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DISSOLUTION KINETICS OF SMITHSONITE IN BORIC ACID SOLUTIONS

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Abstract: The dissolution of smithsonite in boric acid solutions was investigated. The influence of the reaction temperature, acid concentration, solid-to-liquid ratio, particle size and stirring speed on the zinc extraction were determined in the experiments. The results show that the dissolution rate increases with increasing acid concentration and reaction temperature, and with decreasing particle size and solid-to-liquid ratio. The dissolution results were analyzed by reaction control models. The activation energy of smithsonite in boric acid solution was also calculated.

Keywords: *dissolution, leaching, kinetics, reaction engineering, smithsonite, zinc borate*

Introduction

A total of 0.2 teragrams per year of boric acid is produced in Turkey by ETI Mine. In this facility, dissolution of colemanite concentrates in an aqueous solution of sulfuric acid at 85 ^{o}C is followed by a filtering and crystallization process. The boric acid produced has the chemical formula H_3BO_3, 56.25% B_2O_3 content and 60–1000 μm particle size. The main application areas of boric acid are in the glass and fiberglass industries.

Zinc is produced mostly from zinc sulfide ores because the sulfides can be easily separated from gangue and concentrated by conventional flotation techniques. Oxidized zinc ores, such as smithsonite, willemite, hydrozincite, zincite and hemimorphite have also long been an important source of zinc. However, their concentration was difficult and, until relatively recently only rich ores were exploited, using limited concentration by washing and gravity methods. The exploitation and metallurgy of low-grade oxidized zinc ores was very limited (Chenglong et al. 2008). In recent years, the dissolution kinetics of smithsonite in acid or alkaline solutions have been studied. The dissolution kinetics of smithsonite ore in aqueous gluconic

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acid solutions were studied by Hursit et al. (2009). They found that the rate of dissolution of smithsonite in gluconic acid is independent of stirring speed, which indicates that the reaction is not controlled by the diffusion in the liquid phase. The reaction rate was very sensitive to temperature in the range of 30–80 ^{o}C. They also reported that the dissolution rate increased with decreasing particle size. The dissolution kinetics follow a shrinking core model with the surface chemical reaction as the rate-controlling step. The dissolution kinetics of smithsonite ore in ammonium chloride solution were investigated by Ju et al. (2005). Zinc exists as smithsonite and hemimorphite in the lead flotation tailings from the Dandi mineral processing plant in north western Iran. The extraction of zinc from tailings was studied in the Dandi plant using sulfuric acid. A maximum zinc recovery rate of 98% was obtained by dissolution with 2M sulfuric acid for 2 h at 60°C with a solid-to-liquid ratio of 25% and agitation at 480 rpm. Analysis of the experimental data indicates that the dissolution of zinc carbonate consists of a single rate controlling step (Espiari et al. 2006). The results of a dissolution kinetics study of low-grade zinc silicate ore with sulfuric acid by Abdel-Aal (2000) showed that dissolution of about 94% of zinc is achieved using 200–270 mesh ore particle size at a reaction temperature of 70 ^{o}C for 180 min reaction time with 10% sulfuric acid concentration. Dissolution kinetics indicate that diffusion through the product layer is the rate-controlling process during the reaction. Terry and Monhemius (1983) reported on the dissolution kinetics of natural hemimorphite and natural and synthetic willemite. They found that the dissolution was diffusion-controlled for hemimorphite dissolution and chemically-controlled for willemite dissolution. Santos et al. (2010) studied the dissolution kinetics of zinc silicate ore in sodium hydroxide solutions. Their results indicated that 5 h was required for the complete dissolution of the ore and that zinc extraction could reach 90% at the highest temperature tested. The temperature strongly influenced the zinc dissolution, as an increase of 20 °C in this variable (from 70 °C to 90 °C) enhanced the dissolution from 36% to 90%.

Zinc borates have been used as flame retardants, smoke suppressants, after-glow suppressants, antibacterials and additives to protect wood products above ground from insect and fungal attacks, and as antitracking agents in both halogen-containing and halogen-free polymers. Zinc borate can be isolated as a crystalline material in various forms with different chemical compositions and structures. One of these is crystalline zinc borate which has the formula of $2ZnO.3B_2O_3.7/2H_2O$, and the unusual property of retaining its water of hydration at temperatures of up to 290 ^{o}C. This thermal stability makes it attractive as a fire retardant additive for plastics and rubbers that require high processing temperatures. The most widely zinc borates are those with compositions of $3ZnO\cdot 2B_2O_3\cdot 7/2H_2O$, $2ZnO\cdot 3B_2O_3\cdot 3H_2O$ and anhydrous $2ZnO\cdot 3B_2O_3$ (Tian et al. 2008; Roskill 2002; Shete et al. 2004; Shengli et al. 2010).

The aim of the present study is to investigate the dissolution kinetics of smithsonite in boric acid solutions, to describe the dissolution kinetics model, to calculate the activation energy of the system, and to find the effective parameters of the dissolution rate. The homogeneous and heterogenous control model will be described for smithsonite in boric acid solutions. The activation energy of smithsonite in boric acid solution will be determined from the Arrhenius equation. This study will be the first investigation of the kinetics model of smithsonite in boric acid solution.

Experimental procedure

Smithsonite ore was obtained from Hakkari, Turkey. The sample was crushed using a jaw crusher and then a roll crusher. The sample was sieved at 200 µm, 355 µm, 500 µm, 1000 m and 1250 µm. ICP-OES was used for the chemical analysis of the smithsonite. The sample of smithsonite was examined by X-ray diffraction (Philips PW 3710 BASED).

The dissolution experiments were carried out in a 250-cm^3 three-necked glass reactor at atmospheric pressure. A mechanical stirrer with a digital display was used to agitate the solution. The heating or cooling of the reactor was carried out by means of a bath. All reagents were of analytical grade. In the dissolution process, 50 cm^3 of boric acid solution was placed in the reactor, and the stirring was started. After the desired reaction temperature was reached, a given amount of sample was added to the solution. After a certain period of time, the solution was filtered by filter paper without any change in temperature. Each experiment was repeated at least twice.

The dissolved Zn is given as a percentage:

$$\%\ Dissolved\ Zn = \frac{M_1}{M_o}100 \tag{1}$$

where M_1 is the amount of Zn in the solution, and M_o is the amount of Zn in the original sample.

The solution obtained from dissolution was filtered at a high temperature, and the filtrate was allowed to cool in order to determine its zinc content. When it cooled, solid crystals were formed. In order to determine the zinc content of these crystals by ICP-OES instrument, solid samples were re-dissolved in sulphuric acid solution; this solution was taken and chemical analysis was performed by ICP-OES. The experimental parameters used in the dissolution treatments are given in Table 1.

Table 1. Parameters and their values

Parameters	Values				
Reaction temperature, °C	26	30	35	40	60
Acid concentration, mol/dm^3	0.1	0.3	0.5	0.7	0.9
Solid-to-liquid ratio, % w/v	0.5	1	2	10	-
Stirring speed, rpm	100	300	500	1000	-

Results and discussions

The chemical analysis of the smithsonite ore showed that it contained 37.74% ZnO, 19.46 % PbO and 2.05% Fe_2O_3 (Table 2). X-ray diffraction of smithsonite ore is shown in Figure 1. The major minerals are smithsonite ($ZnCO_3$), hidrozincite ($Zn_5(OH)_6(CO_3)_2$), cerrussite ($PbCO_3$), and the minor minerals are hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$) and hematite (Fe_2O_3).

Table 2. Chemical analysis of smithsonite ore

Oxides	%
ZnO	37.74
PbO	19.46
Fe_2O_3	2.05
SO_3	0.12
P_2O_5	0.09
WO_3	0.38
SiO_2	0.70
Al_2O_3	0.09
MgO	0.20
Na_2O	0.11
CaO	0.32
MnO	0.43
ZrO	0.07
Others	3.12
LOI	35.50

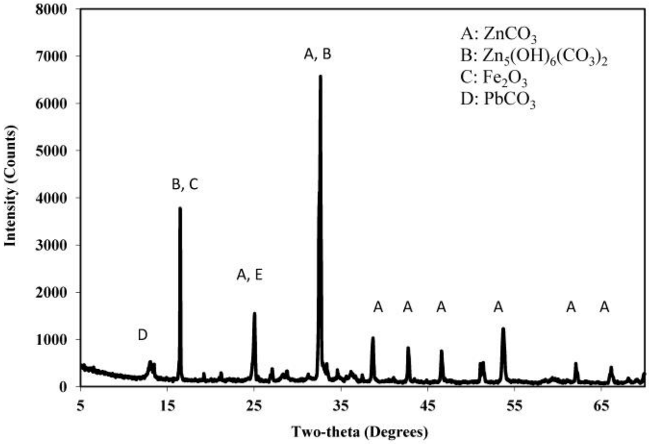

Fig. 1. XRD pattern of the smithsonite sample

The effect of particle sizes of 200, 500, and 1000 μm on the dissolution rate of smithsonite was investigated at 40 °C in a 0.9 mol/L boric acid concentration with a solid to liquid ratio of 1 % and a stirring speed of 700 rpm. It is shown in Figure 2 that the dissolution of smithsonite for 60 minutes attained 94.81 % Zn at +200 μm particle size, and 64.47 % Zn at +1000 μm particle size. The dissolution rate increased with decreasing particle size. This can be explained by the fact that as the particle size is reduced, the total surface area is increased. As the surface area increases, contact between the reactive and the particle surface increases. Similar results were observed for the dissolution of smithsonite ($ZnCO_3$) and zinc silicate ore in sulfuric acid solutions (Espiari et al. 2006; Abdel Aal, 2000).

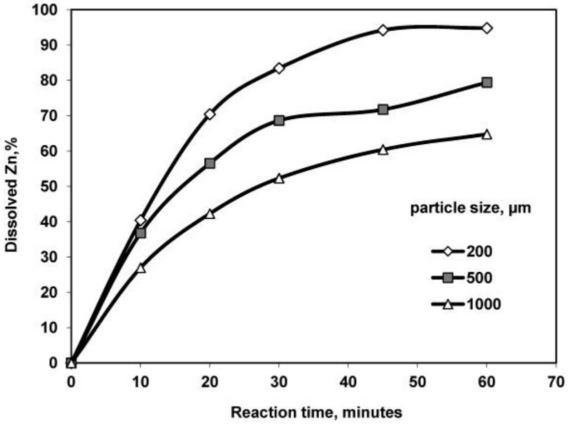

Fig. 2. Effects of particle size (40 °C, 0.9 mol/L boric acid 1 % solid, 700 rpm) on the dissolution of smithsonite

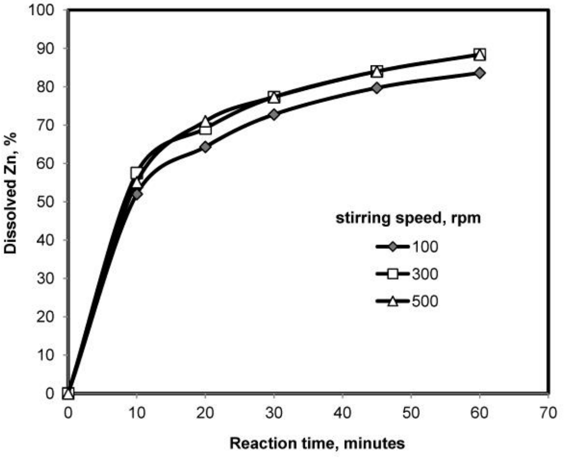

Fig. 3. Effects of stirring speed (40 °C, 0.9 mol/L boric acid, 1 % solid, 200 μm) on the dissolution of smithsonite

The effect of stirring speeds of 100, 300, 500, 700 and 900 rpm on the dissolution rate of smithsonite was investigated at 40 °C in a 0.9 mol/dm^3 boric acid concentration with a solid-to-liquid ratio of 1 % and a particle size of 200 μm (Figure 3). An increase in the stirring speed did not have a significant effect on the dissolution rate.

The experiments were performed over the 0.1–0.9 mol/dm^3 acid concentration range with a solid to liquid ratio of 1%, a particle size of 200 μm and a stirring speed of 700 rpm at 40 °C for 30 minutes. The dissolution rate of smithsonite in boric acid was determined and is shown in Figure 4. Dissolution rate increased with increasing boric acid concentration. However, boric acid crystals were observed in the boric acid solutions when the experiments were performed at high acid concentrations (above 0.9 mol/dm^3). The crystallization temperature of boric acid was determined to be 35 °C (Kuskay and Bulutcu 2011). This behavior was observed in previous studies by Souza et al. (2009), who studied the effect of sulfuric acid solutions on zinc silicate ore.

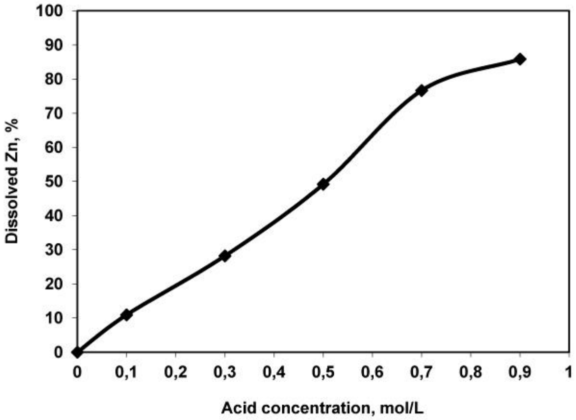

Fig. 4. Effect of boric acid concentration (40 °C, 1 % solid, 200 μm, 30 min, 700 rpm) on the dissolution of smithsonite

The effect of solid-to-liquid ratio on the dissolution rate of smithsonite was investigated in a 0.9 mol/dm^3 boric acid concentration with a particle size of 200 μm and stirring speed of 700 rpm at 40°C. The results are shown in Figure 5. The results show that the dissolution rate of smithsonite decreases with increasing solid-to-liquid ratio. This may be due to faster saturation of the liquid.

The experiments were carried out at different temperatures: 26, 30, 35, 40 and 60 °C. The effect of the temperature on the dissolution rate of smithsonite was investigated in a boric acid concentration of 0.9 mol/dm^3 with a solid-to-liquid ratio of 1 %, a particle size of 200 μm and a stirring speed of 700 rpm. As shown in Figure 6, the dissolution rate of smithsonite in boric acid solution increases with increasing temperature. Similar results were also obtained by Bodas (1996) and Espiari et al. (2006), who carried out dissolution experiments with a zinc silicate ore containing hemimorphite and smithsonite as major zinc minerals.

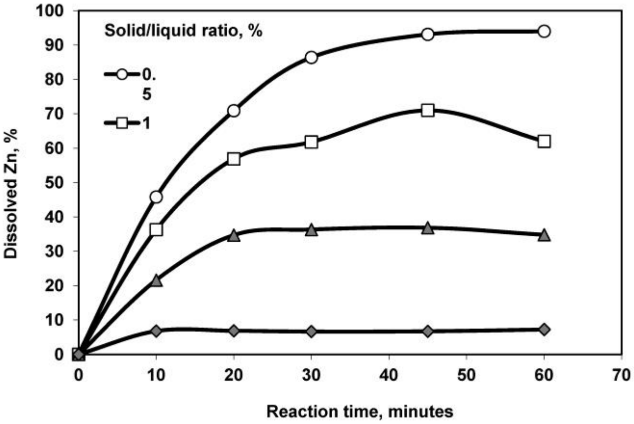

Fig. 5. Effects of solid-to-liquid ratio (40 °C, 0.9 mol/L boric acid, 200 μm, 700 rpm) on the dissolution of smithsonite

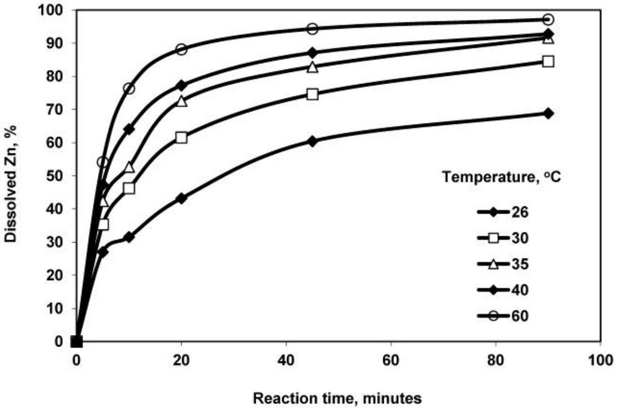

Fig. 6. Effect of reaction temperature (0.9 mol/L boric acid, 1 % solid, 200 μm, 700 rpm) on the dissolution of smithsonite

The rate of reaction between a solid and a liquid can be described with heterogeneous or homogeneous control models. Fluid-solid heterogeneous reaction systems have important applications in chemical and metallurgical processes. A successful reactor design for this process depends mainly on kinetic data. Reactions occurring between fluid and spherical solid particles can be expressed as follows (Levenspiel, 1999).

$$A_{(f)} + bB_{(s)} \longrightarrow products \qquad (2)$$

The results of dissolution rates of smithsonite at different temperatures are given in Figure 6. The experimental data were analyzed using equations of the homogeneous kinetic models and heterogeneous kinetic models. The regression coefficient values R^2 were found to be in the range of 0.8675–0.9483 for the first order pseudo homogeneous control model, 0.5673–0.8862 for the film diffusion control model, 0.7694–9214, for the chemical reaction control model and 0.7801–9739 for the product layer diffusion control model. This indicates that these models cannot be fitted due to nonlinear regression. The results for the dissolution rate of smithsonite in boric acid fit the second-order reaction control model. The kinetics of this model is given by the following equation:

$$\frac{X}{1-X} = kt \tag{3}$$

The R^2 value was close to 1 and the plots of $X/(1 - X)$ versus time (t) had high linearity. X is defined as follows:

$$X_{Zn} = \frac{Dissolved\ amount\ of\ Zn}{Total\ amount\ of\ Zn\ in\ the\ sample} \tag{4}$$

The results indicated that the k values increase with the dissolution temperature. The k values increased by nearly 17 times as the dissolution temperature increased from 26 to 60 °C.

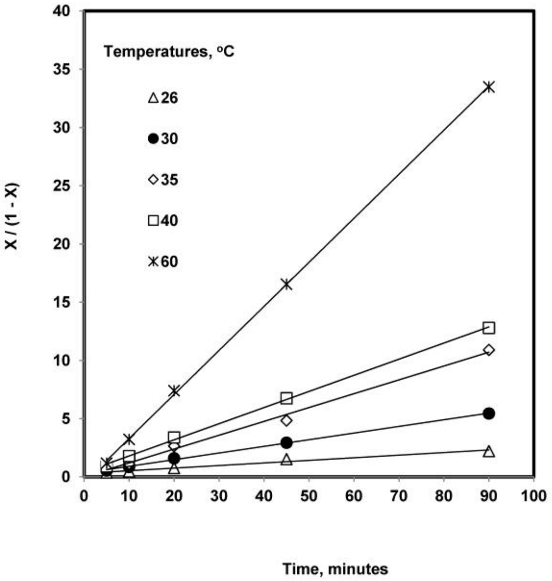

Fig. 7. The variation in $X/(1 - X)$ with time at different temperature

A plot of the pseudo-second-order homogeneous reaction control model, $X/(1–X)$, versus time results in a linear relationship at different temperatures is shown in Figure 7. The reaction control model of smithsonite in boric acid solution was determined to follow a second-order reaction control model. The activation energy of the dissolution was calculated from the Arrhenius equation (5).

$$k = Ae^{(-E/RT)} \tag{5}$$

As seen in Figure 8, ln$k$ versus $1/T$ is plotted and ln$k$ versus $1/T$ gives a straight line of slope $–E/R$. The A values and the activation energy, E, of the dissolution rate of smithsonite in boric acid was determined as follows from the slope of this line: E = 62.03 kJ/mol.

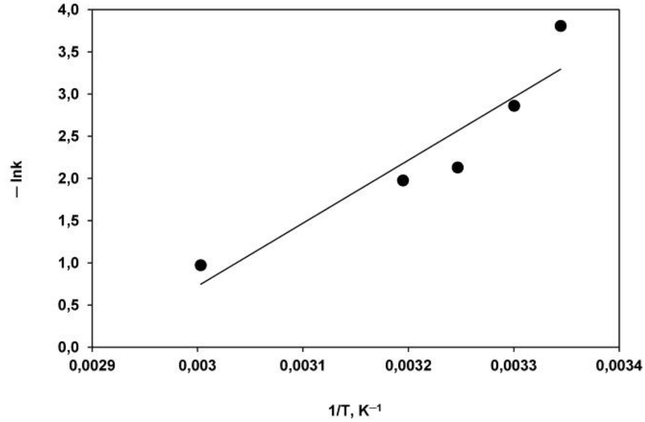

Fig. 8. Arrhenius plot for the leaching of smithsonite

The activation energy of smithsonite in boric acid solution was calculated to be 62.03 kJ/mol. The activation energies calculated by different authors for smithsonite and similar mineral are given in Table 3.

Table 3. Selected values of activation energies reported for the leaching of smithsonite or zinc silicates

Minerals	Leachants	Activation energy kJ/mol	References
Smithsonite	Gluconic acid solutions	47.9	Hursit et al., 2009
Smithsonite	Ammonium chloride solutions	21.3	Ju et al., 2005
Smithsonite	Hydrochloric acid solutions	59.5	Dhawan et al., 2011
Smithsonite	Boric acid solutions	62.0	*This study*
Zinc silicate ore	Sulfuric acid solutions	13.4	Abdel-Aal, 2000
Zinc silicate ore	Sodium hydroxide solutions	67.8	Santos et al., 2010
Zinc silicates	Sulfuric acid solutions	66.8	Souza et al., 2009
Calcined zinc silicates	Sulfuric acid solutions	59.5	Souza et al. 2009

The activation energy of smithsonite in boric acid solution was determined as 62.03 kJ/mol, which is within the range of activation energies of 13.4–67.8 kJ/mol reported for zinc ores.

The dissolution process of smithsonite in boric acid solution takes place via the following set of reactions. The dissolution of boric acid is obtained in an aqueous medium as follows:

$$B(OH)_{3(s)} + H_2O \longrightarrow B(OH)_4{}^-{}_{(aq)} + H^+{}_{(aq)} \tag{6}$$

The dissolution of smithsonite in boric acid proceeds as follows:

$$ZnCO_{3(s)} + 4B(OH)_4{}^-{}_{(aq)} + 4H^+{}_{(aq)} \longrightarrow ZnB_4O_{7(s)} + CO_{2(g)} + 10H_2O_{(l)} \tag{7}$$

The reaction between smithsonite and boric acid results in zinc borate.

The solution, which was obtained in the experiment by dissolution carried out under optimum conditions, was filtered at a high temperature. The filtrate (the liquid phase) was left to cool and the resulting crystals were dried at room temperature.

The X-ray diffractogram of the crystallized product is given in Figure 9. The crystals were analyzed by X-ray diffractometer and found to be zinc borate (ZnB_4O_7). A SEM (Philips PW 3710 BASED) image of the crystallized product is given in Figure 10. Zinc borate crystals consisting of irregular platelets were formed.

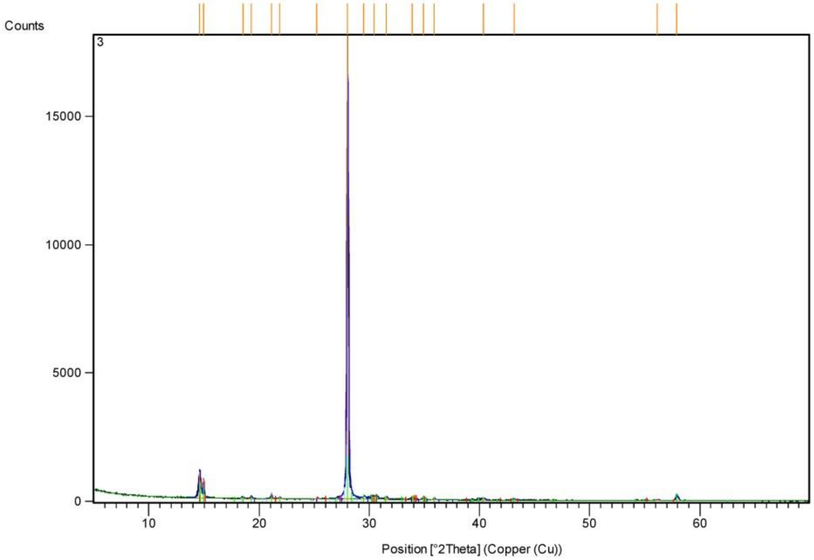

Fig. 9. XRD pattern of leaching product zincborate (200 µm, 40°C, 0.9 M, 700 rpm)

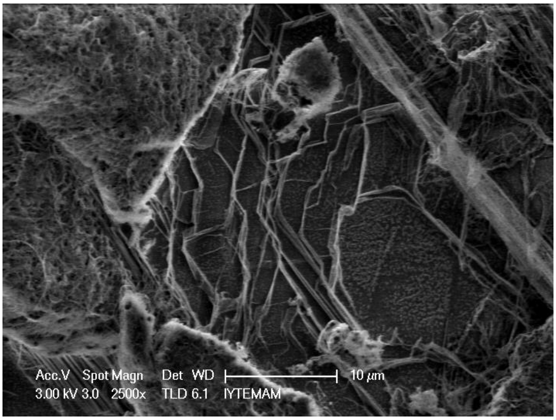

Fig. 10. SEM image of leaching product zincborate (200 µm, 40°C, 0.9 M, 700 rpm)

Conclusions

In this study, the kinetics model of smithsonite was investigated in boric acid solution. When the dissolution kinetics of zinc borate from smithsonite in boric acid solutions were studied in a batch reactor, the results showed that the dissolution rate increases with increasing reaction temperature and decreasing solid-to-liquid ratio. The most important parameter affecting the dissolution rate was found to be the reaction temperature, while the least important was found to be the stirring speed. The reaction control model of smithsonite in boric acid solution was determined to follow a second-order reaction control model, and the activation energy of smithsonite in boric acid solution was calculated to be 62.03 kJ/mol.

The reaction between smithsonite and boric acid results in zinc borate. The formed zinc borate passed into the liquid phase. The cerrussite, hemimorphite and hematite remained on the solid phase. As the liquid phase cooled, zinc borate crystals were precipitated.

The leaching kinetics of this laboratory-scale study was determined by the mathematical models. The findings of this study can be very useful for designing reactor on an industrial scale.

A number of substances are used as fire retardants in industry. The majority of organic fire retardants are halogenated compounds. However, the combustion products of these fire retardants are released as harmful toxic gases into the environment. The dissolution product of smithsonite and boric acid, zinc borate, is a non-toxic compound which is used as a fire retardant in industry. The dissolution of smithsonite and boric acid is also cheaper than using zinc oxide and sulphuric acid.

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