetics of Thermally Dehydrated Colemanite in Perchloric Acid Solutions

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In this study, the dissolution of thermally dehydrated colemanite in aqueous perchloric acid solutions was investigated in a batch reactor employing the parameters of solid to liquid ratio, particle size, temperature and acid concentration. It was found that the dissolution rate increased with increasing temperature and acid concentration, decreasing particle size and solid to liquid ratio. No important effect of stirring speed was observed. The dissolution kinetics of colemanite was examined according to heterogeneous and homogeneous reaction models and it was found that the dissolution rate was controlled by heterogeneous chemical reaction. The activation energy of the process was determined to be 41.07 kJ mol^{-1}. The experimental data were tested by graphical and statistical methods and it was found that the following model best fit the experimental data

$$1 - (1\text{-}X)^{1/3} = 7.56 \times 10^5 (Rp)^{-0.1076} \times (C_A)^{0.4629} \times (S/L) - 0.2525 \times e^{-4938.7/T} \times t$$

Key Words: Boron mineral, Colemanite, Dissolution kinetics, Perchloric acid.

INTRODUCTION

Boron is not directly used in industrial area, however its compounds are widely consumed in the production of glass, fibers, heat resistant materials, material processing, nuclear reactors, fire retardants, catalysis and detergents, *etc*. The most important boron reserves are colemanite, ulexite and tincal. Colemanite has a monoclinic crystal structure with a chemical formula[1] of $2CaO \cdot 3B_3O_3 \cdot 5H_2O$. Commercially, the most used boron compound is boric acid. The production of boric acid has substantially increased recently due to the increasing use of this compound in preparation of many boron chemicals including boron phosphate, borate esters, fluoroborates, boron carbide and metal alloys[2]. Currently, boric acid is produced through the reaction between colemanite and sulfuric acid The overall reaction is as follows:

$$2CaO\cdot 3B_3O_3\cdot 5H_2O(s) + 2H_2SO_4\,(aq) + 6H_2O \longrightarrow 6H_3BO_3(aq) + 2CaSO_4\cdot 2H_2O(s) \quad (1)$$

Calcium sulphate dihydrate, gypsum, forms as a by-product through the reaction. After filtration of gypsum, crystallization of boric acid in high purity and efficiency is a crucial process. This process has some disadvantages such as sulphate contamination in product and disposal of gypsum that causes soil and water pollution because of its boron content[3]. There are many investigation about the dissolution and mechanism of boron minerals in various acid solutions[4-11].

The dissolution of ulexite was investigated in acetic acid solutions and found that the dissolutions rate was maximum at relatively low acid concentration (10-20 w %) and over these concentration the dissolutions rate decreased. It was also reported that the process was controlled by diffusion[12]. It was carried out a work on the dissolution of ulexite in H_3PO_4 solution and reported that in the dissolutions of ulexite in 5 wt. % H_3PO_4 solutions H_3BO_3 solid film formed on crystals, this restricted the dissolution rate of the mineral[13]. Dissolution kinetics of calcined ulexite in ammonium chloride solutions and dissolution kinetics of calcined ulexite in ammonium chloride solutions at high solid-to-liquid ratios were investigated[14,15]. Kucuk *et al.*[16] studied the dissolution kinetics of Kestelek's colemanite containing clay in water saturated with SO_2 and found that the dissolution rate was controlled by chemical reaction and the activation energy for the process was 39.53 kJ mol^{-1}. Gür *et al.*[17] investigated optimization of ulexite in aqueous perchloric acid solution and they reported as the optimum conditions are 0.15 g/mL for solid to liquid ratio 215 μm for particle size, 24 min for reaction temperature and 2 M for acid concentration. Under these conditions, they also determined that the conversion fraction of ore was reached a value of 100 %.

In literature no study was found concerning the dissolution kinetics of thermally dehydrated colemanite in perchloric acid solutions. Thus, in this study, the dissolution kinetics of colemanite in aqueous perchloric acid solution was investigated. The effects of the particle size, solution concentration, reaction temperature, solid-to-liquid ratio and stirring speed on the dissolution rate were evaluated and the best fitted kinetic model designed by means of the experimental data according to heterogeneous and homogeneous reaction models.

EXPERIMENTAL

The colemanite ore used in this study was obtained from Emet-Mine (Kütahya-Turkey). The sample was crushed and ground and sieved by using ASTM standard sieves to obtain 14 ± 30, 30 ± 50 and 80 ± 100 mesh size fractions. The colemanite sample used in the experiments were thermally dehydrated at 723 K in ash furnace. Chemical composition of the natural ore was determined by volumetric and gravimetric methods. Trace elements were analyzed by atomic absorption spectrophotometer. The chemical composition of colemanite ore is given in Table-1.

TABLE-1
COMPOSITION OF THE COLEMANITE USED IN THE EXPERIMENTS

Main mineral	Per cent
B_2O_3	47.27
CaO	25.34
H_2O	20.37
SiO_2	4.11
Al_2O_3	0.80
Fe_2O_3	0.37

All the other chemicals used in the experiments and analysis were purchased in reagent grade from Merck. The dissolution process of the mineral was carried out in a 250 mL spherical glass reactor equipped with a mechanical stirrer having a digital controller unit. A thermostat for controlling the reaction temperature and a back cooler to avoid the loss of solution by evaporation. First, 100 mL of perchloric acid solution at a given concentration was put into the reactor, then 1 g of the mineral was added into the solution while the content of reactor was stirred with a determined speed. As soon as the process finished, the contents were filtrated and B_2O_3 in the solution was analyzed by volumetric method[18].

RESULTS AND DISCUSSION

Dissolution reactions

Effects of parameters: The data obtained were plotted in the form of a conversion fraction, described as $X_{B_2O_3}$ = the amount of dissolved B_2O_3/ the amount of B_2O_3 in original mineral, *versus* time.

In order to investigate the effect of stirring speed on the dissolution rate, experiments were carried out using three different stirring speeds (300, 500 and 700 rpm) at particle size of 30 ± 14 mesh, a reaction temperature of 296 K, a solid-to-liquid ratio of 1 g/100 mL and an acid concentration of 0.2 mol dm^{-3}. The experimental results show that the dissolution rate is practically independent of the stirring speed. Similar result for dissolution kinetics of colemanite in aqueous acetic acid solutions[19].

In order to determine the effect of the particle size on the dissolution rate, experiments were carried out using four different particle sizes of the sample (30 ± 14, 50 ± 30 and 100 ± 80 mesh) at a reaction temperature of 296 K, a stirring speed of 500 rpm, a solid-to-liquid ratio of 1 g/100 mL and an acid concentration of 0.2 mol dm^{-3}. As can be seen in Fig. 1, as the particle size decreases, the dissolution rate increases. This situation can be attributed to the increasing contact surface of the samples as the particle size decreases.

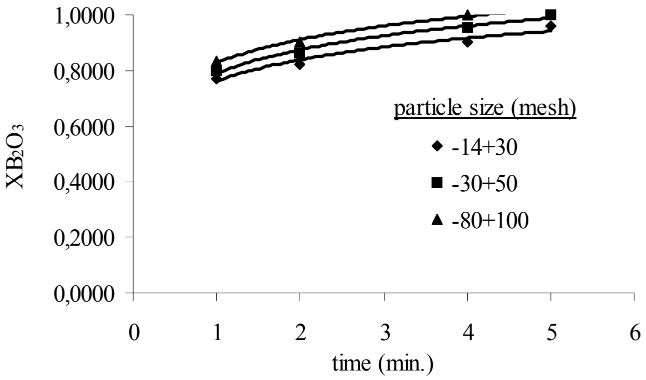

Fig. 1. Effect of the particle sizes on dissolution rate

In order to determine the effect of ammonium chloride concentration on the dissolution rate, experiments were performed with four different ammonium chloride concentrations (0.10, 0.15, 0.20 and 0.25 mol dm^{-3}) at a reaction temperature of 296 K, a stirring speed of 500 rpm, a solid-to-liquid ratio of 1 g/100 mL and a particle size of 14 ± 30 mesh. The fraction reacted under the above conditions is shown in Fig. 2, indicating that the dissolution rate increased with increasing solution concentration.

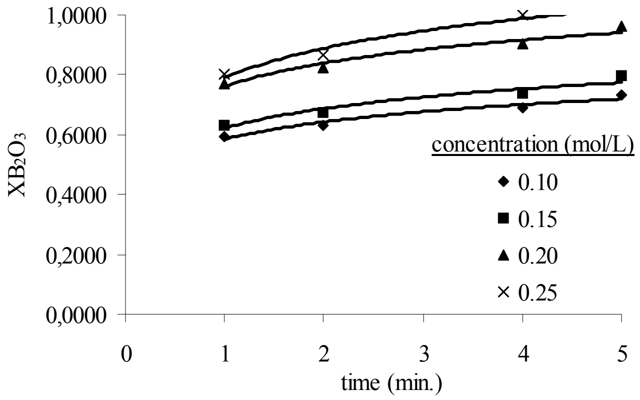

Fig. 2. Effect of the solution concentration on dissolution rate

In order to investigate the effect of solid-to-liquid ratio on the dissolution rate, experiments were carried out using five different solid-to-liquid ratios (0.03, 0.02, 0.015 and 0.010 g/mL) at a reaction temperature of 296 K, a stirring speed of 500 rpm, a particle size of 30 ± 14 mesh and an acid concentration of 0.2 mol dm^{-3}. Fig. 3 shows that the dissolution rate increased with decreasing solid-to-liquid ratios.

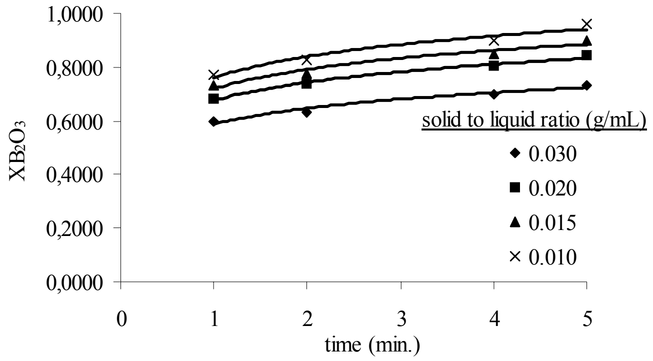

Fig. 3. Effect of the solid to liquid ratio on dissolution rate

The effect of the temperature on the dissolution rate was studied using four different reaction temperatures (293, 296 and 298 K) at a particle size of 30 ± 14 mesh, a stirring speed of 500 rpm, a solid-to-liquid ratio of 1 g/100 mL and an acid concentration of 2 mol dm^{-3}. Fig. 4 shows that increasing the reaction temperature increases the dissolution rate, as expected from the exponential dependence of the rate constant in the Arrhenius equation.

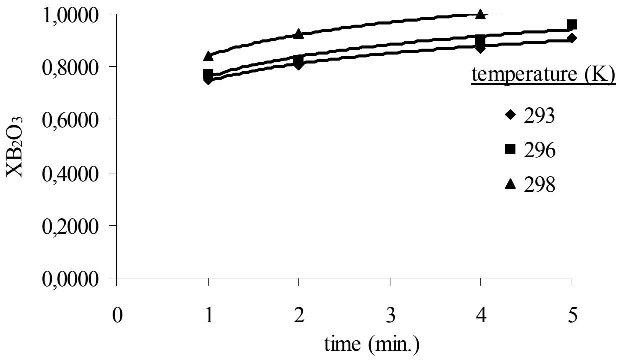

Fig. 4. Effect of the reaction temperature on dissolution rate

Kinetic analysis: The fluid-solid reactive reaction rate can be obtained using the heterogeneous and homogeneous reaction models. In the homogeneous reaction model, it is visualized that a reactant liquid enters the particle and reacts throughout the particle at all times. Thus the solid reactive behave as if it were dissolved. As a result the rate of the reaction can be given in the same form as for a homogeneous reaction. In heterogeneous model, the reaction is considered to take place at the outer surface of the unreacted particle. With increase in conversion the unreacted core of the particle shrinks and the layer of the solid product thickens. According to this model the following five steps are considered to occur in succession during reaction

(1) Diffusion of the fluid reactant through the film surrounding the particle to the surface of the solid. (2) Penetration and diffusion of the fluid reactant through the blanket of ash to the surface of the unreacted core. (3) Fluid-solid chemical reaction at the reaction surface. (4) Diffusion of the fluid products through the ash to the outer surface of the solid. (5) Diffusion of the fluid products through the film into the main body of fluid. It is stated that steps 4 and 5 do not generally contribute to reaction the resistance. It may also be considered that the step with the highest resistance is the rate-controlling step.

The fact that the reaction zone is limited to the outer surface of the unreacted core of a particle is also another assumption for this mode. According to the steps given above a heterogeneous reaction may be controlled by the fluid film diffusion (step 1), the product layer diffusion (step 2), or chemical reaction (step 3). The derived integrated rate equations for these three steps can be given as follows:

(1) film diffusion control: $t = t^* X$ (1)

(2) surface chemical reactions control: $t = t^* [1-(1-X)^{1/3}]$ (2)

(3) product layer (or ash layer) diffusion control:

$$t = t^*[1-3(1-X)^{2/3} + 2(1 - X)] \quad (3)$$

In eqn. 1, t* is

$$t^* = \rho_B Ro^2/6bDC_A \quad (4)$$

where t* is the time for complete conversion (min), ρ_B is the molar density of solid reactant (mol m^{-3}), R_0 is the radius of a sphere (m), b is the stoichiometric coefficient of the solid, D is the effective diffusion coefficient (m^2 s^{-1}) and C_A is the concentration of A in the bulk solution (mol m^{-3}). The fact that the dissolution rate was independent of the stirring speed, as mentioned above, indicates that the diffusion through the fluid film does not act as a rate-controlling step. Because of solid product layer formed during the leaching reaction, the possibility of product layer diffusion being the rate-controlling step should be taken into account.

As mentioned previously the kinetics of the reaction between colemanite and ammonium chloride were statistically and graphically studied by using heterogeneous and homogeneous reaction models. The kinetic analysis performed by taking into consideration the heterogeneous fluid-solid reaction models showed that the process fitted to $t = t^*[1-(1-X)^{1/3}]$.

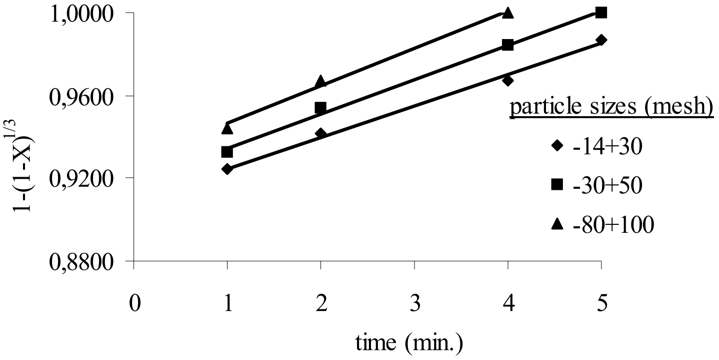

Fig. 5. Plot of 1-(1-X)$^{1/3}$ for different particle size

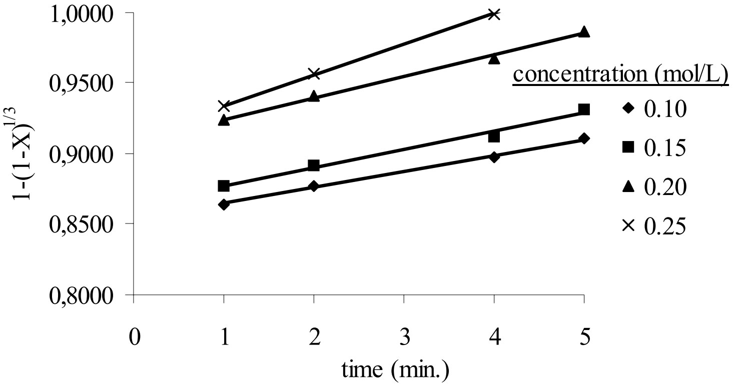

Fig. 6. Plot of 1-(1-X)$^{1/3}$ for different concentrations

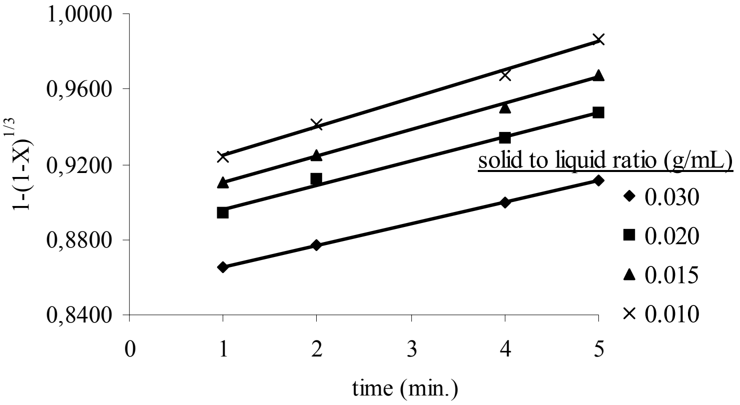

Fig. 7. Plot of 1-(1-X)$^{1/3}$ for different solid to liquid ratios

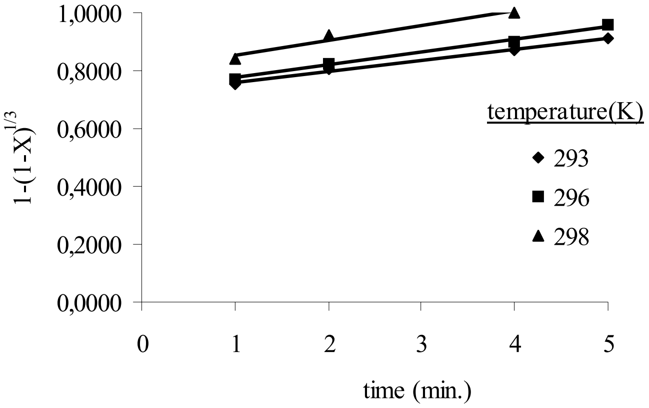

Fig. 8. Plot of $1-(1-X)^{1/3}$ for different temperatures

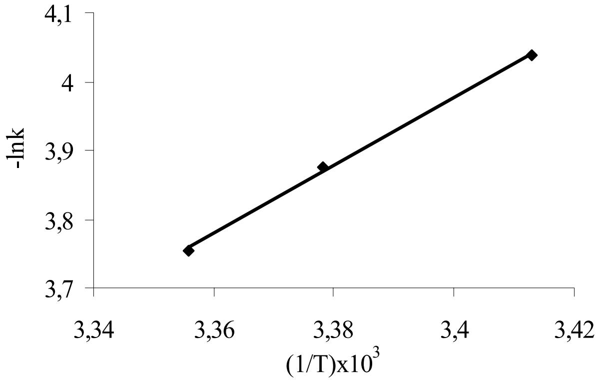

Fig. 9. Arrhenius plot

Conclusion

In this work, the dissolution of colemanite in aqueous perchloric acid solutions was investigated in a batch reactor and was determined by graphical and statistical methods that the chemical reaction control model fits the experimental data. It was found that the dissolution rate increased with decreasing particle size, increasing temperature and increasing acid concentration, but it was not affected by stirring speed. An empirical equation for the process was derived as

$1 - (1\text{-}X)^{1/3} = 7.56 \times 10^5 (Rp)^{-0.1076} \times (C_A)^{0.4629} \times (S/L) -0.2525 \times e^{-4938.7/T} \times t$

The activation energy of the process was found to be 41.07 kJ mol^{-1}.

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