

A SEMIEMPRICAL KINETICS MODEL FOR DISSOLUTION OF COLEMANITE IN AMMONIUM CHLORIDE SOLUTIONS

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ABSTRACT

At the industrial area, it is very important that boron compounds are produced from boron ores. In this study, the dissolution of colemanite in aqueous ammonium chloride solutions was investigated in a batch reactor employing the parameters of stirring speed, particle size, reaction temperature, solid-to-liquid ratio and solution concentration. It was found that the dissolution rate increased with increasing temperature, increasing solution concentration and decreasing particle size, decreasing solid-to-liquid ratio. And it was determined that there was no important effect of stirring speed on dissolution rate. Colemanite could be dissolved up to 100 percent in aqueous ammonium chloride solutions. The dissolution kinetics of colemanite was examined according to heterogeneous and homogeneous reaction models; the analysis of the experimental data, the fact that activation energy is very high, indicate that the dissolution rate based on homogeneous reaction models, can be expressed as: $(1-X)^{-1} - 1 = 7.73 \cdot 10^{13} (Rp)^{3.1142} \cdot [C_{NH_4Cl}]^{1.5124} \cdot (S/L)^{-1.2592} \cdot e^{-4622/T}$. T. The activation energy of the process was determined to be 38,427 kJ. mol⁻¹. The experimental data were tested by graphical and statistical methods and it was found that the above model best fit the experimental data.

Keywords: Colemanite, Dissolution kinetics, Ammonium chloride

INTRODUCTION

Turkey has approximately 60% of the world boron reserves. In the boron ores colemanite, which has a large portion in the deposits, is one of the most important underground riches of Turkey. and it. When colemanite having a $2CaO \cdot 3B_2O_3 \cdot 5H_2O$ formula is mined naturally, it contains various clay minerals. Huge portions of the Turkey's commercially recoverable boron reserves are colemanite, ulexite and tincal. Colemanite has a monoclinic crystal structure with a chemical formula of $2CaO \cdot 3B_2O_3 \cdot 5H_2O$. Although the boron is not used directly, its compounds are widely consumed in the production of glass, fibers, heat resistant materials, material processing, nuclear reactors, fire retardants, catalysis and detergents, etc.¹ 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. In Turkey, boric acid is produced through the reaction between colemanite and sulfuric acid.² 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 very 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 some study about the dissolution of boron minerals in hydrochloric acid,⁴ sulfuric acid⁵, oxalic acid⁶, phosphoric acid⁷, chlorine saturated water⁸ and sulfur dioxide saturated water⁹ etc. and 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.^{10,11} Furthermore, in a study¹² to investigate the mechanism of the dissolution process by nitric acid solutions, it was found that the film layer of the product formed on the mineral surface affects the reaction rate

and the level of this effect differs for every acid, in another study, dissolution mechanism of colemanite in sulphuric acid solutions was investigated.¹³ In another study dissolutions of colemanite, ulexite, inyoite and hydroboracite in H_3PO_4 solutions were investigated and it was found that dissolution of borates in H_3PO_4 solutions presents a diffusion limited character¹⁴. Many investigations, most of which have been patented, have been conducted to produce various boron compounds from boron minerals.¹⁵⁻¹⁸ In another study in which borax production from ulexite ore was investigated, the dissolution of natural and calcinated Ulexite in sodium carbonate-sodium bicarbonate solutions was investigated comparatively.¹⁹ The investigators found that the ore achieved activity and the B_2O_3 concentration as higher when it was calcinated. Imamutdinova and Bikchurova²⁰ studied the dissolution of inyoite, ulexite, colemanite, and hydroboracite minerals in HNO_3 and proved the mechanism proposed earlier by Imamutdinova to be true. According to the mechanism, a H_3BO_3 product film forms on the crystals to be dissolved, which limits the dissolution. They also reported the dissolution process to be diffusional-type based on the calculated rate constants and activation energies. In another study in which the dissolution kinetics of ulexite in ammonia solutions saturated with CO_2 was investigated, the investigators concluded that the dissolution rate of ulexite can be defined according to pseudo-first-order kinetics.²¹ Özmetin et al. found that the activation energy to be 55 kJmol^{-1} .²²

No detailed study was found concerning the dissolution kinetics of natural colemanite in ammonium chloride solutions. Therefore, in this study, the dissolution kinetics of colemanite in aqueous ammonium chloride solution was investigated. The effects of the particle size, solution concentration, reaction temperature, solid-to-liquid ratio and stirring speed on the dissolution rate have been evaluated. The dissolution kinetics of colemanite were examined according to heterogeneous and homogeneous reaction models, and the best fitted equation to the experimental data was determined.

EXPERIMENTAL

The colemanite ore used in this study was obtained from Emet-Mine (Kütahya-Turkey). After cleaning the mineral manually from visible impurities, it was crushed and ground and then sieved by using ASTM standard sieves to obtain the nominal particle size fractions of 0.450, 0.275, 0.215 and 0.165 mm in diameter. Chemical composition of the 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. In addition, X-ray diffraction analysis illustrating basic contents of the colemanite ore is given in Fig.1. 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 used for controlling the reaction temperature within $\pm 0.5^\circ\text{C}$. Also, the reactor was fitted a back cooler to prevent the losses by evaporation. After the reactor containing 100 ml of ammonium chloride solution was heated to reaction temperature, 1g of sample was added into it while stirring was maintained. given concentration was put into the reactor. As soon as the process finished, the contents were filtrated, and B_2O_3 in the solution was analyzed by volumetric method²³. The parameters, expected to effect the dissolution were chosen as the stirring speed, particle size, solid-to-liquid ratio, acid concentration and temperature. The parameters and their ranges and values are given in Table 2. The analysis of the dissolved mineral in the solution was performed volumetrically. As the aqueous solution of boric acid have too weak acidic character, it cannot be determined directly by titration with a basic solution. Therefore, the addition of mannitol in to the solution gives a character of mild acid to boric acid by a basic solution, such a potassium hydroxide, as follows:

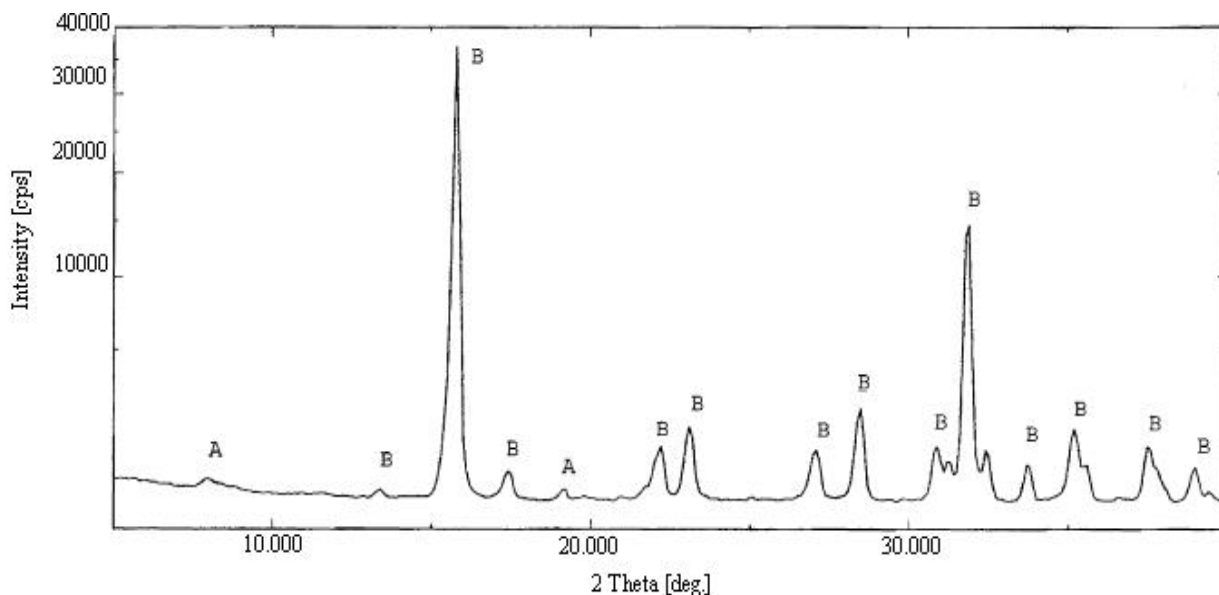
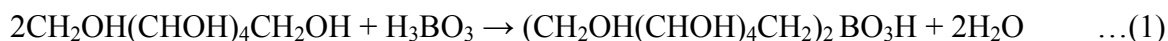


Fig 1 X-ray diffractogram of colemanite ore: (A) SiO_2 ; (B) $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

Table-1 :Composition of the colemanite used in the experiments

Main mineral	Percent
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

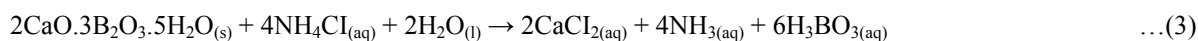
Table-2 : Parameters and their ranges used in the experiments

Parameter	Value				
Particle size (mm)	0.450	0.275*	0.215	0.165	
Acid concentration (mol dm^{-3})	0.5	1	2*	4	
Temperature ($^\circ\text{C}$)	20	30	40	55	75*
Solid-to-liquid ratio (g/100ml)	1*	4	8	12	16
Stirring speed (rpm)	300	500*	700		

*The constant values used when the effect of other parameters was investigated

RESULTS AND DISCUSSION

Dissolution reactions. When colemanite is added into the ammonium chloride solution, the overall reaction can be written as follows:



The Effects of the parameters. The effects of parameters on the dissolution process were investigated using the values given in Table 2 for each parameter. In the experiments, while the effect of one parameter was studied, the values of the other parameters shown with asterisks in Table 2 were kept constant. 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.

To observe 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 0.275 mm, a reaction temperature of 75 °C, a solid-to-liquid ratio of 1g/100ml and an acid concentration of 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 solutions²².

To investigate the effect of the particle size on the dissolution rate, experiments were carried out using four different particle sizes of the sample (0.450, 0.275, 0.215, and 0.165 mm) at a reaction temperature of 75 °C, a stirring speed of 500 rpm, a solid-to-liquid ratio of 1g/100ml and an acid concentration of 2 mol dm⁻³. As can be seen in Fig. 2.a, 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.

In order to investigate the effect of ammonium chloride concentration on the dissolution rate, experiments were performed with four different ammonium chloride concentrations (0.5, 1, 2 and 4 mol dm⁻³) at a reaction temperature of 75 °C, a stirring speed of 500 rpm, a solid-to-liquid ratio of 1g/100ml and a particle size of 0.275 mm. The fraction reacted under the above conditions is shown in Fig. 2.b, indicating that the dissolution rate increased with increasing solution concentration.

To investigate the effect of solid-to-liquid ratio on the dissolution rate, experiments were carried out using five different solid-to-liquid ratios (1, 2, 4, 6 and 8 g/100ml) at a reaction temperature of 75 °C, a stirring speed of 500 rpm, a particle size of 0.275 mm and an acid concentration of 2 mol dm⁻³. Fig. 2.c shows that the dissolution rate increased with decreasing solid-to-liquid ratios.

The effect of the temperature on the dissolution rate was studied using four different reaction temperatures (20, 30, 40, 55 and 75 °C) at a particle size of 0.275 mm, a stirring speed of 500 rpm, a solid-to-liquid ratio of 1g/100ml and an acid concentration of 2 mol dm⁻³. Fig. 2.c shows that increasing the reaction temperature increases the dissolution rate, as expected from the exponential dependence of the rate constant in the Arrhenius equation.

Kinetic analysis: The fluid–solid reactive reaction rate (Eq. (3)) 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

resistance²⁴. It may also be considered that the step with the highest resistance is the rate-controlling step²⁵.

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 mode²⁶. 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:

$$(1) \text{ film diffusion control : } t = t^* X \quad \dots (4)$$

$$(2) \text{ surface chemical reactions control : } t = t^*[1 - (1 - X)^{1/3}] \quad \dots(5)$$

$$(3) \text{ product layer (or ash layer) diffusion control : } t = t^*[1 - 3(1 - X)^{2/3} + 2(1 - X)] \quad \dots(6)$$

Where;

$$t^* = \rho_B R_0^2 / 6bDC_A \quad \dots(7)$$

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 ($\text{m}^2 \text{s}^{-1}$) and C_A is the concentration of A in the bulk solution (mol m^{-3}). D values calculated from Eq. (7) were given in Table 3.

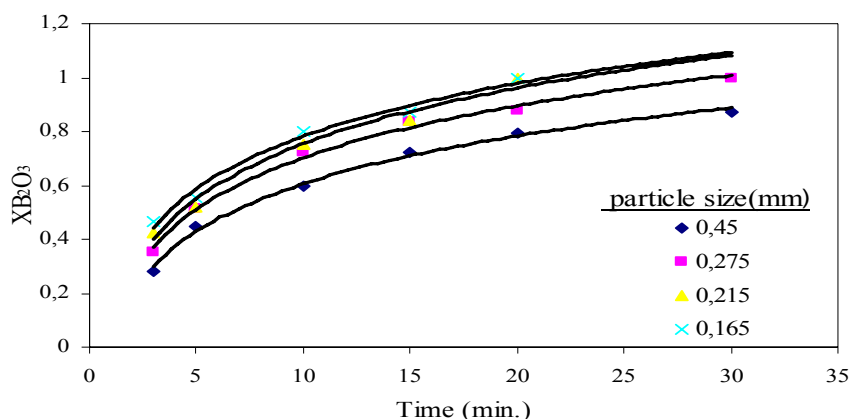


Fig.2.a The effect of the particle sizes on dissolution rate.

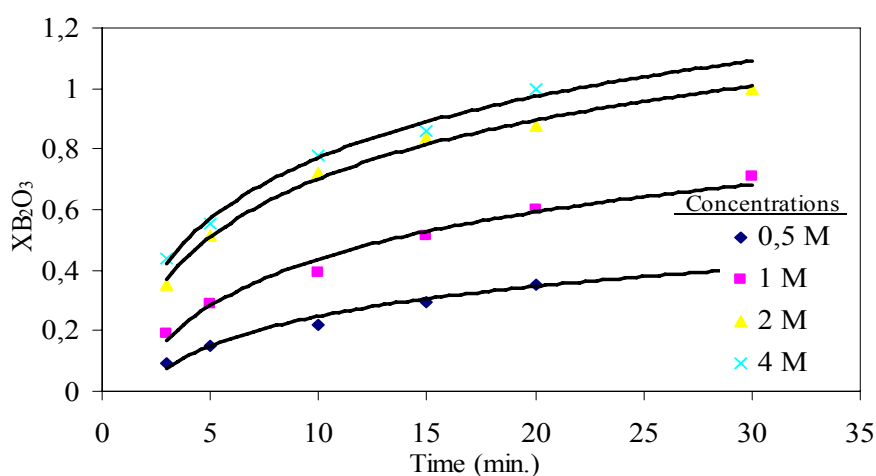


Fig.2.b The effect of the solution concentration on dissolution rate.

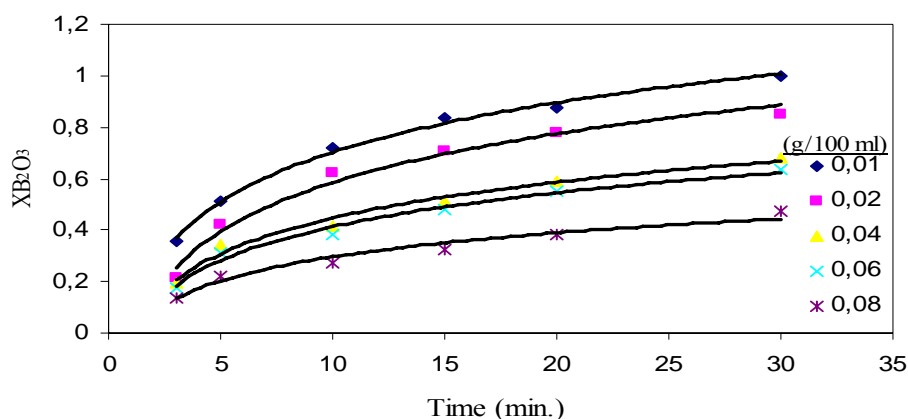


Fig.2.c The effect of the solid to liquid ratios on dissolution rate.

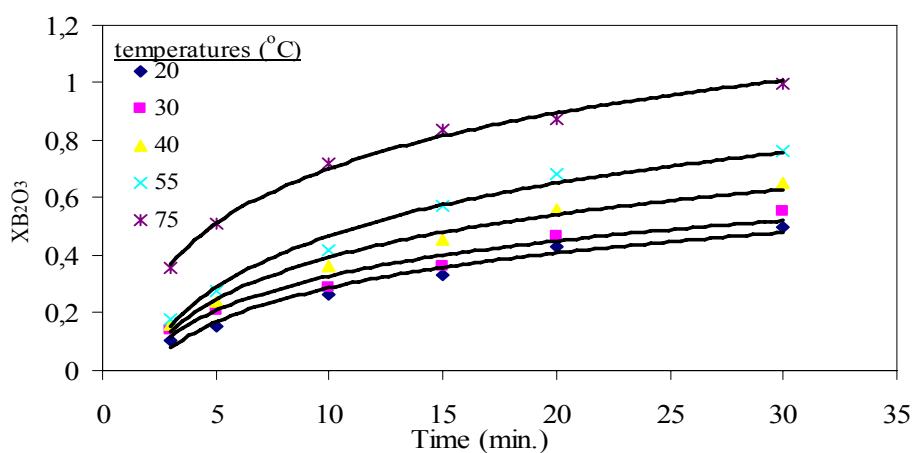


Fig.2.d The effect of the reaction temperature on dissolution rate.

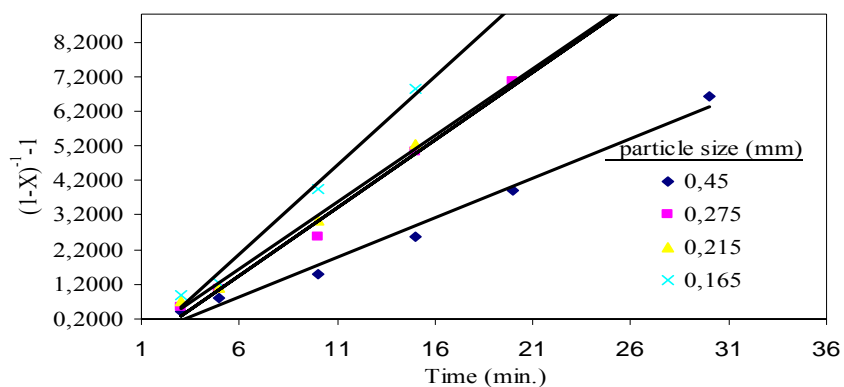
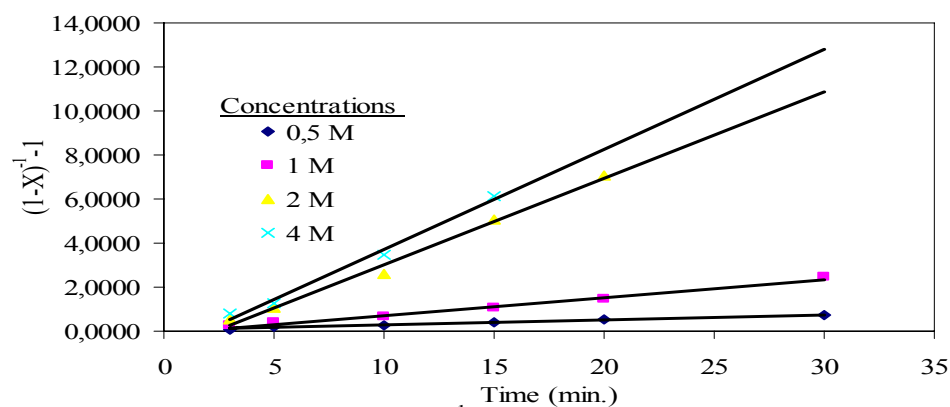
The fact that the dissolution rate was independent of the stirring speed, as mentioned above, indicates that the diffusion through the fluid film does not

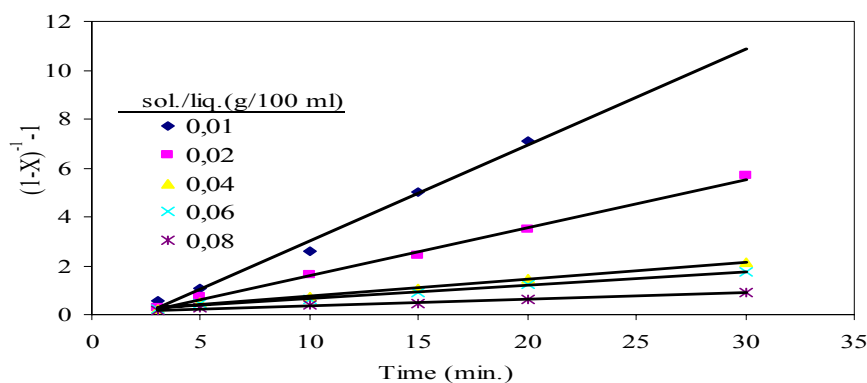
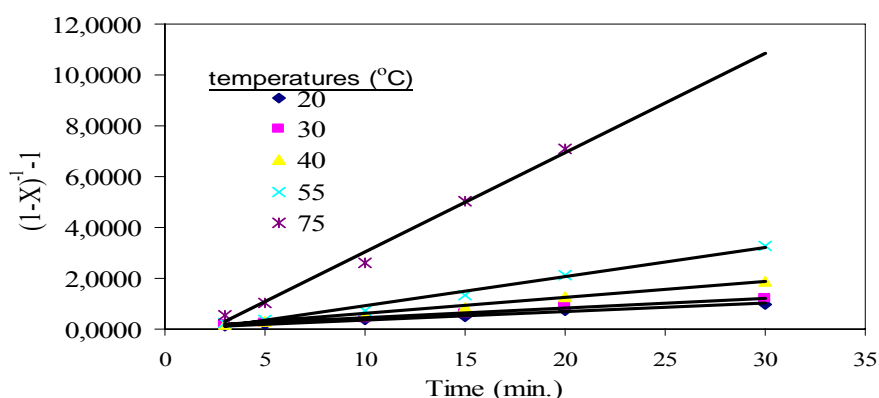
act as a rate-controlling step. Because of solid product layer formed during the leaching reaction, the possibility of product layer diffusion being the rate-controlling step should be taken into account²⁷. As mentioned previously the kinetics of the reaction between colemanite and ammonium chloride were statistically and graphically studied by using heterogeneous and homogeneous reaction models. The kinetic analysis performed by taking into consideration the homogeneous fluid–solid reaction models showed that the process fitted to $(1-X)^{-1}-1$. The plots of $(1-X)^{-1}-1$ versus time gave straight lines for all samples with correlation coefficients between 0.9932 and 1 as can be seen in Table 3. The straight lines shown in Fig. 3.a–d can adequately represent the dissolution process. In accordance with these results, the equation representing the kinetics of these process can be expressed as-

$$t = t^* (1-X)^{-1} - 1^{26}.$$

Table-3: r-Values calculated for the homogeneous reaction model

Concentration (mol dm ⁻³)	Temperature (°C)	Stirring speed (rpm)	Solid-to-liquid ratio (g/100ml)	Particle size (mm)	Kinetic equation [(1-X)] ⁻¹ -1 r
0.5	75	500	1	0.275	0.9963
1	75	500	1	0.275	0.9941
2	75	500	1	0.275	0.9953
4	75	500	1	0.275	0.9941
2	20	500	1	0.275	0.9947
2	30	500	1	0.275	0.9955
2	40	500	1	0.275	0.9968
2	55	500	1	0.275	0.9942
2	75	500	2	0.275	0.9984
2	75	500	4	0.275	0.9965
2	75	500	6	0.275	0.9966
2	75	500	8	0.275	0.9943
2	75	500	1	0.450	0.9932
2	75	500	1	0.215	0.9952
2	75	500	1	0.165	0.9941

Fig.3.a Plot of $(1-x)^{-1}-1$ against for various time.Fig.3.b Plot of $(1-X)^{-1}-1$ against for various time.

Fig.3.c Plot of $(1-X)^{-1}$ against for various time.Fig.3.d Plot of $(1-X)^{-1}$ against for various time.

Activation energies. The temperature dependence of the chemical reactions can be given by the Arrhenius equation as follows:

$$\ln D = \ln D_0 - Ed/RT$$

...(8)

According to Eq. (8), a plot of $\ln D$ versus $1/T$ should be a straight line with a slope $-Ed/R$ and intercept $\ln D_0$ when experimental data follows Arrhenius equation. The Ed value calculated from this equation is $38,427 \text{ kcal mol}^{-1}$ and D_0 frequency factor was found to be $7.73 \cdot 10^{13}$ for process.

CONCLUSION

In this paper, the conversion of colemanite to boric acid was investigated in ammonium chloride solutions. The chosen parameters were the particle sizes, stirring speed, solution concentration, solid-to-liquid ratio and temperature. The dissolution kinetics of colemanite were examined according to heterogeneous and homogeneous reaction models, and the best fitted equation to the experimental data was determined. According to statistical and experimental analysis; reaction rate could be expressed using the homogeneous reaction model. The activation energy was found as $38,427 \text{ kJ mol}^{-1}$.

Currently boric acid is produced by dissolving colemanite ore in H_2SO_4 solution, the overall reaction is as follows: $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}_{(s)} + 2\text{H}_2\text{SO}_{4(aq)} + 6\text{H}_2\text{O} \rightarrow 6\text{H}_3\text{BO}_{3(aq)} + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}_{(s)}$. This process is not good, due to difficulties that encountered in filtration of the reaction mixture and crystallization. Additionally in this process, a form of gypsum is as a by product and causes severe environmental pollution³. The aim of this work was to investigate the dissolution kinetics of colemanite in ammonium chloride solutions, as a basis for improving environmentally sensitive boric acid technology.

The advantage this process: It was determined that colemanite could be dissolved completely in ammonium chloride solutions, and The ammonium chloride process mentioned in this paper more advantageous than the classical sulphuric acid process, because there is no borogypsum byproduct that causes environmental pollution.

Appendix A. Nomenclature

t reaction time (min)

t^* time for complete conversion (min)

X fractional conversion

D effective diffusion coefficient

D_0 frequency factor for process

E_d activation energy for diffusion process (kcal mol⁻¹)

R universal gas constant (kcalK⁻¹ mol⁻¹)

T temperature (K)

r regression coefficient

S/L solid-to-liquid ratio.

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