

硝酸铵溶液浸提硬硼酸钙的动力学研究

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摘要: 对硬硼酸钙在硝酸铵水溶液的溶解在间歇式反应器中就搅拌速度、粒径大小、反应温度、固液比和溶液的浓度等参数的影响进行了研究。结果表明溶解速度随温度、硝酸铵水溶液的浓度以及粒径和固液比的增加而增加, 但搅拌速度对溶解速度无重要影响。硬硼酸钙在硝酸铵水溶液中可以高达 100%。硬硼酸钙的溶解动力学根据多相和均相反应模型进行了检验。实验数据表明有高的活化能, 说明基于多相反应动力学模型的溶解速度可表达为: $1 - (1 - X)^{1/3} = 3.28 \times 10^4 \cdot D^{-0.6537} \cdot C^{1.2958} \cdot (SL)^{-0.4909} \cdot e^{-41.40/(RT)}$ 。反应过程的活化能为 $41.40 \text{ kJ} \cdot \text{mol}^{-1}$ 。

关键词: 硼材料; 硬硼酸钙; 溶解动力学; 硝酸铵; 硼酸

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A Kinetic Study on Leaching of Colemanite in Ammonium Nitrate Solutions

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Abstract: The dissolution of colemanite in aqueous ammonium nitrate solutions was investigated in a batch reactor in terms of stirring speed, particle size, reaction temperature, solid-to-liquid ratio and solution concentration. The results showed that the dissolution rate increased with increasing temperature and concentration of ammonium nitrate solution as well as decreasing particle size and solid-to-liquid ratio, while no important effect of stirring speed was observed on dissolution rate. Colemanite could be dissolved up to 100 percent in aqueous ammonium nitrate solutions. The dissolution kinetics of colemanite was examined according to heterogeneous and homogeneous reaction models. The experimental data revealed high activation energy, indicating that the dissolution rate based on heterogeneous reaction models can be expressed as $1 - (1 - X)^{1/3} = 3.28 \times 10^4 \cdot D^{-0.6537} \cdot C^{1.2958} \cdot (SL)^{-0.4909} \cdot e^{-41.40/(RT)}$. The activation energy of the process was found to be $41.40 \text{ kJ} \cdot \text{mol}^{-1}$.

Key words: boron minerals; colemanite; leaching kinetics; ammonium nitrate; boric acid

The production of boron compounds has substantially increased recently due to the increasing demand for these compounds in nuclear technology, in rocket engines as fuel, in the production of heat resistant materials such as refractories and ceramics, in high quality steel, in heat-resistant polymers, in catalysts, etc. Commercially, the most-used compounds of boron are boric acid, boron oxides and sodium perborates. Ulexite and colemanite have been used for the production of these

compounds as raw materials. Colemanite has a monoclinic crystal structure with a chemical formula of $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}^{[1]}$. Ulexite, a hydrated calcium-sodium borate with the chemical formula $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$, is commercially important boron mineral commonly used in the production of fire-resistant materials, isolators and fiberglass^[2]. Boron minerals are generally extracted in the form of boric acid (H_3BO_3) by acid leaching of borate minerals. As colemanite ($2\text{CaO} \cdot$

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$3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) are used as the borate mineral in the sulphuric acid leaching process, which is the process used in Turkey, gypsum is formed as a by-product, leading to several environmental problems^[3]. There are a lot of patented studies dealing with the production of boron compounds especially boric acid and borax, from boron minerals, such as the production of boric acid from ulexite using the mixture of sodium carbonate-bicarbonate solution^[4] and the dissolution kinetics of ulexite in CO_2 -saturated water^[5] and in SO_2 -saturated water^[6]. There are some studies in the dissolution of boron minerals in hydrochloric acid^[7], nitric acid^[8], acetic acid (Özmetin et al.^[9] found the activation energy to be $55 \text{ kJ} \cdot \text{mol}^{-1}$), the dissolution kinetics of colemanite in CO_2 -saturated water^[10]. It has also been investigated in SO_2 -saturated water and it has been found that the dissolution is controlled by surface reaction with an activation energy of $54 \text{ kJ} \cdot \text{mol}^{-1}$ in the case of colemanite^[11].

In another work, the dissolution kinetics of colemanite in oxalic acid solutions were studied and it was found that the dissolution rate was controlled by the product layer (ash layer) diffusion process, the activation energy of the process was found to be $39.75 \text{ kJ} \cdot \text{mol}^{-1}$ ^[12].

Many investigations, most of which have been patented, have been conducted to produce various boron compounds from boron minerals^[13,14]. Imamutdinova and Bikchurova 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 diffusion-type based on the calculated rate constants and activation energies^[15]. In another study in which the dissolution kinetics of ulexite in ammonia solutions saturated with CO_2 was investigated, the researchers concluded that the dissolution rate of ulexite can be defined according to pseudo-first-order kinetics^[16]. There are some studies on the use of ammonium salt for the leaching ores in literature. Ammonium carbonate solutions were used as extractant for malachite, because basic ores often consume acid, therefore a more basic solvent than sulphuric acid may

be attractive^[17]. The leaching of malachite with ammonium sulphate solutions has been carried out^[18] and the leaching of magnesite with ammonium chloride solution has also been conducted^[19]. 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^[20,21].

The aim of this work is to determine the leaching kinetics of colemanite in ammonium nitrate solutions. Because no detailed study has been found with the dissolution kinetics of colemanite in ammonium nitrate solutions to the best of our knowledge, the effects of the particle size, solution concentration, reaction temperature, solid-to-liquid ratio and stirring speed on the dissolution rate are evaluated in this work. The dissolution kinetics of colemanite is examined according to heterogeneous and homogeneous reaction models, and the best fitted equation to the experimental data is determined.

1 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 - 1400+600, - 600+300, - 250+180 and - 180+150 μm . Chemical composition of the ore was determined by volumetric and gravimetric methods. Trace elements were analyzed by atomic absorption spectrophotometry. The chemical composition of colemanite ore is given in Table 1. In addition, X-ray diffraction

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
Others	1.74

analysis illustrating the 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 quality from Merck.

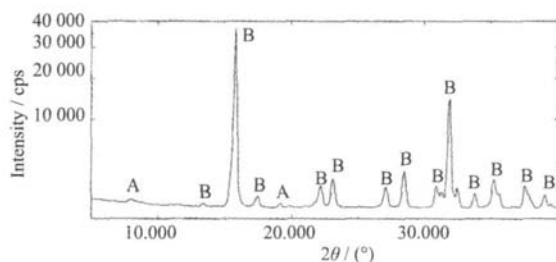


Fig.1 XRD pattern of colemanite ore: (A) SiO_2 ; (B) $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

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 was within ± 0.5 . Also, the reactor was fitted a reflux cooler to prevent losses by evaporation. After the reactor containing 100 mL of ammonium nitrate solution (1, 1.5, 2 and $2.5 \text{ mol} \cdot \text{L}^{-1}$) was heated to reaction temperature, 1g of sample was added into it while stirring was maintained. As soon as the process came to an end (5, 10, 15, 20, 30, 40 and 50 min) the contents were filtrated, and B_2O_3 in the solution was analyzed by a volumetric method [22]. The parameters expected to affect 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.

Table 2 Parameters and their ranges used in the experiments

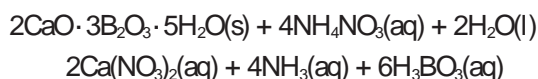
Parameter	Value			
Particle size / μm	* - 1 400+600	- 600+300	- 250+180	- 180+150
NH_4NO_3 / $\text{mol} \cdot \text{dm}^3$	1	1.5	2*	2.5
Temperature / K	297.15	305.15	313.15*	321.15
Solid-to-liquid ratio / ($\text{g} \cdot \text{L}^{-1}$)	5	10*	20	30
Stirring speed / ($\text{r} \cdot \text{min}^{-1}$)	300	500*	700	

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

2 Results and discussion

2.1 Dissolution reactions

When colemanite is added into the ammonium nitrate solution, the overall reaction can be written as follows:



2.2 Effects of parameters

The effects of parameters on the dissolution process were investigated using the values given in Table 2 for each parameter. In experiments, while the effect of one parameter was studied, the values of 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 =the amount of dissolved B_2O_3 /the amount of B_2O_3 in original mineral, versus time.

To determine the effect of stirring speed on the

dissolution rate, experiments were carried out using three different stirring speeds (300 , 500 and $700 \text{ r} \cdot \text{min}^{-1}$) at particle size of $- 1400+600 \mu\text{m}$, a reaction temperature of 313.15 K , a solid-to-liquid ratio of $10 \text{ g} \cdot \text{L}^{-1}$ and a solution concentration of $2 \text{ mol} \cdot \text{L}^{-1}$. The experimental results show that the dissolution rate is practically independent of the stirring speed. Similar results were obtained for the dissolution kinetics of colemanite in SO_2 -saturated water^[9].

The effect of the particle size on the dissolution rate was determined by using $- 1400+600$, $600+300$, $- 250+180$, $- 180+150 \mu\text{m}$ fractions while ammonium nitrate concentration, solid/liquid ratio, stirring speed, reaction temperature were kept constant at $2.00 \text{ mol} \cdot \text{L}^{-1}$, $1/100 \text{ g} \cdot \text{mL}^{-1}$, $500 \text{ r} \cdot \text{min}^{-1}$ and 313.15 K , respectively. As can be seen from Table 3, 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.

Table 3 Values of conversion factor ($X(\text{B}_2\text{O}_3)$) calculated from experimental data

Effect of the particle sizes (Reaction temperature: 313.15 K, stirring speed: 500 $\text{r} \cdot \text{min}^{-1}$, NH_4NO_3 concentration: 2 $\text{mol} \cdot \text{L}^{-1}$, solid to liquid ratio: 10 $\text{g} \cdot \text{L}^{-1}$)				
t / min	- 1 400+600 μm	600+300 μm	- 250+180 μm	- 180+150 μm
5	0.222 1	0.281 1	0.352 1	0.401 2
10	0.361 6	0.441 6	0.601 3	0.651 8
15	0.471 7	0.572 3	0.692 9	0.842 1
20	0.592 9	0.630 1	0.821 6	0.972 4
30	0.751 5	0.683 6	0.971 1	—
40	0.841 4	0.841 1	—	—
50	0.932 3	0.955 4	—	—
Effect of the NH_4NO_3 concentration (Particle size: - 1 400+600 μm , stirring speed: 500 $\text{r} \cdot \text{min}^{-1}$, temperature: 313.15 K, solid to liquid ratio: 10 $\text{g} \cdot \text{L}^{-1}$)				
t / min	1 $\text{mol} \cdot \text{L}^{-1}$	1.5 $\text{mol} \cdot \text{L}^{-1}$	2 $\text{mol} \cdot \text{L}^{-1}$	2.5 $\text{mol} \cdot \text{L}^{-1}$
5	0.08	0.141 4	0.222 1	0.272 2
10	0.152 8	0.231 8	0.361 6	0.451 3
15	0.241 4	0.300 6	0.471 7	0.581 6
20	0.321	0.412 1	0.592 9	0.682 5
30	0.421 2	0.525	0.751 5	0.831 7
40	0.531 8	0.630 1	0.841 4	0.954 8
50	0.604 6	0.698 4	0.932 3	0.999 8
Effect of the solid to liquid ratio (Reaction temperature: 313.15 K, stirring speed: 500 $\text{r} \cdot \text{min}^{-1}$, NH_4NO_3 concentration: 2 $\text{mol} \cdot \text{L}^{-1}$, particle size: - 1 400+600 μm)				
t / min	30 $\text{g} \cdot \text{L}^{-1}$	20 $\text{g} \cdot \text{L}^{-1}$	10 $\text{g} \cdot \text{L}^{-1}$	5 $\text{g} \cdot \text{L}^{-1}$
5	0.072 1	0.132 3	0.222 1	0.321 7
10	0.192 9	0.261 2	0.361 6	0.482 1
15	0.298 4	0.391 4	0.471 4	0.599 3
20	0.371 2	0.541 8	0.592 9	0.721 6
30	0.496 6	0.632 4	0.751 5	0.851 9
40	0.602 9	0.735 5	0.841 4	0.969 5
50	0.682 6	0.841 6	0.932 3	—
Effect of the reaction temperature (Particle size: - 1 400+600 μm , stirring speed: $\text{r} \cdot \text{min}^{-1}$, NH_4NO_3 concentration: 2 $\text{mol} \cdot \text{L}^{-1}$, solid to liquid ratio: 10 $\text{g} \cdot \text{L}^{-1}$)				
t / min	297.15 K	305.15 K	313.15 K	321.15 K
5	0.073 2	0.146 8	0.221 2	0.353 2
10	0.171 3	0.244 2	0.361 6	0.574 9
15	0.271 5	0.352 1	0.471 4	0.712 1
20	0.342 3	0.444 6	0.592 9	0.824 1
30	0.442 2	0.561 4	0.751 5	0.941 1
40	0.534 3	0.671 3	0.841 4	0.989 9
50	0.604 1	0.768 9	0.932 3	—

To investigate the effect of the ammonium nitrate concentration on dissolution rate, experiments were carried out at 1, 1.5, 2, 2.5 $\text{mol} \cdot \text{L}^{-1}$ concentrations while the temperature, particle size, stirring speed and solid/liquid

ratio were kept constant at 313.15 K, - 1 400+600 μm , 500 $\text{r} \cdot \text{min}^{-1}$, 1/100 $\text{g} \cdot \text{mL}^{-1}$, respectively. The results listed in Table 3 show that the dissolution rate increases with an increase in solution concentration.

In order to study the effect of solid-to-liquid ratio on the dissolution rate, experiments were carried out using four different solid-to-liquid ratios ($\text{g} \cdot \text{mL}^{-1}$) as 0, 0.5/100, 1/100, 2/100, and 3/100. In experiments, solution concentration, particle size, stirring speed and reaction temperature were kept constant at $2 \text{ mol} \cdot \text{L}^{-1}$, $-1\,400+600 \text{ } \mu\text{m}$, $500 \text{ r} \cdot \text{min}^{-1}$, 313.15 K , respectively. Table 3 shows that the dissolution rate decreases with increased solid-to-liquid ratio. This situation can be explained by the increase in the amount of solid per amount of reagent in the reaction mixture.

To observe the effect of the reaction temperature on the dissolution rate, experiments were performed with four different reaction temperatures. Reaction temperatures at 297.15 , 305.15 , 313.15 , 321.15 K were studied while ammonium nitrate concentration, particle size, solid/liquid ratio and stirring speed were kept constant at $2 \text{ mol} \cdot \text{L}^{-1}$, $-1\,400+600 \text{ } \mu\text{m}$, $1/100 \text{ g} \cdot \text{mL}^{-1}$ and $500 \text{ r} \cdot \text{min}^{-1}$, respectively. The experimental results plotted in Fig.3 and Table 3 show that the dissolution rate increases with an increase in reaction temperature. This result is expected according to the exponential dependence of the rate constant in the Arrhenius equation.

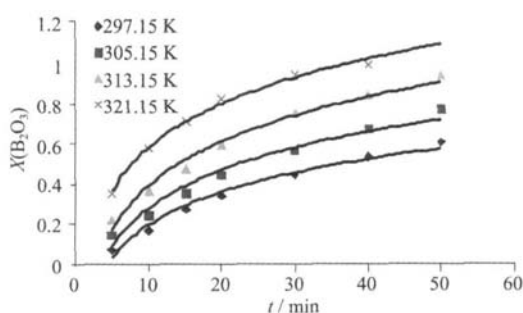


Fig.2 Effect of reaction temperature on dissolution rate

2.3 Kinetics analysis

Fluid-solid heterogeneous reaction systems have many applications in chemical and hydrometallurgical processes. The reaction between a solid and a fluid may be represented by



The rate of reaction between a solid and a fluid can be expressed by homogeneous or heterogeneous models. The data obtained in the present work were analysed for the homogeneous model, but it is seen that

the homogeneous model is inappropriate. Therefore, the experimental data obtained were analysed on the basis of the unreacted shrinking core model. According to the heterogeneous reaction 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. In this model, the following five steps are considered to occur in succession during reaction^[23].

- i. Diffusion of the fluid reactant through the film surrounding the particle to the surface of the solid.
- ii. Penetration and diffusion of the fluid reactant through the blanket of ash to the surface of the unreacted core.
- iii. Fluid-solid chemical reaction at the reaction surface.
- iv. Diffusion of the fluid products through the ash to the outer surface of the solid.
- v. Diffusion of the fluid products through the film into the main body of fluid.

The resistance of these five steps is different from each other. The steps iv and v do not generally contribute to the resistance. Therefore, to derive the rate equations of reactions, the resistance that corresponds to steps i, ii and iii is taken into consideration. It is accepted that the step with the greatest resistance controls the reaction rate. According to these three steps, in noncatalytic fluid-solid heterogeneous reactions, the rate of reaction may be controlled by diffusion through a fluid film (step i), by diffusion through the ash or product layer (step ii), or by a surface chemical reaction (step iii). As mentioned in section 2.1, the stirring speed is ineffective on the dissolution rate. So, the diffusion through a fluid film is unsuitable for a rate-controlling step. A solid product layer is not formed on the surface of the particle during the dissolution reaction. For these reasons, the diffusion through the ash or product layer does not act as a rate-controlling step. If the process is controlled by the resistance of surface chemical reaction (step iii), then the integrated rate equation for this step can be given as follows.

$$1 - (1 - X)^{1/3} = (m \cdot k_s \cdot C_A / R \rho_B) \cdot t \quad (2)$$

Where X is the fraction reacted, m is the stoichiometric coefficient of the solid reactant.

metric coefficient of the reagent, k_s is the rate constant for surface reaction ($\text{cm} \cdot \text{s}^{-1}$), C_A is the bulk concentration of the fluid ($\text{mol} \cdot \text{cm}^{-3}$), R is the average radius of solid particle (cm), ρ_B is the molar density of B in the solid ($\text{g} \cdot \text{cm}^{-3}$) and t is reaction time (s). The relation between the left side of Eq.2 and time must be linear. In the present study, it is observed that the experimental data fit into the surface chemical reaction model. The experimental data were examined by statistical and graphical methods. For this model, the plots of $1 - (1 - X)^{1/3}$ versus time give straight lines for all samples with high correlation coefficients (Table 4). The plots of $1 - (1 - X)^{1/3}$ versus time are shown in Fig.3 for different reaction temperatures. From the slope of the straight lines, the apparent rate constants are evaluated. Furthermore, the activation energy of the process is as high as $41.40 \text{ kJ} \cdot \text{mol}^{-1}$. Thus, these two situations confirm that the dissolution rate is

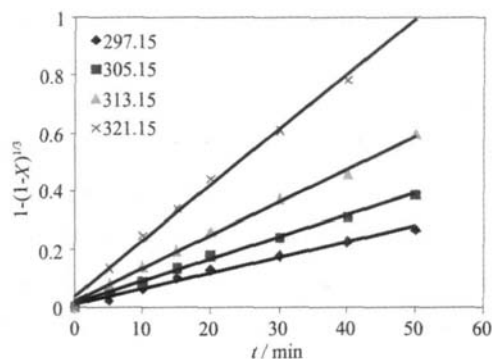


Fig.3 $1 - (1 - X)^{1/3}$ vs various reaction temperatures

chemically controlled. In accordance with these results, the equation representing the kinetics of this process can be expressed as $1 - (1 - X)^{1/3} = k \cdot t$.

The dependence of the rate constant, k , on the concentration, particle size, solid-to-liquid ratio and reaction temperature may be given by

$$k = k_0 \cdot D^a \cdot C^b \cdot (SL)^c \cdot e^{E/(RT)} \quad (3)$$

Table 4 R-values calculated for the heterogeneous reaction model

Concentration / ($\text{mol} \cdot \text{L}^{-1}$)	Temperature /	Stirring speed / ($\text{r} \cdot \text{min}^{-1}$)	solid-to-liquid ratio / ($\text{g} \cdot \text{L}^{-1}$)	Particle size / μm	Kinetic equation [$1 - (1 - X)^{1/3}$] Correlation coefficient
1	40	500	10	- 1400+600	0.9979
1.5	40	500	10	- 1400+600	0.9969
2	40	500	10	- 1400+600	0.9989
2.5	40	500	10	- 1400+600	0.9917
2	24	500	10	- 1400+600	0.9935
2	32	500	10	- 1400+600	0.9988
2	48	500	10	- 1400+600	0.9990
2	40	500	5	- 1400+600	0.9953
2	40	500	20	- 1400+600	0.9933
2	40	500	30	- 1400+600	0.9965
2	40	500	10	- 600+300	0.9982
2	40	500	10	- 250+180	0.9947
2	40	500	10	- 180+150	0.9925

The values of the constants a , b and c in Eq.3 are calculated to be - 0.653 7, 1.295 8 and - 0.490 9, respectively. The temperature dependence of the chemical reactions is expressed by the Arrhenius equation. From this equation, the activation energy of the dissolution process can be determined. Using the apparent rate constants in Fig.3, the plot of $\ln k$ versus $1/T$ is constructed in Fig.4 which shows a straight line. From the slope of this line, the activation energy of process is calculated to be $41.40 \text{ kJ} \cdot \text{mol}^{-1}$, and the intercept is

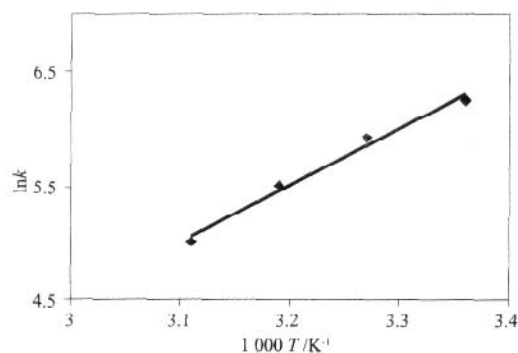


Fig.4 Arrhenius plot

calculated as 3.28×10^4 . Finally, the following mathematical model can be written to represent the reaction kinetics of this dissolution process.

$$1 - (1 - X)^{1/3} = 3.28 \times 10^4 \cdot D^{-0.6537} \cdot C^{1.2958} \cdot (S/L)^{-0.4909} \cdot e^{-41.40/(RT)} \cdot t$$

3 Conclusion

The dissolution rate was found to increase with decreasing particle size and solid to liquid ratio, with increasing reaction temperature and concentration of ammonium nitrate solution, but unaffected by stirring speed. The increasing effect of reaction temperature, solution concentration, solid to liquid ratio, particle size and ineffectiveness of stirring rate on dissolution process, the straight lines obtained with t vs. $1 - (1 - X)^{1/3}$ plots, the relatively better regression constants obtained with the chemical reaction-controlled model, and the activation energy of $E > 40 \text{ kJ} \cdot \text{mol}^{-1}$ all show that the current process is controlled by chemical reaction on the particle surface^[24]. Colemanite is leached with sulphuric acid in Turkey, this mineral could not be dissolved completely because of anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) formation on the surface of this mineral during the reaction. In addition anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) cause severe environmental problems. Colemanite can be totally dissolved in ammonium nitrate solutions, and this process is more environmentally friendly than boric acid extraction by the sulphuric acid process. The investigation of leaching conditions and kinetics of colemanite in ammonium nitrate solutions will help to solve possible problems in the process of boric acid production.

Nomenclature:

- m =stoichiometric coefficient, in Eq.1
 C =concentration of ammonium nitrate, in Eq.3 ($\text{mol} \cdot \text{cm}^{-3}$)
 C_A =bulk cocentration of the fluid, in Eq.2 ($\text{mol} \cdot \text{cm}^{-3}$)
 D =particle diameter, in Eq.3 (mm)
 S/L =solid to liquid ratio, in Eq.1 ($\text{g} \cdot \text{cm}^{-3}$)
 R =average radius of solid particle, in Eq.2 (cm)
 ρ_B =molar density of B in the solid, in Eq.2 ($\text{g} \cdot \text{cm}^{-3}$)
 T =temperature (K)

t =reaction time(s)

X =conversion fraction

k =reaction rate constant (s^{-1})

k_s =rate constant of surface reaction, in Eq.2 ($\text{cm} \cdot \text{s}^{-1}$)

a, b, c, k_0 =constants, in Eq.3

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