Dissolution of thermally dehydrated colemanite in sulphuric acid solutions

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ABSTRACT

Boron and boron compounds are widely used in industrial applications. In the boron reserves colemanite is one of the most important underground riches. In this study, the dissolution of thermally dehydrated colemanite in aqueous sulphuric acid solutions was investigated in a batch reactor employing the parameters of dehydration temperature, acid concentration and reaction temperature. It was found that the dissolution rate increased with increasing dehydration temperature, acid concentration and reaction temperature.

Key words: Boron, boric acid, sulphuric acid, colemanite, dissolution kinetics, dehydration.

INTRODUCTION

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 disinfectant and as food preservative. Borax is widely used in welding and brazing of metals, and more recently, boron compounds have found applications for hand cleansing, high-energy fuels, cutting fluids and catalysts[1]. Turkey possesses approximately 60% of the world's boron reserves. The known borate reserves in Turkey are located in four main districts, namely Emet, Bigadiç, Kýrka and Mustafakemalpaþa[2]. Boron in general is found as calcium or sodium borates or both in nature. Colemanite together with other borates is chiefly found in Bigadiç town in Balýkesir province and Emet town in Kütahya province in Turkey.

There have been many investigations on the kinetics and mechanisms of the dissolution of boron minerals in aqueous solutions. In a study performed on the extraction of boric acid with carbon dioxide gas in aqueous media from colemanite and optimum working conditions were found to be 70 °C reaction temperature, 0,1 g/ml solid-to-liquid ratio, 273.58 kPa gas pressure and 120 min reaction time. Under these optimum conditions, the boric acid extraction efficiency from calcined colemanite was 99.55% [3]. Imamutdinova investigated the dissolution of boron minerals such as inyoite, ulexite, colemanite, and hydroboracite by using various mineral acids[4]. It was reported that the dissolution curves of the borates were the same type with respect to all the mineral acids used, and the maximal dissolution changed according to the nature of the mineral acid as well as the medium temperature. In the studies in which the dissolution kinetics of some boron minerals was investigated in basic media, films of metal oxides or metal hydroxides have been observed to form on the surface of product crystals at base concentrations above certain values, and these films appeared to

limit the dissolution[5,6]. Some studies on the use of ammonium salt for the leaching ores are found in literature: Dissolution mechanism of colemanite in H_2SO_4 was investigated and it was seen that when the concentration of SO_4^{-2} increases the dissolution rate decreases[7]. 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[8,9]. Furthermore the Taguchi method was used to determine optimum conditions for the dissolution of ulexite in NH_4Cl solution[10]. Ammonium carbonate solutions were used as leachant for malachite, because basic ores often consumeacids, and therefore a basic matter more lixiviant than sulphuric acid, may be attractive[11]. In another study the leaching of malachite with ammonium sulphate solutions has been investigated[12]. The leaching of magnesite with ammonium chloride solution has also been investigated[13]. 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[14]. 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 5wt. % H_3PO_4 solutions H_3BO_3 solid film formed on crystals , this restricted the dissolution rate of the mineral[15].

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[16]. It was found that the ore achieved activity and the B_2O_3 concentration was higher when it was calcined. 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[17]. Alkan and Kocakerim, conducted research to determine the dissolution kinetics of pure ulexite in water saturated with SO_2 and found that the process was controlled by chemical reaction and the activation energy was 58.01 kJ,mol^{-1}[18]. Kucuk et al., 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}[19]. In literature no work was found about the dissolution kinetics of thermally dehydrated colemanite in sulphuric acid solution. Therefore in the current study, the dissolution of thermally dehydrated colemanite was investigated. Dehydration temperature, acid concentration, and reaction temperature were chosen as parameters and their effects on dissolution rate were evaluated.

EXPERIMENTAL

The colemanite mineral used in the study was obtained from Emet-Mine (Kütahya-Turkey).The sample mineral was first broken into small pieces, ground, and sieved with ASTM standard sieves to have three samples with the particle sizes of -600+212 μm. The chemical composition of colemanite ore is given in Table1. 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.

Dissolution experiments were performed in a 250 mL jacketed glass reactor equipped with gas inlet and outlet tubing. Reactor content was stirred with a mechanical stirrer with tachometer, and the temperature was controlled with a constant temperature circulator. At the and of the desired period the time, the constant of the vessel was filtered as soon as the process finished ,and B_2O_3 in the solution was analyzed as titrimetically using a digital titrator. The fraction of our sample reacted is defined:

XB_2O_3 = the amount of dissolved B_2O_3/ the amount of B_2O_3 in original sample.

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
Other	1.74

RESULTS AND DISCUSSION

While the effect of one of the parameters was being determined, the values of all the others were kept constant. The data obtained were plotted as time vs. conversion fraction (the amount of B_2O_3 taken into solution/the amount of B_2O_3 in the original sample).

The samples thermally dehydrated previously at temperatures of 80,150, 250, 350 and 450 °C were used to determine of the effect of the dehydration temperature on the dissolution. The concentration and reaction temperature of the acid

solution were 1.5 M and 40 °C. During the dehydration process the way colemanite loses its crystal water depends on the temperature. It is suggested that deyhdroxylation occur in two pace, first involving the formation of water from hydroxyl groups, and the second involving the breaking of water and B-O-B bonds, followed by the explosive escape of the hydroxyl water at a temperature of around 400 °C [20]. It was seen that dissolution rate increased with increasing dehydration temperature (Fig.2, table 2)

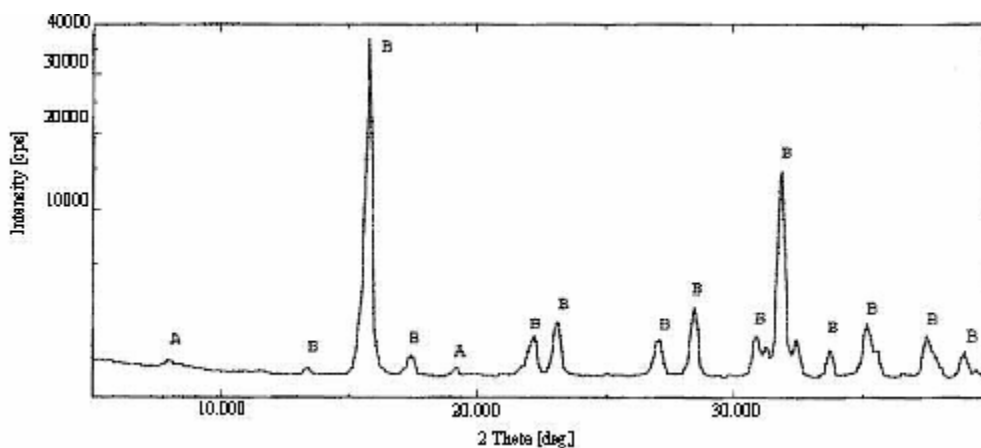The effect of acid concentration on dissolution rate was investigated by using four

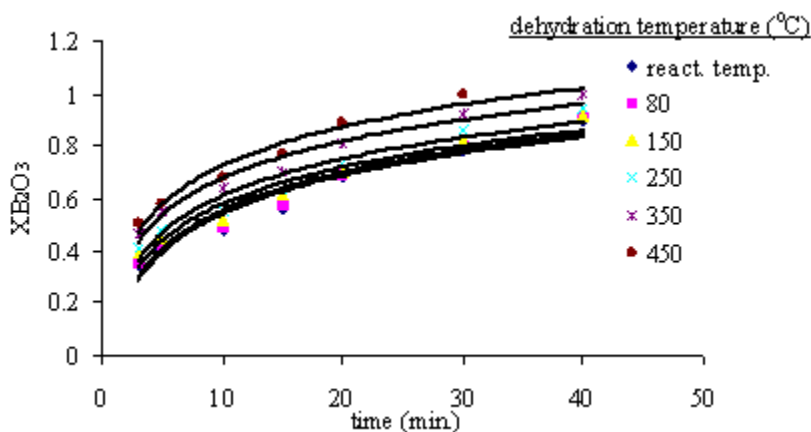Fig. 1: X-ray diffractogram of colemanite ore: (A) SiO_2, (B) $Ca_2B_6O_{11}$, $5H_2O$

Fig. 2: The effect of dehydration temperature on the dissolution rate

different concentrations (0. 5, 1, 0.15 and 2 mol. L^{-1}). In these experiments, the reaction temperature was kept constant as 25 °C, particle size as -600+212 μm, solid/liquid ratio as 1g/100mL, and stirring speed as 500 min^{-1}. The results, as showed in Fig.3 and Table 2, show that the dissolution rate increases acid concentration increases.

The effect of reaction temperature on dissolution rate was investigated by using the reaction temperatures 20, 30, 40 and 50°C and keeping the other parameters constant: particle size as -600+212 μm, stirring speed at 500 min^{-1}, acid concentration 1.5 molL^{-1} and solid/liquid ratio as 1 g/100mL. According to the results given in Fig. 4 and Table 2, the dissolution rate of colemanite increased as the temperature was increased, this finding was attributed to the positive effect of reaction temperature on dissolution rate.

Table 2: The values of conversion factor (XB$_2$O$_3$) calculated from experimental data

Effect of the H$_2$SO$_4$ concentration (Particle size: -600+212 μm, stirring speed: 500 rpm, reaction temperature: 40 °C, solid to liquid ratio: 1g/100cm^3)				
t/min.	0.5 mol /dm^3	1 mol/dm^3	1.5 mol/dm^3	2 mol/dm^3
0.4107	0.3644	0.3421	0.3013	
5	0.4378	0.4241	0.4013	0.3424
10	0.5116	0.4908	0.4818	0.4416
15	0.5935	0.5818	0.5612	0.5313
20	0.7323	0.6909	0.6837	0.6523
30	0.8419	0.7986	0.7828	0.7221
40	0.9722	0.9009	0.8998	0.8186

Effect of the dehydration temperature (Solid to liquid ratio: 1g/100cm3 , stirring speed: 500 rpm, H$_2$SO$_4$ concentration: 1.5 mol/dm^3, particle size: -600+212 μm)					
t/min.	80°C	150 °C	250°C	350°C	450°C
3	0.3515	0.3889	0.4121	0.4629	0.5026
5	0.4222	0.4424	0.4818	0.5512	0.5783
10	0.4888	0.5212	0.5516	0.6423	0.6804
15	0.5742	0.6111	0.6323	0.7021	0.7717
20	0.6912	0.7022	0.7332	0.8111	0.8929
30	0.8026	0.8216	0.8644	0.9218	0.9989
40	0.9098	0.9171	0.9429	0.9998	-

Effect of the reaction temperature (Particle size: -600+212 μm, stirring speed: 500 rpm, H$_2$SO$_4$ concentration: 1.5mol/dm^3, solid to liquid ratio: 1g/100cm^3)				
t/min.	20 °C	30 °C	40 °C	50°C
3	0.2212	0.2736	0.3421	0.3818
5	0.2608	0.3198	0.4013	0.4724
10	0.3713	0.4213	0.4818	0.5978
15	0.4361	0.4726	0.5612	0.7033
20	0.5400	0.6121	0.6837	0.7926
30	0.6316	0.7286	0.7828	0.8910
40	0.7414	0.8301	0.8998	0.9798

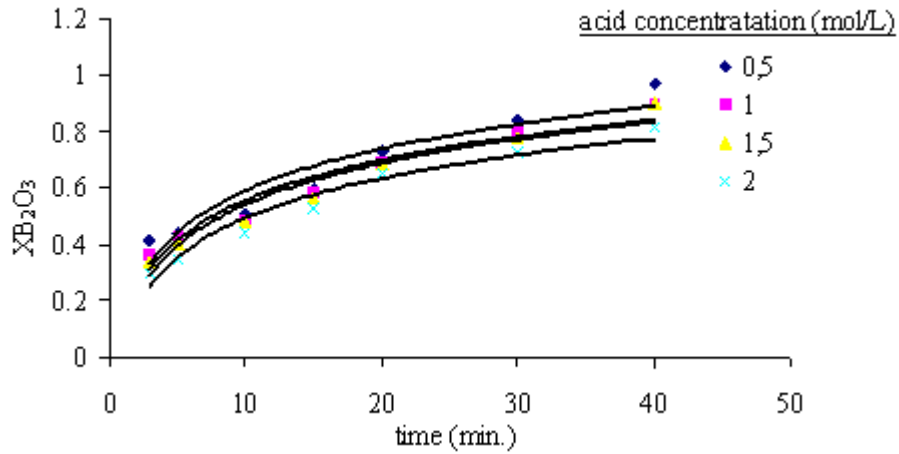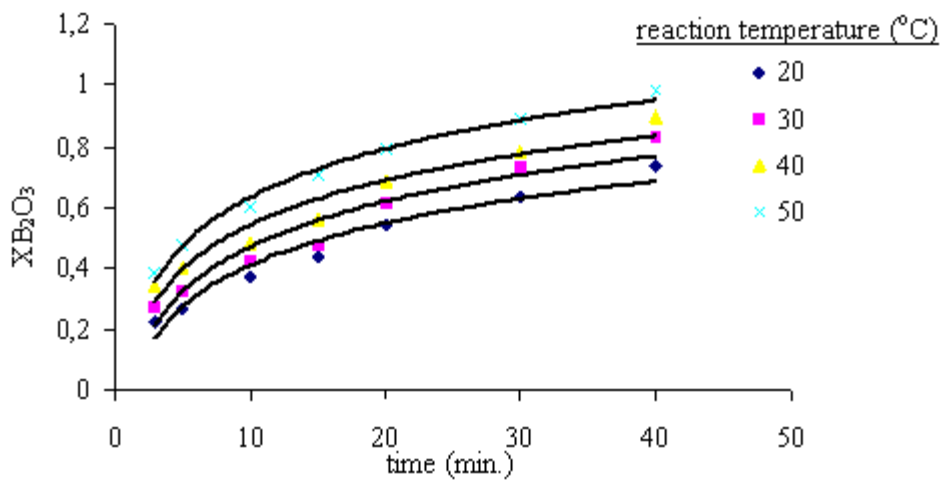**Fig. 3: The effect of sulphuric acid concentration on the dissolution rate**

Fig. 4: The effect of the reaction temperature on the dissolution rate

CONCLUSIONS

In this work it is seen that colemanite can be dissolved in sulphuric acid solutions. The dissolution rate was found to increase with increasing dehydration temperature, reaction temperature and acid concentration. And it is also say that dehydration process has a important effect on dissolution rate, because dissolution rate increased with increasing giving off water from colemanite ore.

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