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Dissolution and Mechanism of Tincal in Ammonium Carbonate Solutions

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In this paper the dissolution and mechanism of tincal, sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), in ammonium carbonate solutions using the effects parameters of reaction temperature, solution concentration, solid to liquid ratio, particle size and stirring speed. 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 exerted no significant effect on dissolution rate.

Key Words: Tincal, Ammonium carbonate, Boric acid, Boron.

INTRODUCTION

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. Recently, boron compounds 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 optimization, kinetics and mechanisms of the dissolution of boron minerals in aqueous solutions[5-8]. 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 favourable in the leaching processes, allowing impurities

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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], colemanite[11], ulexite[12], malachite[13] and tincal[14,15] were reported by several workers.

Tincal, sodium tetra borate decahydrate ($Na_2B_4O_7{\cdot}10H_2O$), crystals are odourless, white, monoclinic prisms with a relative density of 1.715. Based on the crystal structure, borax is best represented by the formula $Na_2[B_4O_5(OH)_4].8H_2O$, with 2 mol of water existing as hydroxyl groups and 8 mol as crystal water[16]. 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[17].

No study is found that ammonium carbonate may used as the leaching reactant for tincal in the literature. Hence, the goal of this investigation were to investigate the dissolution of tincal using ammonium carbonate solution and to determine the effects of the experimental parameters, including solution concentration, solid-to-liquid ratio, particle size and temperature. Ammonium carbonate solutions have a weakly acidic character. When ammonium carbonate ionizes in aqueous media, it yields ammonium and carbonate ions. When the ammonium ions hydrolyze, they provide the protons required for the dissolution reaction. The solutions obtained from the dissolution of tincal in the ammonium carbonate include sodium, carbonate, 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.

EXPERIMENTAL

Preparation of materials: The samples tincal obtained from Kirka Boron Plant, Eskisehir, 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 34.3 % B_2O_3, 16.30 % Na_2O, 44.5 % H_2O and 4.8 % the others. These values and the X-ray diffractogram of tincal were shown in Table-1 and Fig. 1, respectively[14].

Apparatus and procedure: In the experimental section 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 100 mL of ammonium carbonate 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 finished at a certain time period, the solution was filtered.

TABLE-1
CHEMICAL CHARACTERISTICS OF USED MATERIAL

Content	Per cent	Content	Per cent
B_2O_3	34.3	Others	4.8
Na_2O	16.3	H_2O	44.5

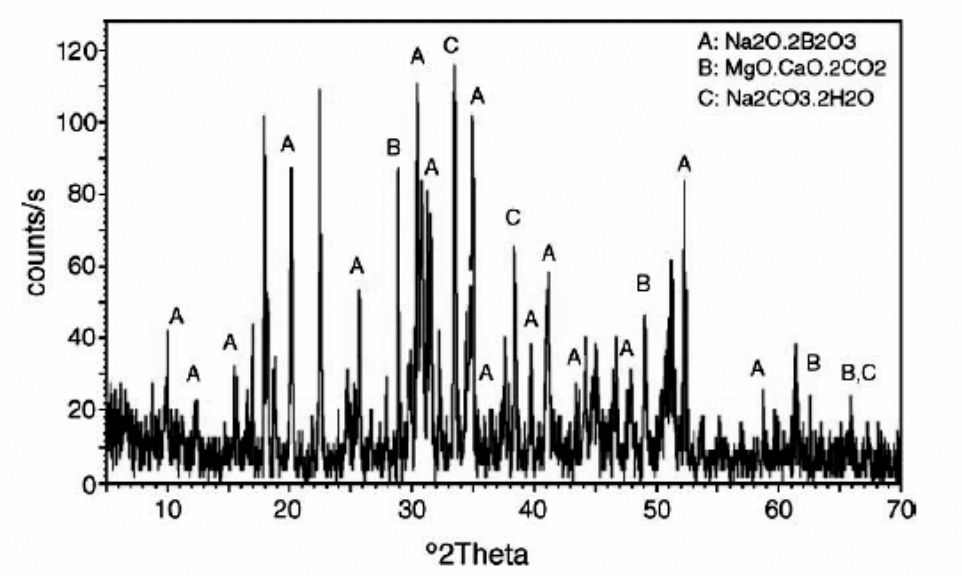

Fig. 1. X-ray diffractogram of tincal ore

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-2.

TABLE-2
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 (mol/L)	(0.010)	*(0.020)	(0.030)	(0.40)
Solid-to-liquid ratio (g/mL)	(0.01)*	(0.02)	(0.04)	(0.06)
Reaction temperature (K)	(288)	*(295)	(303)	(310)
Stirring speed (rpm)	(400)*	(500)	(600)	

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

RESULTS AND DISCUSSION

The effect of stirring speed was investigated on dissolution rate. The experiments were performed at stirring speeds of 400, 500 and 600 rpm 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 M, 1-0,6 mm, 1/100 g/mL and 305 K, respectively. It was found that the conversion factors were the same obtained from experimental results. From these results it can say that the reagent amounts of particles were fully suspended in the solution. Thus, it can be inferred that the effect of stirring speed exerts no important effect on the dissolution rate[15,19].

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

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_4^+{}_{(aq)} + CO_3^{2-}{}_{(aq)} \quad (1)$$

The hydrolysis of NH_4^+ ions gives:

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)} \quad (2)$$

The reaction of tincal in aqueous medium is:

$$Na_2B_4O_5{\cdot}8H_2O(s) \longrightarrow 2Na^+{}_{(aq)} + B_4O_5^{2-}{}_{(aq)} + 8H_2O_{(aq)} \quad (3)$$

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

$$Na_2B_4O_5(OH)_4{\cdot}8H_2O(s) + (NH_4)_2CO_{3(aq)} \longrightarrow$$
$$2Na^+ + 2NH_{3(aq)} + CO_3^{2-}{}_{(aq)} + 4H_3BO_{3(aq)} + 5H_2O_{(l)} \quad (5)$$

Effects of parameters: The effect of parameters on the dissolution process was investigated for each parameter using the values given in Table-2. In the experiments, while the effect of one parameter was studied, the values of the other parameter shown with asterisks in Table-2 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. 2 indicate that the particle size has a significant effect on the dissolution of tincal. As seen in Fig. 2, as the particle size decreases, the dissolution rate increases, which can be attributed to the increase of the contact surface, with the decrease of the particle size per amount of the solid.

The effect of the ammonium carbonate concentration on dissolution rate, the experiments was carried out in concentrations of 0.010, 0.020, 0.030 and 0.040 M. The experiments to see the effect of ammonium carbonate concentration (Fig. 3) on dissolution rate with increased with increasing solution concentration; the concentration of H_3O^+ increases, therefore the dissolution rate of tincal increases with an increase of ammonium carbonate concentration[15,20,21].

The effect of solid-to-liquid ratio on the dissolution of tincal, the solid-to-liquid ratio was studied in the range of 1/100-6/100 g/mL and Fig. 4 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[19-21].

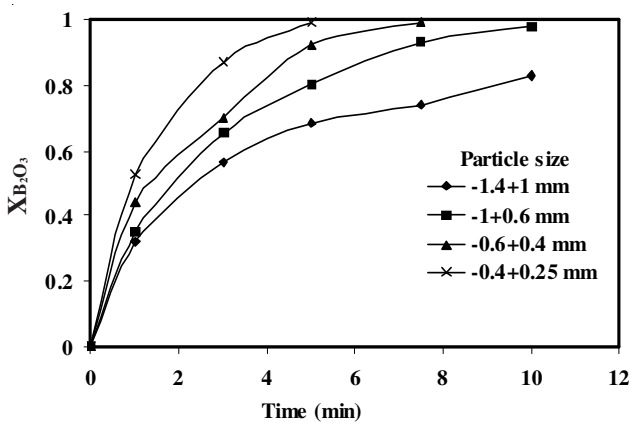

Fig. 2. Effect of the particle size on dissolution rate

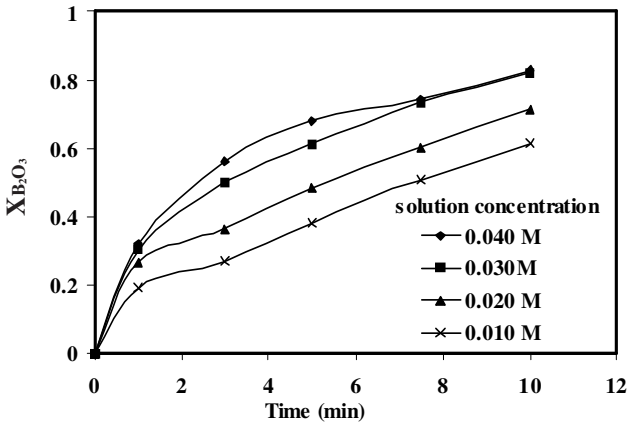

Fig. 3. Effect of the solution concentration on dissolution rate

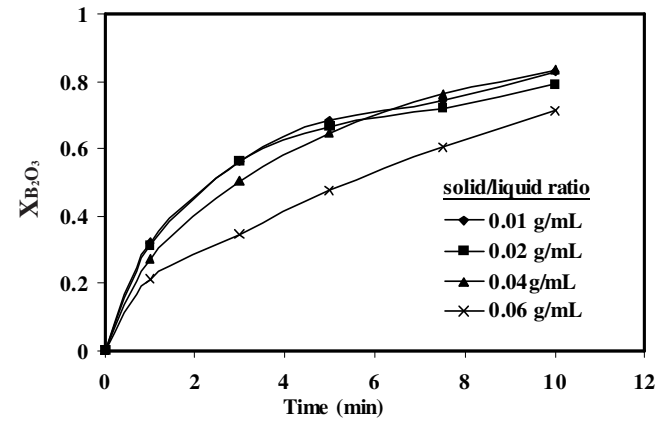

Fig. 4. Effect of the solid/liquid ratio on dissolution rate

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. 5. 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.

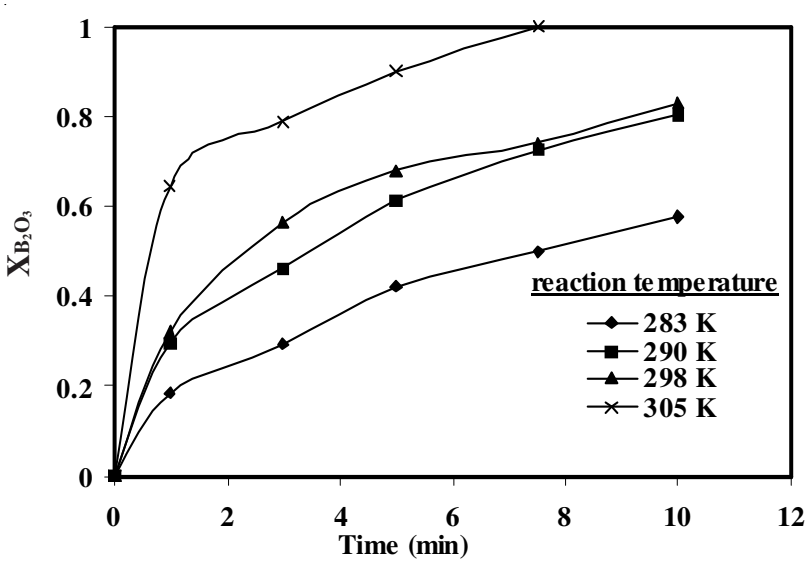

Fig. 5. Effect of the reaction temperature on dissolution rate

Conclusions

In this study, the dissolution kinetics of tincal was investigated in ammonium carbonate solutions in a batch reactor. The dissolution rate increases with increasing ammonium carbonate concentration, reaction temperature and with decreasing particle size and solid to liquid ratio. It was found that tincal could be dissolved in ammonium carbonate solution in short period of time, low temperature and at much diluted solution concentration[15]. This mean that leaching tincal in ammonium carbonate is both economical and do not contribute to environmental pollution. Consequently, it can say that ammonium carbonate can be used as a good leachant for tincal mineral at industrial area.

Nomenclature

C = Concentration of ammonium carbonate, (mol/L)
S/L = Solid-to-liquid ratio, (g/mL)
R = Universal gas constant, (J/mol K)
T = Temperature, (K)
t = Reaction time, (min)
X = Reacted fraction of B_2O_3

REFERENCES

1. S. Sahin, *Desalination*, **143**, 35 (2002).
2. A. Gür, *Chin. J. Inorg. Chem.*, **24**, 467 (2008).
3. E. Çetin, I. Eroglu and S. Özkar, *J. Crystal Growth*, **231**, 559 (2001).
4. C. Özmetin, M.M. Kocakerim, S. Yapici and A. Yartasi, *Ind. Eng. Chem. Res.*, **35**, 2335 (1996).
5. A. Gür and A. Selçuk, *Asian J. Chem.*, **19**, 3345 (2007).
6. M. Alkan, M. Oktay, M.M. Kocakerim and Z. Karagölge, *Hydrometallurgy*, **26**, 255 (1991).
7. A. Gür, *Korean J. Chem. Eng.*, **44**, 588 (2007).
8. A. Gür, A. Yildiz, H. Çelik and A. Selçuk, *Asian J. Chem.*, **20**, 2929 (2008).
9. A.M. Ranjitham and P.R. Khangaonkar, *Hydrometallurgy*, **23**, 177 (1990).
10. P. Raschman, *Hydrometallurgy*, **56**, 109 (2000).
11. A. Gür and E. Alkan, *J. Chem. Eng. Japan*, **41**, 354 (2008).
12. A. Gür, *Acta Phys.-Chim. Sin.*, **22**, 1287 (2006).
13. A. Ekmekyapar, R. Oya and A. Künkül, *Chem. Biochem. Eng. Q.*, **17**, 261 (2003).
14. Y. Abali, U.S. Bayca and E. Mistincik, *Chem. Eng. J.*, **123**, 25 (2006).
15. A. Gür and M. Kandilcik, *Chin. J. Inorg. Chem.*, **25**, 767 (2009).
16. W. Gerhartz, Ullmann's Encyclopedia of Industrial Chemistry, Wiley, Germany, Vol. A4 (1985).
17. T. Dickson, Etibank at Kirka from Ore to Derivatives, Industrial Minerals (1985).
18. W.W. Scot, Standard Method of Chemical Analysis, D. Van Nostrand, New York (1963).
19. A. Gur, A. Yildiz and H. Ceylan, *Asian J. Chem.*, **18**, 2002 (2006).
20. M. Tunc, M.M. Kocakerim, A. Gur and A. Yartasi, *Energy, Educ. Sci. Technol.*, **3**, 1 (1999).
21. M. Tunc, A. Gur, M.M. Kocakerim and A. Yartasi, *Energy, Educ. Sci. Technol.*, **3**, 32 (1999).

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