Dissolution of colemanite in $(NH_4)_2SO_4$ solutions

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Abstract−Turkey is the country having the richest boron ores in the world, and colemanite, tincal and ulexite are the ores being mined mostly in Turkey. These ores are used in the production of various boron compounds of which the production methods are generally patented. Colemanite ore also is reacted with sulfuric acid to product boric acid. Produced by this method, boric acid contains various impurities which reduce the market value and are difficult to remove. This study investigated the reaction between colemanite and ammonium sulfate as an alternative method to produce boric acid. Particle size, ammonium sulfate concentration, solid to liquid ratio and reaction temperature were chosen as parameters. In results, the conversion rate was increased by decreasing particle size and solid to liquid ratio, by increasing ammonium sulfate concentration and temperature. A semi-empirical model with 40.46 kJmol^{-1} activation energy representing this process was found as follows: $1-(1-X)^{1/3}=2.12 \times 10^2 \cdot C^{1.38} \cdot R^{-0.75} \cdot (S/L)^{-0.44} \cdot e^{-4866/T} \cdot t^{0.61}$

Key words: Ammonium Sulfate, Colemanite, Dissolution, Dissolution Kinetics

INTRODUCTION

In ancient Egypt and Rome, boron was used in durable glass production and mummification. At present, boron compounds are used in various industries, such as glass and ceramics, cleaning products, textile, agriculture and production of fire retardant. These compounds are obtained from boron ores, especially from colemanite $(2CaO \cdot 3B_2O_3 \cdot 5H_2O)$, ulexite $(Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O)$ and tincal $(Na_2B_4O_7 \cdot 10H_2O)$. Boric acid from colemanite and sulfuric acid and sodium borates and perborates from tincal are the principal boron products of Turkey having 72% of the reserves of the world boron ores.

Many researches have been carried out to clarify the kinetics and mechanisms of dissolutions of boron minerals in various acid solutions. It was stated in some researches dealing with which boron minerals were dissolved with inorganic acid solutions that the reaction products formed a product layer in mineral surface and this film decreased the reaction rate [Imamutdinova, 1967, 1978; Zdanovskii, 1982]. In a study in which the dissolutions of colemanite, ulexite and pandermite were investigated in disodium EDTA solutions, it was found that these minerals dissolved completely in EDTA solutions [Gülensoy and Savcı, 1976]. Leaching kinetics of colemanite by EDTA solutions was examined and it was determined that the dissolution rate increased with decreasing the particle size and pH and increasing the temperature and EDTA concentration [Karagölge et al., 1992]. Dissolution kinetics of colemanite were studied in CO_2-saturated waters and it was found that reaction rate was controlled chemically [Alkan et al., 1985]. Ceyhun et al. [1999] studied dissolution kinetics of colemanite in chlorine saturated waters and stated that dissolution rate increased with decreasing particle size and solid to liquid ratio, and in-creasing temperature. For this process activation energy was found to be 35.46 kJ·mol^{-1}. Okur et al. [2002] study-ing ultrasound effect on dissolution of colemanite found by nonlinear regression analysis that kinetics data fitted to Avrami model with 30 kJ·mol^{-1} of activation energy. Imamutdinova [1967] and Temur et al. [2000] examined dissolution of colemanite in phosphoric acid solutions. The former showed that maximum dissolution carried out in 10-15% H_3PO_4 solutions and $CaHPO_4$ might form. The latter determined that dissolution rate was surface chemical controlling with 53.91 kJ·mol^{-1} of activation energy. Küçük et al. [2002] studied the dissolution of Kestelek's colemanite in water saturated with SO_2 and the dissolution process was found to be chemically reaction-controlled. Özmetin et al. [1996] investigating dissolution of colemanite in acetic acid solutions determined that dissolution rate of colemanite obeyed the first order pseudo-homogeneous reaction model in the form of $-\ln(1-X)=k.t$. In another study, the investigators studied dissolution kinetics of colemanite in oxalic acid solutions and found that the dissolution rate was controlled by product layer (or ash layer) diffusion process [Alkan and Doğan, 2004]. Yartaşı et al. [1998] investigated kinetics and mechanism of leaching colemanite in boric acid solutions and showed that reaction rate was controlled by diffusion through product film around unreacted core of colemanite particles. X-ray diffractometer examinations in this study showed that solid product from crystallization of leaching solution contained H_3BO_3, $Ca(H_2BO_3)_2 \cdot 4H_2O$, $Ca[B(OH)_4]_2 \cdot 2H_2O$, $CaB_2O_4 \cdot 2H_2O$, $CaB_2O_4 \cdot 4H_2O$ and $CaB_2O_4 \cdot 5H_2O$. In other study, Küçük et al. [2005] studied the optimization of dissolution of ulexite in $(NH_4)_2SO_4$ solutions. Also, Küçük [2006] studied the application of Taguchi method in the optimization of dissolution of Ulexite in NH_4Cl solutions. Kum et al. [1994] studied the leaching kinetics of calcinated colemanite in ammonium chloride solutions and found that the dissolution rate fitted a homogeneous first order reaction model with 89 kJ·mol^{-1} activation energy. In this study, dissolution reaction was stated as follows:

$$2CaO \cdot 3B_2O_3 \cdot nH_2O + 4NH_4Cl + (7-n)H_2O \rightarrow 2CaCl_2 + 4NH_3 + 6H_3BO_3$$
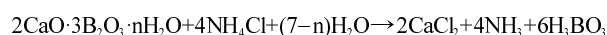
Here, the by-products are $CaCl_2$ and NH_3. NH_3 passes to gas phase

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when reaction mixture is heated, but $CaCl_2$ remains in the solution, and when boric acid is crystallized, Ca^{2+} and Cl^- brings about contaminations in solid boric acid phase. On the other hand, also, the pH of solution is too low in the currently used sulfuric acid process and in this pH(pH=1-2), Fe and Al dissolve, and solubility of gypsum ($CaSO_4 \cdot 2H_2O$) being a by-product of the reaction increases. In addition to these, the amount of sulfate ion in the reaction medium is too much. For these reasons, the produced boric acid is contaminated with above-mentioned ions and refined by using additional processes which increase production cost. ZareNezhad [2003] experimentally investigated the reaction of oxalic acid crystals with borax solution in a 1.5 L batch reactor at different operating conditions. The activation energy of the dissolution process also was determined as 12.89 kJ mol^{-1}. ZareNezhad [2004] investigated the production of boric acid through reaction of borax crystals with propionic acid in batch mode. Sevim et al. [2006] investigated kinetic analysis of thermal decomposition of boric acid from thermogravimetric data.

The aim of this study was to investigate dissolution of colemanite in ammonium sulfate solutions and to determine formation conditions of boric acid, as an alternative method to both sulfuric acid and ammonium chloride processes.

MATERIAL AND METHOD

Colemanite ore from Bigadiç, Turkey was cleaned externally, crushed ground and sieved to the fractions of $-10+18, -20+40, -60+80$ and $-120+140$ mesh by ASTM standard sieves. The chemical analysis showed that the ore contained 27.01% CaO, 50.37% B_2O_3, 21.70% H_2O and 0.92% others. The chemicals were supplied from Fluka. Particle size, solid to liquid ratio, ammonium sulfate concentration and reaction temperature were chosen as parameters in dissolution experiments. The values of parameters are given in Table 1.

Dissolution experiments were carried out in a 250 mL round bottom flask equipped with a mechanical stirrer to set the stirring speed to 400 rpm, a constant temperature circulator to control the reaction temperature within ±0.5 °C and a condenser to avoid solution loss by evaporation. In each dissolution experiment, after 100-mL $(NH_4)_2SO_4$ solution was put in the reactor and the temperature of reactor content was adjusted to a predetermined value, colemanite sample was added to the reactor and the content was stirred at 400 rpm. After the experiment ended, the reactor content was filtered and B_2O_3 in the filtrate was analyzed by the carmine method spectrophotometrically [Greenberg et al., 1985].

pHs of reaction mixtures were measured by a pH meter during the experiments, and it was seen that pHs changed from about 5 to 7. Conversion fraction of colemanite was calculated as follows:

X=(B_2O_3 amount passing to the solution)

/(B_2O_3 amount in original sample)

EXPERIMENTAL

We investigated the effects of particle size, ammonium sulfate concentration, solid to liquid ratio and reaction temperature on the conversion rate of colemanite in ammonium sulfate solutions. In all the experiments, the stirring speed was taken constant at 400 rpm.

While a parameter was being investigated the others were kept constant; for example, when particle size effect was studied the reaction temperature was taken as 20 °C, ammonium sulfate concentration 2 M and solid to liquid ratio 2/100 g·mL^{-1}.

1. The Effect of Parameters

The particle size effect was examined by using the fractions of $-2.000+1.000, -0.850+0.425, -0.250+0.180$ and $-0.125+0.106$ mm. In these experiments, the reaction temperature was 293 K, ammonium sulfate concentration 2 M and solid-to-liquid ratio 2/100 g·mL^{-1}. The results in Fig. 1 show that conversion rate increases with decreasing the particle size.

The effect of ammonium sulfate concentration was identified by using 0.5, 1, 2 and 3 M concentrations of ammonium sulfate. In these experiments, particle size, temperature and solid-to-liquid ratio were $-0.850+0.425$ mm, 293 K and 2/100 g·mL^{-1}, respectively. The results in Fig. 2 show that the conversion rate increased with increasing ammonium sulfate concentration.

To determine the effect of solid to liquid ratio, we used 2/100, 4/100, 6/100 and 8/100 g·mL^{-1} of solid to liquid ratios. The values of
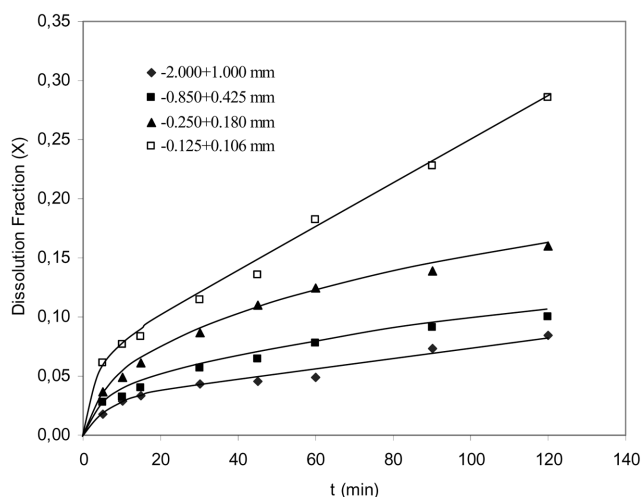

Fig. 1. The effect of particle size on the dissolution rate of colemanite in ammonium sulfate solutions (T, 293 K; S/L, 0.02 g·mL^{-1}; W, 400 min^{-1} and C, 2 M).

Table 1. Parameters and their values

Parameters	Chosen parameter values
Particle size (mm)	$-2.000+1.000, -0.850+0.450*, -0.250+0.180, -0.125+0.106$
Solid to liquid ratio (g·mL^{-1})	2/100*, 4/100, 6/100, 8/100
Ammonium sulfate concentration (mol·L^{-1})	0.5, 1, 2*, 3
Reaction temperature (K)	293*, 308, 318, 333, 353

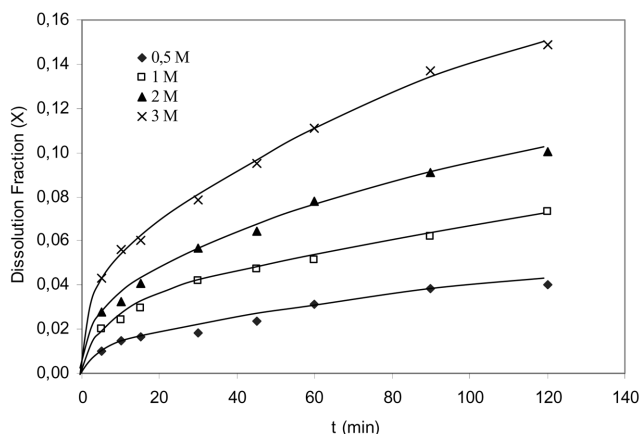*The parameters kept constant while each parameter was studying.

Fig. 2. The effect of ammonium sulfate concentration on the dissolution rate of colemanite in ammonium sulfate solutions (D, 0.850-0.425 mm; T, 293 K; W, 400 min⁻¹ and S/L, 0.02 g·mL⁻¹).
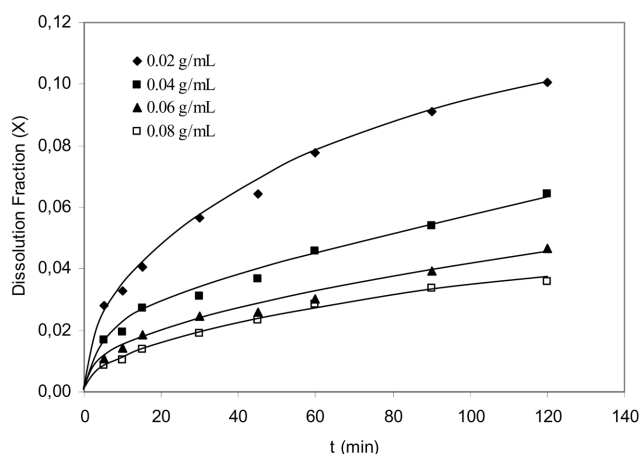

Fig. 3. The effect of solid-to-liquid on the dissolution rate of colemanite in ammonium sulfate solutions (D, 0.850-0.425 mm; T, 293 K; W, 400 min⁻¹ and C, 2 M).

parameters kept constant were −0.850+0.425 mm for particle size, 293 K for temperature and 2 M for ammonium sulfate concentration. The results in Fig. 3 show that the conversion increased with decreasing solid to liquid ratio.

The effect of reaction temperature was investigated at 293, 308, 318, 333 and 353 K. In these experiments, particle size was taken −0.850+0.425 mm, solid-to-liquid ratio 2/100 g·mL⁻¹ and ammonium sulfate concentration 2 M. Fig. 4 shows that conversion rate increased with increasing reaction temperature.

2. Reactions

Reactions occurring between colemanite and ammonium sulfate solutions are as follows [Küçük et al., 2005]:
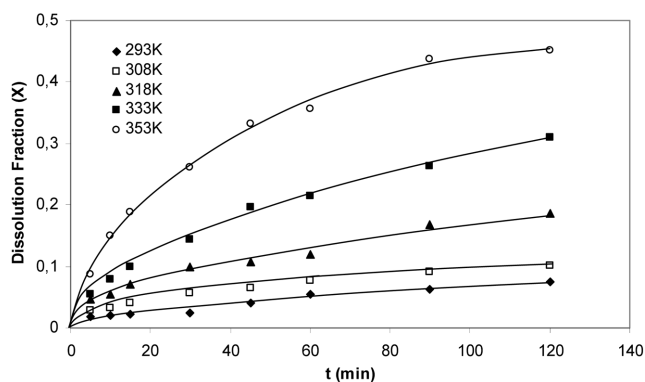
$$(NH_4)_2SO_{4(aq)} \rightarrow 2NH_{4(aq)}^+ + SO_{4\ (aq)}^{2-} \tag{1}$$

$$NH_{4(aq)}^+ + H_2O_{(aq)} \Leftrightarrow NH_{3(aq)} + H_3O_{(aq)}^+ \tag{2}$$

$$2CaO\cdot 3B_2O_3\cdot 5H_2O_{(s)} + 4H_3O_{(aq)}^+ \rightarrow 2\ Ca_{(aq)}^{2+} + 6H_3BO_{3(aq)} + 2\ H_2O \tag{3}$$

$$Ca_{(aq)}^{2+} + SO_{4\ (aq)}^{2-} + 2H_2O \Leftrightarrow CaSO_4\cdot 2H_2O_{(s)} \tag{4}$$
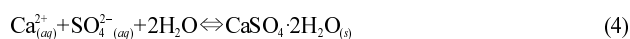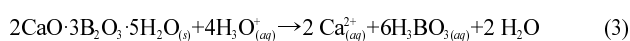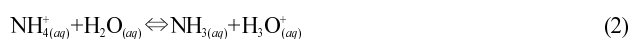

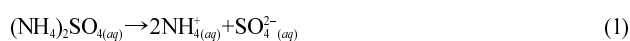**Fig. 4. The effect of temperature on the dissolution rates of colemanite in ammonium sulfate solutions (D, 0.850-0.425 mm; S/L, 0.02 g·mL⁻¹; W, 400 min⁻¹ and C, 2 M).**

3. Kinetics

If the non-catalytic reaction between a fluid and a solid is taken into account as A(fluid)+bB (solid)⇔ product (fluid and/or solid), all or some of the following physical and chemical phenomena occur:

Step 1. Diffusion of fluid reactant through fluid film on solid product

Step 2. Diffusion of fluid reactant through solid product on the surface of solid reactant

Step 3. Reaction between solid reactant and fluid reactant

Step 4. Diffusion of fluid products through solid product film to fluid film

Step 5. Diffusion of fluid products through fluid film to bulk fluid

The resistance of each step above is different than that of another. In such situations, it is accepted that the step with the biggest resistance controls the rate. In order to derive the rate equations of such reactions, the resistances corresponding to Steps 1, 2 and 3 are taken into consideration and the others are omitted. Accordingly, non catalytic fluid-solid reactions may be presented with one of three control mechanisms: gas film diffusion control, chemical reaction control and product film diffusion control. There is an integrated rate equation for each control and particle geometry [Levenspiel, 1999]. In addition to these models, pseudo-homogenous models may be also used to derive the rate equations in such systems, as follows:

$$-\ln(1-X)=kt \quad \text{for the first order pseudo-homogenous model} \tag{5}$$

$$X/1-X=kt \quad \text{for the second order pseudo-homogenous model} \tag{6}$$

$$F(X)=kt^m \quad \text{for Avrami and modified Avrami models} \tag{7}$$

In deriving a rate equation for the reaction between colemanite and ammonium sulfate in aqueous medium, experimental data were applied to integrated rate equations by using a PC, and a modified Avrami model with 40.46 kJmol⁻¹ activation energy as the following was found out to be the most appropriate, statistically.

$$1-(1-X)^{1/3}=2.12\times 10^2\cdot C^{1.38}\cdot R^{-0.75}\cdot (S/L)^{-0.44}\cdot e^{-4866/T}\cdot t^{0.61} \tag{8}$$

To compare values predicted from this model with observed values a graph of observed values versus predicted values was drawn as seen in Fig. 5 and also this graph showed that the model fit.
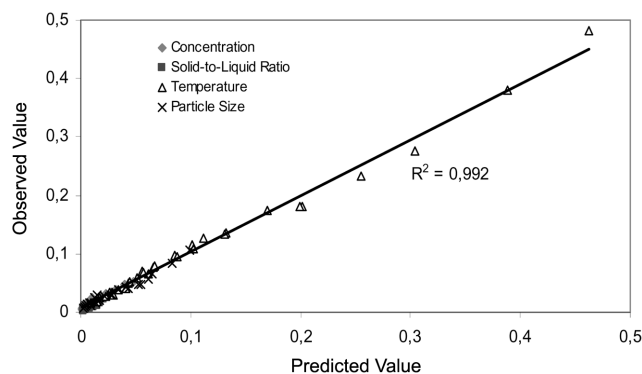
Fig. 5. The experimental and theoretical dissolution fraction data for all the parameters.
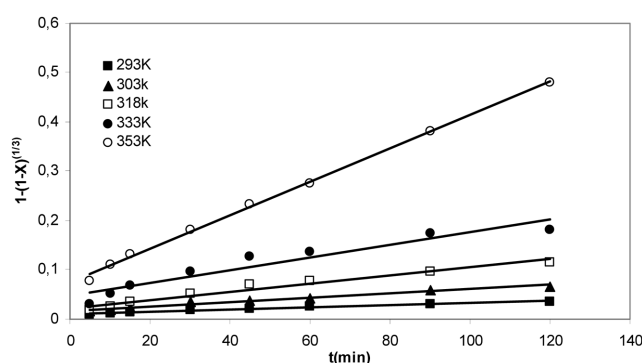

Fig. 6. Dissolution of colemanite in ammonium sulfate solutions; plots of $1-(1-X)^{1/3}$ versus t for different temperatures (D, 0.850-0.425 mm; S/L, 0.02 g·mL^{-1}; W, 400 min^{-1} and C, 2 M).

On the other hand, graphs of $1-(1-X)^{1/3}$ versus t were plotted for all the examined parameters, and it is seen that $1-(1-X)^{1/3}$ changes versus time were linear (Fig. 6). Due to the causes mentioned above, the modified Avrami model found statistically was concluded to represent the system. The Avrami model was derived originally for systems in which the crystallization phenomenon occurs [Avrami, 1939]. In the system studied, $CaSO_4 \cdot 2H_2O$ crystallized and precipitated on unreacted colemanite particles. For this reason, it has been thought that the Avrami model is appropriate for this system.

CONCLUSIONS

The dissolution kinetics of colemanite in ammonium sulfate solutions was investigated. The dissolution rate of colemanite was determined to increase by increasing ammonium sulfate concentration and temperature and also, decreasing particle size and solid to liquid ratio. A mathematical model which represents dissolution kinetics and has activation energy of 40.46 kJmol^{-1} was found as follows:

$$1-(1-X)^{1/3}=2.12\times10^2 \cdot C^{1.38} \cdot R^{-0.75} \cdot (S/L)^{-0.44} \cdot e^{-4866/T} \cdot t^{0.61} \qquad (8)$$

As a result, it is thought that boric acid can be produced by this process. Boric acid is contaminated with ions such as Fe^{2+}, Al^{3+} and SO_4^{2-} in the sulfuric acid process and with ions such as Ca^{2+} and Cl^- in ammonium chloride process, and this case causes additional cost for boric acid purification. For these reasons, the ammonium

sulfate process may be more attractive than other processes in boric acid production.

NOMENCLATURE

X : fractional conversion
t : time [min]
b : stoichiometric coefficient of B (solid) reacting with each mole of A (fluid)
R : particle size [mm]
T : reaction temperature [K]
S/L : solid-to-liquid ratio [g·mL^{-1}]
C : concentration of $(NH_4)_2SO_4$
k : reaction rate constant
b : stoichiometric coefficient of B (solid) reacting with each mole of A (fluid)
m : constant

REFERENCES

Alkan, M. and Dogan, M., "Dissolution kinetics of colemanite in oxalic acid solutions," *Chem. Eng. Process*, **43**, 867 (2004).

Alkan, M., Kocakerim, M. M. and Çolak, S., "Dissolution kinetics of colemanite in water saturated by CO_2," *J. Chem. Tech. Biotechnol.*, **35A**, 382 (1985).

Avrami, M., "Kinetics of phase change," *J. Chem. Phys.*, **7**, 1103 (1939).

Ceyhun, I., Kocakerim, M. M., Sarac, H. and Colak, S., "Dissolution kinetics of colemanite in chlorine saturated water," *Theoretical Foundations of Chemical Engineering*, **33**, 253 (1999).

Greenberg, A. E., Trussel, R. R. and Clesceri, L. S., *Standard methods for the examination of water and wastewater*, American Public Health Association, Washington, (16 th. Ed.), pp. 276-277 (1985).

Gülensoy, H. and Savcı, H., "Solubilities of some calcium minerals and prepared calcium compounds in EDTA solutions," *Bulletin of the Mineral Research and Exploration Institute of Turkey*, **86**, 77 (1976).

Imamutdinova, V. M., "Kinetics of dissolution of borates in mineral acid solutions," *Zh. Prikl. Khim.*, **40**(11), 2593 (1967).

Imamutdinova, V. M., "Rates of dissolution natural borates in phosphoric acid solutions," *Zh. Prikl. Khim.*, **40**(11), 2596 (1967).

Imamutdinova, V. M., "Role of films of the reaction products in the acid dissolution of borates," *Zh. Pricl. Khim.*, **51**(2), 260, *J. Appl. Chem. U.S.S.R.*, **51**(2), 249 (1978).

Karagölge, Z., Alkan, M. and Kocakerim, M. M., "Leaching kinetics of colemanite by aqueous EDTA solutions," *Metall. Trans. B*, **23B**, 409 (1992).

Küçük, Ö., Kocakerim, M. M., Çopur, M. and Yartaşı, A., "Optimization of dissolution of ulexite in $(NH_4)_2SO_4$ solution," *Canadian Metallurgical Quarterly*, **44**(1), 53 (2005).

Küçük, Ö, "Application of Taguchi method in the optimization of dissolution of ulexite in NH_4Cl solutions," *Canadian Metallurgical Quarterly*, **44**(1), 53 (2005).

Küçük, Ö., Kocakerim, M. M., Yartaşı, A. and Çopur, M., "Dissolution of Kestelek's colemanite containing clay minerals in water saturated with sulfur dioxide," *Ind. Eng. Chem. Res.*, **41**, 2853 (2002).

Kum, C., Alkan, M. and Kocakerim, M. M., "Dissolution kinetics of calcined colemanite in ammonium chloride solution," *Hydrometallurgy*, **36**, 359 (1994).

Levenspiel, O., *Chemical reaction engineering*, 2nd End. John Wiley and Sons, New York, pp. 566-586 (1999).

Okur, H., Tekin, T., Ozer, A. K. and Bayramoglu, M., "Effect of ultrasound on the dissolution of colemanite in H_2SO_4," *Hydrometallurgy*, **67**, 79 (2002).

Özmetin, C., Kocakerim, M. M., Yapıcı, S. and Yartaşı, A., "A semi-empirical kinetic model for dissolution of colemanite in aqueous CH_3COOH solutions," *Ind. Eng. Chem. Res.*, **35**, 2355 (1996).

Sevim, F., Demir, F., Bilen, M. and Okur, H., "Kinetic analysis of thermal decomposition of boric acid from thermogravimetric data," *Korean J. Chem. Eng.*, **23**, 736 (2006).

Temur, H., Yartaşı, A., Çopur, M. and Kocakerim, M. M., "The kinetics of dissolution of colemanite in H_3PO_4 solution," *Ind. Eng. Chem. Res.*, **39**, 4114 (2000).

Yartaşı, A., Özmetin, C., Kocakerim, M. M. and Demirhan, M. H., "Kinetics and mechanism of leaching colemanite in boric acid solution," *Chimica Acta Turcica*, **26**(2) (1998).

ZareNezhad, B., "Direct production of crystalline boric acid through heterogeneous reaction of solid borax with propionic acid: Operation and simulation," *Korean J. Chem. Eng.*, **21**, 956 (2004).

ZareNezhad, B., "Experimental and theoretical investigation of boric acid production through reactive dissolution of oxalic acid crystals in borax aqueous solution," *Korean J. Chem. Eng.*, **20**, 44 (2003).

Zdanovskii, A. B., "Kinetics of borate dissolution in acids," *Issled. Sint. Boratev, Chem. Abs.*, **97**(18), 151479s (1982).