

粗硼砂的氯化铵溶液浸提动力学

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摘要: 研究了反应温度、溶液浓度、固液比、固体粒径大小和搅拌速度对氯化铵溶液浸提粗硼砂(十水四硼酸钠, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) 动力学的影响。结果表明反应速率随反应温度、溶液浓度的增加和固体粒径、固液比的减小而增加, 但搅拌速度对溶解速率无显著影响。根据均相和多相反应动力学模型研究了粗硼砂的溶解过程。结果表明溶解速率遵从假一级均相反应模型。粗硼砂在氯化铵溶液中溶解的活化能为 $82.73 \text{ kJ} \cdot \text{mol}^{-1}$ 。

关键词: 硼矿石; 粗硼砂; 氯化铵; 浸提动力学; 硼酸

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Leaching Kinetics of Tincal in Ammonium Chloride Solutions

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Abstract: The effects of reaction temperature, solution concentration, solid to liquid ratio, particle size and stirring speed were investigated on leaching kinetics of tincal, sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), in ammonium chloride solutions. The results showed that the dissolution rate increased with increasing solution concentration and reaction temperature, and increased with decreasing particle size and solid to liquid ratio. It was also determined that stirring speed had no significant effect on dissolution rate. The dissolution process was examined according to homogeneous and heterogeneous reaction kinetic model. The dissolution rate was found to be based on the first order pseudo homogeneous reaction model. The activation energy of the dissolution of tincal in ammonium chloride solutions was determined to be $82.73 \text{ kJ} \cdot \text{mol}^{-1}$.

Key words: boron minerals; tincal; ammonium chloride; leaching kinetics; boric acid

Borates are commonly used in chemical, metallurgical, and nuclear engineering and in many related industries. The most common boron compounds commercially used are boric acid, anhydrous borax, borax hydrates, and sodium per borates, which are generally obtained from colemanite, ulexite, and tincal. Boric acid and boron salts have extensive industrial use in the manufacture of glass and porcelain, in wire

drawing, the production of leather, carpets, cosmetics and photographic chemicals, for fireproofing fabrics, and weatherproofing wood. Boron compounds are used in certain fertilizers for the treatment of boron deficient soils. Boric acid, which has mild bactericidal and fungicidal properties, is used as a disinfectant and as a food preservative. Borax is widely used in welding and brazing of metals, and more recently, boron compounds

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have found applications for hand cleansing, high-energy fuels, cutting fluids and catalysts^[1]. Boric acid is commercially produced in Turkey by the heterogeneous solid-liquid reaction of sulfuric acid and colemanite. In this process, colemanite ore is reacted with sulfuric acid at 95 °C. Gypsum forms as a by-product and precipitates in the reactor while boric acid remains in the liquid phase through the reaction. After gypsum is removed by filtration, boric acid is crystallized by cooling the solution. Filtration of gypsum has an important role in boric acid production because it affects the efficiency, purity, and crystallization of boric acid. This present process has some disadvantages, such as sulfate contamination in the final product and environmental pollution^[2-4]. There have been many investigations on the kinetics and mechanisms of the dissolution of boron minerals in aqueous solutions. Decrepitation properties of colemanite ore have also been studied to some extent. These studies indicate that although most boron minerals exhibit various degrees of hydration, only colemanite appears to undergo decrepitation^[5]. Because of these disadvantages, various studies have been performed on the kinetics and mechanism of dissolution of boron minerals in aqueous solutions. The dissolution kinetics of inderite and inyoite in water saturated with carbon dioxide was investigated^[6]. The dissolution of colemanite was examined in different solutions^[7,8]. In the hydrometallurgical processes, inorganic acids are generally used as the leaching agents. However, the acid methods are uneconomical because basic ores consume excessive acid during the leaching. Furthermore, some undesired impurities can pass into the leaching media when inorganic acids are used. Therefore, more basic lixiviants than inorganic acids (or weakly acidic reagents) may be more favorable in the leaching processes, allowing impurities in the solution to be separated more effectively. Some ammonium salts have been employed by researchers as the lixiviant. The dissolution kinetics of magnesite^[9,10], ulexite^[11], malachite^[12] and dissolution mechanism of colemanite have been studied^[13].

Tincal, sodium tetra borate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot$

$10\text{H}_2\text{O}$), crystals are odorless, white, monoclinic prisms with a relative density of 1.715. Based on the crystal structure, borax is best represented by the formula $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$, with 2 mol of water existing as hydroxyl groups and 8 mol as crystal water^[14]. The largest tincal deposit known in the world exists in Kirka, some 220 km to the west of Ankara, Turkey. This deposit has been worked by Eti Mine Boron Works since 1970 by open pit methods. The run of mine is upgraded and sold as a tincal concentrate^[15]. A tincal concentrate is produced from ore that has been blasted and carried in trucks to the concentration plant. The ore is crushed, milled and screened several times to obtain 6 mm tincal size. A fraction of +1 mm is washed and classified to remove fine clay. A final product, tincal concentrate, has a particle size of -6 mm, moisture of 6wt%~8wt% and B_2O_3 of 32 percent^[16]. Boric acid (H_3BO_3) is produced commercially by reactions of sulfuric acid with sodium borate in the United States and sulfuric acid with colemanite in Europe and Turkey^[17]. Many studies have been carried out on the dissolution kinetics of colemanite and ulexite to produce boric acid.

Although tincal is an important potential source for production boric acid and sodium perborate, there is few leaching study in literature about tincal. We aimed to both contribute to literature and to emphasize important of the leaching kinetic of tincal. No study was found that ammonium chloride was used as the leaching reactant for tincal in the literature. Therefore, the aims of this present work were to investigate the dissolution of tincal using ammonium chloride solution and to determine the effects of the experimental parameters, including solution concentration, solid-to-liquid ratio, particle size, and temperature. Ammonium chloride is highly soluble in water with a weakly acidic character. When the ammonium ions hydrolyze, Ammonium chloride upon dissolving in water provides the protons required for the dissolution reaction. The solutions obtained from the dissolution of tincal in the ammonium chloride include sodium, chloride, dissolved boric acid, and ammonia/ammonium. Various products, such as boric

acid, sodium borates, and ammonium borates may be obtained from this solution. Sodium and ammonium borates are notable boron compounds. Sodium chloride can form as by-products, and is used as table salt. In light of above, the present study can have an important environmental impact.

1 Experimental

1.1 Preparation of materials

The tincal samples used in this study were provided by Kırka Boron Plant, Eskişehir, Turkey. After cleaning the mineral manually from visible impurities, it was ground and sieved by ASTM standard sieves to obtain the nominal particle size fractions of $-1.4+1$, $-1+0.6$, $-0.6+0.4$ and $-0.4+0.25$ mm in diameter. The original ore sample was analyzed, and the mineral content was determined to be 34.06% B_2O_3 , 1.20% SiO_2 , 4% CaO , 4.46% MgO , 14.88% Na_2O , 41.10% H_2O , and 0.30% insoluble matter.

1.2 Apparatus and procedure

The dissolution rate of tincal was determined as a function of time by changing the solution concentration, particle size, solid-liquid ratio, and reaction

temperature. The dissolution experiments were carried out in a 250 mL glass reactor at atmospheric pressure. A mechanic stirrer was used and a thermostat employed to keep reaction medium at constant reaction temperature. Then 50 mL of ammonium chloride solution was put into the reactor. After the desire reaction temperature was reached, a given amount of tincal was added to the solution medium and stirring was started at constant stirring speed. As soon as reaction time was completed at a certain time period, the solution was filtered. The amount of B_2O_3 in filtrate was determined by volumetric method^[18]. The data obtained were plotted as a function of conversion, described as: X =amount of dissolved B_2O_3 in the solution amount of B_2O_3 in the original sample, versus time. Particle size, solution concentration, solid-to-liquid ratio, reaction temperature, and stirring speed were chosen as parameters in the leaching studies. The dissolution data obtained was plotted as a function of reacted fraction, and the kinetic analysis was performed. Experimental parameters and their values in dissolution process are given Table 1.

Table 1 Parameters and their values used in experiments

Particle size / mm	($-1.4+1$)	($-1+0.6$)*	($0.6+0.4$)	($0.4+0.25$)
Solution concentration / ($\text{mol} \cdot \text{L}^{-1}$)	(0.010)	(0.020)	(0.035)	(0.05)*
Solid-to-liquid ratio / ($\text{g} \cdot \text{mL}^{-1}$)	(0.01)*	(0.02)	(0.04)	(0.06)
Reaction temperature / K	(283)	(290)	(298)*	(305)
Stirring speed / ($\text{r} \cdot \text{min}^{-1}$)	(300)	(400)*	(500)	(600)

*The values with asterisks was used, when the effect of other parameters were investigated.

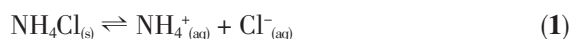
2 Results and discussion

Firstly the effect of stirring speed was investigated on dissolution rate. The experiments were performed at stirring speeds of 300, 400, 500, 600 $\text{r} \cdot \text{min}^{-1}$ to determine of the stirring speed effect on the dissolution rate. In these experiments, solution concentration, particle size, solid-to-liquid ratio, and reaction temperature were kept at 0.05 $\text{mol} \cdot \text{L}^{-1}$, 1~0.6 mm, 0.50/50 $\text{g} \cdot \text{mL}^{-1}$, and 305 K, respectively. It was found that that after a 5 min leaching time, 84.10% of XB_2O_3 at 300 $\text{r} \cdot \text{min}^{-1}$, 85.18% of XB_2O_3 at

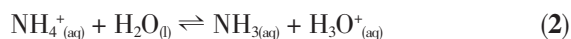
400 $\text{r} \cdot \text{min}^{-1}$, 85.46% of XB_2O_3 at 500 $\text{r} \cdot \text{min}^{-1}$ and 85.98% of XB_2O_3 at 600 $\text{r} \cdot \text{min}^{-1}$ were obtained. From these results it can say that the reagent amounts of particles are fully suspended in the solution. Thus, it can be inferred that the effect of stirring speed is not important on the dissolution rate and thus discarded from the analysis.^[12,19]

2.1 Dissolution reactions

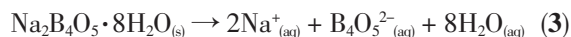
The dissolution process of tincal in ammonium chloride solution occurs to the following reactions. Ammonium chloride ionizes in an aqueous medium according to the following reaction:



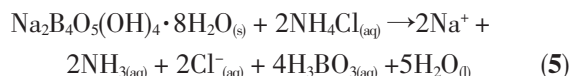
The hydrolysis of NH_4^+ ions gives:



The reaction of tincal in aqueous medium is:

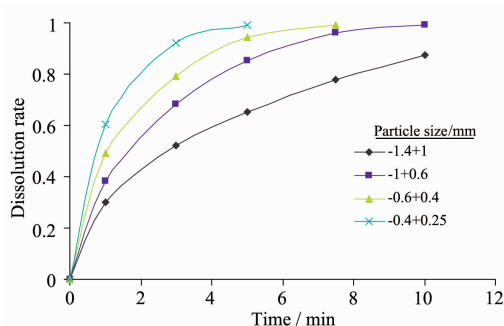


When tincal is added into ammonium chloride solution, the overall reaction occurring in the reaction medium can be written as follows:



2.2 Effects of parameters

The effect of parameters on the dissolution process was investigated for each parameter using the values given in Table 1. In the experiments, while the effect of one parameter was studied, the values of the other parameter shown with asterisks in table 1 were kept constant. The experiments on particle size were carried out using the following size fractions: $-1.4+1$, $-1+0.6$, $-0.6+0.4$, and $-0.4+0.25$ mm. The results shown in Fig.1 indicate that the particle size has a significant effect on the dissolution of tincal. As seen in Fig.1, as the particle size decreases, the dissolution rate increases, which can be attributed to the increase of the contact surface, on which the main dissolution reaction occurs, with the decrease of the particle size per amount of the solid.

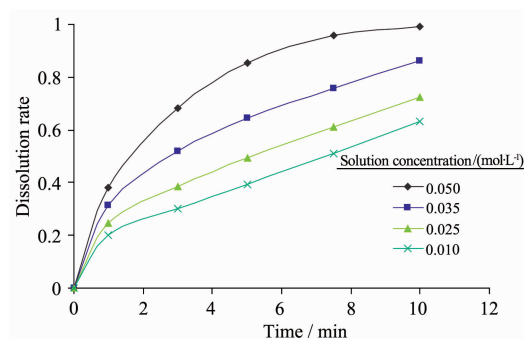


temperature: 298 K; solution concentration: $0.05 \text{ mol} \cdot \text{L}^{-1}$; solid/liquid ratio: $0.5/50 \text{ g} \cdot \text{mL}^{-1}$; stirring speed: $400 \text{ r} \cdot \text{min}^{-1}$

Fig.1 Effect of the particle size on dissolution rate

To investigate the effect of the ammonium chloride concentration on dissolution rate, the experiments were carried out in concentrations of 0.010, 0.020, 0.035 and $0.050 \text{ mol} \cdot \text{L}^{-1}$. The results in Fig.2 show that the effect of ammonium chloride concentration on dissolution rate increases with increasing solution concentration; the

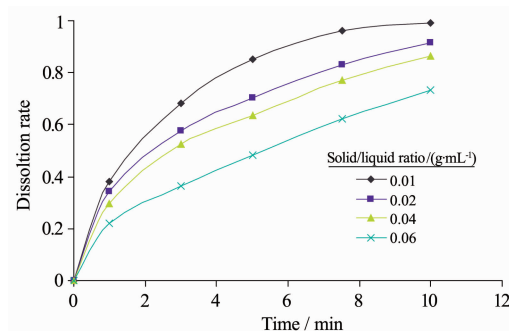
concentration of H_3O^+ increases, therefore the dissolution rate of tincal increases with an increase in ammonium chloride concentration^[20].



temperature: 298 K; particle size: $-1+0.6 \text{ mm}$; solid/liquid ratio: $0.5/50 \text{ g} \cdot \text{mL}^{-1}$; stirring speed: $400 \text{ r} \cdot \text{min}^{-1}$

Fig.2 Effect of the solution concentration on dissolution rate

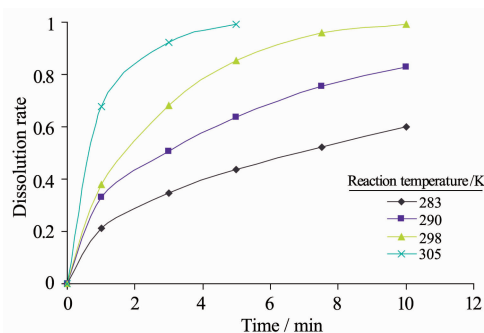
To determine the effect of solid-to-liquid ratio on the dissolution of tincal, the solid-to-liquid ratio was studied in the range of $0.5/50 \sim 3/50 \text{ g} \cdot \text{mL}^{-1}$ and Fig.3 shows the effect of this parameter. This figure shows that the dissolution rate of tincal decreases with an increase in solid-to-liquid ratio, which can be explained by the decrease of solid amount per amount of the reagent in the suspension.



temperature: 298 K; particle size: $-1+0.6 \text{ mm}$; solution concentration $0.05 \text{ mol} \cdot \text{L}^{-1}$; stirring speed: $400 \text{ r} \cdot \text{min}^{-1}$

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

The effect of the reaction temperature on the dissolution rate under certain reaction conditions was investigated in the range of 290 ~ 305 K, where the results are presented in Fig.4 According to results given in Fig.4, increasing reaction temperature has an increasing effect on the dissolution of tincal, as expected owing to the exponential dependence of the rate constant in the Arrhenius equation.



particle size: $-1+0.6$ mm; solution concentration $0.05 \text{ mol} \cdot \text{L}^{-1}$; solid/liquid ratio $0.5/50 \text{ g} \cdot \text{mL}^{-1}$; stirring speed: $400 \text{ r} \cdot \text{min}^{-1}$

Fig.4 Effect of the reaction temperature on dissolution rate

2.3 Kinetic Analysis

The kinetic data of the present study were analyzed according to heterogeneous and homogeneous reaction model using graphical and statistical methods. As the experimental results were analyzed using the non-catalytic heterogeneous reaction models (According to these models, the rate of reaction between solid particle and the leaching reagent may be controlled by one of the following steps: diffusion through the fluid film, diffusion through the product layer, or the chemical reaction at the surface. The particle size can stay constant or decrease during the reaction) by graphical and statistical methods^[21,22], it was found that the data fit none of the heterogeneous reaction kinetic models. When the data were analyzed using the homogeneous models, it was found that the process can be expressed by a first-order pseudo homogeneous reaction kinetic model^[23],

$$dX/dT = k(1-X) \quad (6)$$

or

$$-\ln(1-X) = kt \quad (7)$$

As can be seen graphically in Fig.5, there are in good linear agreement between formula of the first-order pseudo homogeneous reaction kinetic model and time for different reaction temperature. The findings of Imamutdinova and Bikhurova^[24], Imamutdinova and Vladykina^[25] could be salting out of particles from the solution. The process is very complex in nature and can include gradual dissolution of probable boric acid film and diffusion of the reacting reagent through this film in addition to the other steps. The fact that the process can be represented by a first order pseudo homogeneous

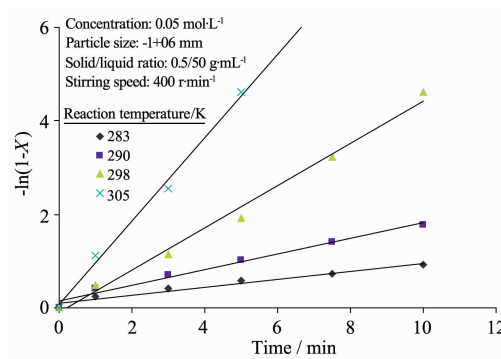


Fig.5 Agreement of experimental data with a first-order pseudo homogeneous kinetic model $[-\ln(1-X)]$ versus time for reaction temperature

reaction model can be explained by the mechanism of one of the fluid-fluid heterogeneous systems^[21]. The concentration of reagent species does not drop appreciably within the film; it can be taken to be constant throughout. Reaction taking place in the reaction zone is fast enough, and the overall system can be represented by a pseudo homogeneous first-order reaction model^[19].

Rate expression for this process can be written as follows:

$$-\ln(1-X) = kt \quad (8)$$

To include the effect of the reaction parameters on the rate constant of reaction, a semi empirical model can be written as follows:

$$k = k_0 D^a C^b (S/L)^c \exp(-E_a/RT) \quad (9)$$

Combining Eqs.(8) and (9), the following equation is obtained:

$$-\ln(1-X) = k_0 D^a C^b (S/L)^c \exp(-E_a/RT) t \quad (10)$$

The constants a , b , and c were estimated from the apparent rate constants given in Table 2. The values of these constants were calculated as -1.1156 , 0.9625 and -0.7043 , respectively. The activation energy of the dissolution process was determined from the Arrhenius equation. The Arrhenius plot of the process is shown in Fig.6. From the slope of the straight line in this figure, the activation energy of the process was calculated to be $82.73 \text{ kJ} \cdot \text{mol}^{-1}$. As a result, the following kinetic expression including the parameters used in this dissolution process can be written:

$$-\ln(1-X) = 7.98 \times 10^{13} D^{-1.1156} C^{0.9625} (S/L)^{-0.7043} \exp(-9951/T) t \quad (11)$$

Table 2 Apparent rate constant and correlation coefficient values

First-order pseudo homogeneous reaction kinetic model $-\ln(1-x)=kt$		
Parameters	k / min^{-1}	R^2
Particle size / mm		
-0.4+0.225	0.185 8	0.998 7
-0.6+0.4	0.461 6	0.994 4
-1+0.6	0.611 5	0.995 7
-1.4+1	0.920 0	0.997 8
Concentration / ($\text{mol} \cdot \text{L}^{-1}$)		
0.010	0.085 4	0.993 2
0.020	0.110 5	0.997 4
0.035	0.173 7	0.996 2
0.050	0.461 6	0.994 4
Solid-to-liquid ratio / ($\text{g} \cdot \text{mL}^{-1}$)		
0.5/50	0.461 6	0.994 4
1/50	0.224 3	0.997 6
2/50	0.178 5	0.997 7
3/50	0.114 0	0.997 0
Temperature / K		
283	0.073 6	0.998 0
290	0.152 8	1.000 0
298	0.461 6	0.994 4
305	0.869 7	0.994 7

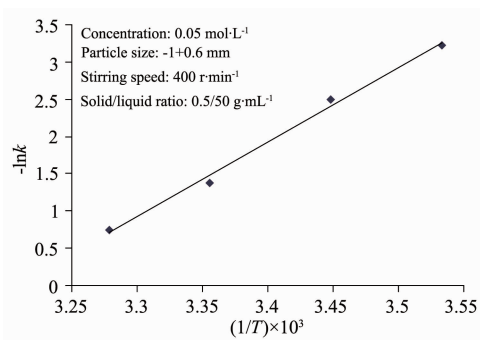


Fig.6 Arrhenius plot for dissolution process

Nomenclature:

C : concentration of ammonium chloride, ($\text{mol} \cdot \text{L}^{-1}$)

D : particle diameter, (mm)

E_a : activation energy, ($\text{J} \cdot \text{mol}^{-1}$)

S/L : solid-to-liquid ratio, ($\text{g} \cdot \text{mL}^{-1}$)

R_0 : average radius of solid particle, (cm)

R : universal gas constant, ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)

T : temperature, (K)

t : reaction time, (min)

X : reacted fraction of B_2O_3

k : apparent rate constant for the surface chemical

reaction, (min^{-1})

k_0 : frequency or pre-exponential factor, (s^{-1})

a, b, c : constants in Eq.(10)

3 Conclusions

In this study, the dissolution kinetics of tincal was investigated in ammonium chloride solutions in a batch reactor. The dissolution rate increases with increasing ammonium chloride concentration, reaction temperature, and with decreasing particle size and solid to liquid ratio. And it was found that tincal could be dissolved in ammonium chloride solution in short period of time, low temperature and at much diluted solution concentration^[11]. This means that leaching tincal in ammonium chloride is both economically beneficial and environmental pollution free. Employing the graphical and statistical methods to heterogeneous and homogeneous reaction kinetic model, it was obtained that dissolution kinetics of tincal in ammonium chloride solutions was described by the first order pseudo homogeneous reaction control model. Finally it can say

that ammonium chloride solution is a good leachant for tincal as mentioned above. The activation energy for dissolution process of tincal in ammonium chloride solution was determined to be $82.73 \text{ kJ} \cdot \text{mol}^{-1}$. A semi empirical mathematical model, which expresses the process well, was developed.

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