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Leaching kinetics of ulexite in oxalic acid

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Abstract. Leaching of ulexite in oxalic acid, which is an organic acid, was studied. The parameters were solid-to-liquid ratio, acid concentration, stirring speed and temperature. The experimental data were applied to the homogeneous and heterogeneous kinetic models to determine the best one. The results showed that the leaching rate increases with increasing reaction temperature, stirring speed, acid concentration, but decreases with solid-to-liquid ratio and particle size. The leaching kinetics of ulexite was determined as the product layer model. The activation energy of the process was calculated.

keywords: concrete aggregates, shape, mechanical resistance, mobile plant, fixed plant

1. Introduction

Ulexite is a hydrated sodium–calcium borate. In Turkey commercially produced boron minerals are colemanite, ulexite, and tincal. These borate mineral are produced in large amounts in Turkey where ulexite is produced in Balikesir – Bigadic. In Bigadic, a ulexite ore is produced in open mines. Ulexite processing is carried out in ore preparation facilities near ore mines in Bigadic. Ulexite is enriched by crushing, wetting in water, washing in a tumbling mill, sieving, triage and classification, and produced in different grain sizes as well as chemical compositions as concentrated ulexite, and offered for sale. A major portion of the ulexite concentrate produced is exported (Bayca, 2009).

Pure boron element does not exist in nature. Rather it is found as boron oxides. Boron minerals, produced as compounds of boron oxide and alkaline or earth alkaline elements exist widely in nature. Although there are many varieties of boron minerals in nature, only a small amount of these varieties can be used commercially (Brotherton, 1995). Ulexite is a sodium-calcium borate mineral with a chemical composition of $NaCaB_5O_9 \cdot 8H_2O$ and contains theoretically 42.95% B_2O_3. The water in the structure of ulexite exists as 3 moles of hydroxyl groups and 5 moles of crystal water ($NaCa[B_5O_8(OH)_6] \cdot 5H_2O$). Ulexite exists as a white parallel fiber and has a triclinic crystal structure. It has relatively low water solubility: 0.5% at 25^{o}C (Brotherton, 1995; Gerhartz, 1985).

The leaching kinetics of boron minerals in various acid solutions has been investigated. The leaching kinetics of colemanite in acetic acid (Ozmetin et al. 1996), phosphoric acid (Temur et al., 2000), citric acid (Cavus et al., 2005), oxalic acid (Alkan et al., 2004a) were studied. The dissolution kinetics of tincal in phosphoric acid (Abali et al., 2007) and oxalic acid (Abali et al., 2006) were studied. Many studies have been carried out on the dissolution kinetics of ulexite in different solutions. Kunkul et al. (2003) investigated the dissolution kinetics of ulexite in ammonium sulfate solutions. They found that the dissolution rate increased with increasing ammonium sulfate concentration, stirring speed, and reaction temperature. However, increasing the particle size and solid-to-liquid ratio decreased the dissolution rate. They determined that the heterogeneous diffusion-controlled ash or product layer may describe the dissolution rate. Demirkiran (2008) studied the dissolution of ulexite in ammonium acetate solutions. He found that the dissolution rate increased with an increase in concentration and reaction temperature, and with a decrease in particle size and solid-to-liquid ratio. No effect of stirring speed was observed on the conversion. It was determined that the dissolution rate fit the chemical reaction control model. Tunc et al. (1999) have investigated the dissolution kinetic of ulexite in aqueous acetic acid solutions. They reported that the dissolution rate increased with increasing temperature and stirring speed and decreasing solid-to-liquid ratio and particle size. Demirkiran and Kunkul (2007) have studied the dissolution kinetics of ulexite in perchloric acid solutions. They found that the dissolution rate increased with increasing concentration, stirring speed, reaction temperature and with decreasing particle size. The dissolution process was described by the Avrami model. Kunkul et al., (1997a) have studied the dissolution kinetics of ulexite in ammonia solutions saturated with CO_2. It was found that the dissolution rate of ulexite can be described by a first-order pseudo-homogenous reaction model. Alkan et al. (2004b) have conducted the dissolution kinetics of ulexite in oxalic acid solutions. They found that the dissolution rate was controlled by product layer diffusion model. Kunkul et al. (1997b) have studied the dissolution of thermally dehydrated ulexite in sulfuric acid solutions. They reported that the process fits the first-order pseudo homogeneous kinetic model.

The aim of this paper is to investigate leaching kinetics of ulexite in oxalic acid solutions. The effects of reaction temperature, solid-to-liquid ratio, stirring speed, particle size, and acid concentration on the leaching rate have been studied. The leaching kinetics of ulexite was examined according to the heterogeneous and homogenous reaction models, and the best fitted equation to the experimental data was determined. Activation energy was calculated by using the best model and Arrhenious equation.

2. Material and methods

Ulexite (3 – 125 mm) used in the present study was obtained from Eti Mine Bigadic Boron Works, Balikesir, Turkey. The sample was crushed by a jaw crusher and sieved using ASTM Standard sieves to obtain the following size fractions: 160 – 315, 315 – 500, 710 – 1000, and 1000 – 1600 µm. The X-ray diffraction analysis is given in the Fig. 1.

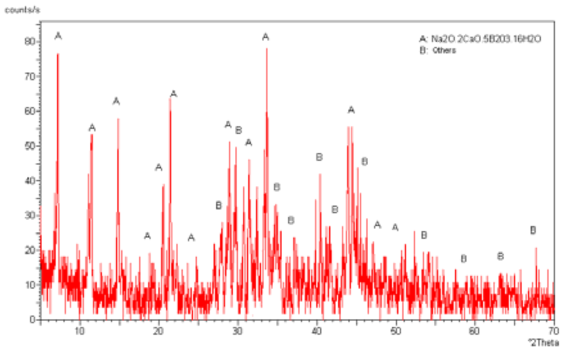

Fig. 1. X-ray diffractogram of ulexite

The chemical analysis of the studied ulexite fraction is shown in Table 1. The boron oxide chemical analysis was determined by the volumetric method (Scott, 1963) and others were determined by X-ray fluorescence (XRF). Oxalic acid and other reagents used were of analytical grade. Distilled water was used to prepare solutions.

Table 1. Chemical analysis of the studied ulexite

Oxides	Percent
B_2O_3	37.3
CaO	15.8
Na_2O	9.2
H_2O	36.4
Others	1.3

The leaching experiments were performed in a 250 dm^3 glass reactor at atmospheric pressure. A mechanical stirrer was used and a thermostat was employed to keep reaction medium at constant temperature. In the dissolution process, 100 dm^3 of oxalic acid solution was placed into the reactor. After the desired reaction temperature was reached, a given amount of ulexite was added to the solution and the stirring was started.

After a certain period of time, the solution was filtered without any change in temperature. The percent of B_2O_3 in the filtrate was determined by volumetric method and experimental parameters used in the dissolution process are given in Table 2.

Table 2. Parameters and their values

Parameters and Values	1	2	3	4
Reaction temperature, °C	13	25	35	60
Acid concentration, % w/v	1	2	5	10
Solid/liquid ratio, % w/v	0.5	1	2	5
Particle size, µm	1000 – 1600	710 – 1000	315 – 500	315 – 160
Stirring speed, rpm	250	450	750	

3. Results and discussion

3.1. Leaching reaction

The dissolution of oxalic acid is as follows:

$$C_2H_2O_{4(aq)} + 4H_2O = 2C_2O_4{}^{2-}{}_{(aq)} + 4H_3O^+{}_{(aq)} \quad (1)$$

while the dissolution of ulexite in oxalic acid solution proceeds as follows:

$$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O_{(s)} + 3C_2H_2O_{4(aq)} + 2H_2O =$$
$$10H_3BO_{3(aq)} + 2Na^+{}_{(aq)} + 2CaC_2O_{4(s)} + C_2O_4{}^{2-}{}_{(aq)} + 6H_2O_{(l)} \quad (2)$$

The reaction between ulexite and oxalic acid leads to boric acid (H_3BO_3), sodium oxalate and calcium oxalate.

3.2. Effects of leaching parameters

The experiments were performed at different particle sizes between 13 and 60°C while other parameters were kept constant.

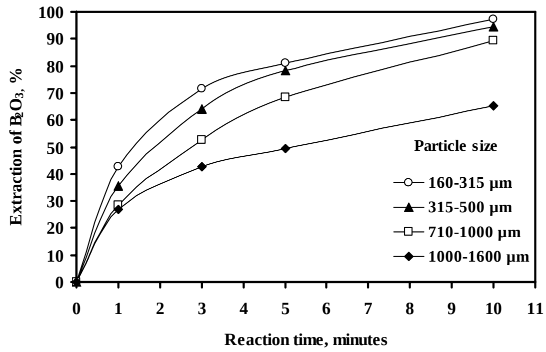

Fig. 2. Effect of time and particle size on the dissolution of ulexite (10% $C_2H_2O_4$, 1% solid, 450 rpm, 25°C)

Figure 2 indicates that the lowest dissolution rate was obtained at 1000 – 1600 µm particle size. The dissolution rate quickly increases when particle size of ulexite reaches 500 µm. Since the particle size decreases, the dissolution rate increases.

Ekmekyapar et al. (2008) reported that the dissolution rate of ulexite in acetic acid solutions increased with decreasing particle size.

Figure 3 shows the effect of time and solid-to-liquid ratio on the dissolution rate of ulexite. The dissolution rate increases from 58.4 to 98.6 % when the solid-to-liquid ratios is reduced from 0.5 to 5%. It might be explained by insufficient dissolution reagent in the medium. It was observed that the dissolution rate increases with decreasing solid-to-liquid ratio. Similar results were found for borogypsum in SO_2 saturated solutions (Demirbas, 2000) and for ulexite in ammonia solutions saturated with CO_2 (Kunkul, 1997).

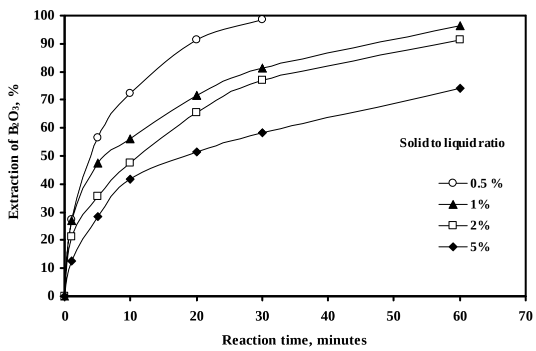

Fig. 3. Effect of time and solid to liquid ratio on the dissolution of ulexite (10% $C_2H_2O_4$, 315 – 500 μm, 450 rpm, 25°C)

It was observed (Fig. 4) that the maximum dissolution rate was 78.2% at 1% acid concentration for 60 min. The boron oxide extraction increased from 78.2 to 96.3% at 10% acid concentration for 60 min. When acid concentration increases the dissolution rate increases.

The effects of temperature on the dissolution rate of ulexite are studied at different temperatures. The results are given in Fig. 5. They show that the maximum dissolution rate was 84.4% at 13°C for 60 minutes.

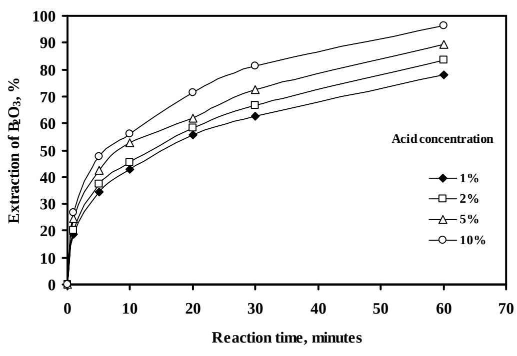

Fig. 4. Effect of time and acid concentration on the dissolution of ulexite (315 – 500 μm, 1% solid, 450 rpm, 25°C)

The extraction of boron oxide increases from 84.4 to 99.9% at 60°C for 60 minutes. The dissolution rate increases with increasing temperature. Demirkiran and Kunkul (2007) found that dissolution of ulexite in perchloric acid solutions increased with increasing temperatures.

The experiments on influence of stirring speed on the dissolution rate of ulexite were performed between 250 and 750 rpm. The results (Fig. 6) indicate that changing the stirring speed from 250 to 750 rpm improves dissolution rate from 58.4 to 73.8% for 10 minutes of stirring. The dissolution rate was increasing with increasing stirring speed.

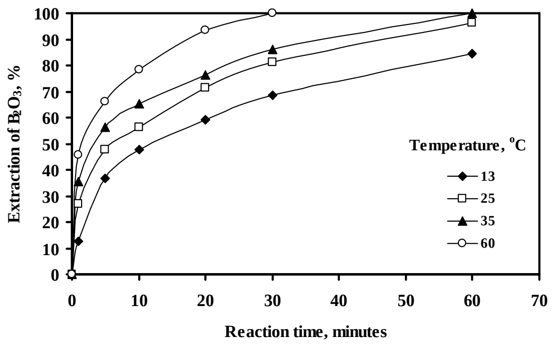

Fig. 5. Effect of time and temperature on the dissolution of ulexite (10% $C_2H_2O_4$, 1% solid, 315 – 500 μm, 450 rpm)

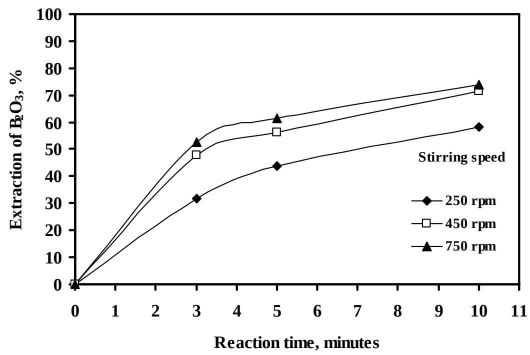

Fig. 6. Effect of time and stirring speed on the dissolution of ulexite (10% $C_2H_2O_4$, 1% solid, 315 – 500 μm, 25°C)

3.3. Kinetic analysis

The rate of reaction between the solid and fluid phases can be expressed in terms of heterogeneous reaction models. The rate may be described by film diffusion, chemical reaction, product layer diffusion models (Levenspiel, 1972). Reaction time *t* is given as a function of fractional dissolution for surface chemical reaction, diffusion through fluid film, and diffusion product layer control model cases.

The kinetics of film diffusion control model is given by:

$$X = \frac{t}{\tau} \quad , \tag{3}$$

the chemical reaction control model by:

$$1-(1-X)^{1/3} = \frac{t}{\tau}, \tag{4}$$

while the product layer diffusion control model by:

$$1-3(1-X)^{2/3} + 2(1-X) = \frac{t}{\tau}. \tag{5}$$

The dissolution rates of ulexite were determined at different temperatures. The results were given in Fig. 4. The results were analyzed using Eq. 3, 4 and 5. The experimental data were analyzed using equations of the homogeneous kinetic models. The regression coefficient values R^2 found in the range of 0.9197 – 0.9958 for the first order pseudo homogeneous control model and as 0.6473 – 0.9824 for the second order pseudo homogeneous control model. It indicates that these models cannot be fitted due to nonlinear regression.

The values for calculated from Eqs. 3-5 are plotted to find regression coefficients. The correlation coefficients (R^2) and k values of heterogeneous models for each temperature were calculated using the slope of the lines. The correlation coefficients was calculated between 0.6858 and 0.7735 for the film diffusion control model, between 0.9045 and 0.9600 for the surface chemical reaction control model and between 0.9939 and 0.9976 for the product layer diffusion control model (Table 3).

Table 3. Values k_f, k_r, k_d and correlation coefficients

Models	Heterogeneous control models					
	Film diffusion		Surface chemical reaction		Product layer diffusion	
Temperature, K	k_f, min^{-1}	R^2	k_r, min^{-1}	R^2	k_d, min^{-1}	R^2
286	0.0124	0.7735	0.0071	0.9045	0.0073	0.9948
298	0.0132	0.7339	0.0100	0.9413	0.0121	0.9976
308	0.0128	0.6637	0.0132	0.9598	0.0155	0.9939
333	0.0258	0.6858	0.0263	0.9600	0.0310	0.9960

The kinetic analysis indicated that the dissolution rate of ulexite in oxalic acid does not fit the film diffusion control model and the surface chemical reaction control model due to nonlinear relationships. However, linear relationships were obtained for the product layer diffusion control model. The dissolution rate of ulexite in oxalic acid results fits the product layer diffusion control model. The dissolution rate increased between 250 and 450 rpm stirring speed (Fig. 6). The solid product layer formed on the surface of ulexite particle is CaC_2O_4. This layer prevents diffusion of oxalic acid to the surface of the particle. The low dissolution rate was due to insufficient, 250 rpm stirring speed. The solid product layer removal from the surface of particle was sufficient at 450 rpm stirring speed (increase in extraction).

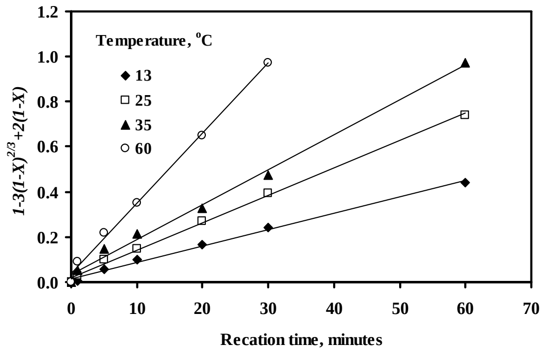

Fig. 7. The variation in $1-3(1-X)^{2/3}+2(1-X)$ with time at different temperatures

Figure 7 shows results of leaching at different temperatures. It indicates that the dissolution rate increases with increasing stirring speed, which may be the result of film layer forming on the surface of ulexite particle. Because the stirring speed of solution increased, the film layer formed on the particle surface was probably removed. The product layer diffusion control model, which was determined for ulexite in oxalic acid solution, confirmed these results. Similar results were reported by Kunkul et al. (2003).

In our process Ca^{2+} ions and $C_2O_4^{2-}$ formed solid CaC_2O_4 while ulexite completely dissolved in oxalic acid solution. This solid formed an insoluble layer on the surface of particles. The layer causes that the kinetics of ulexite in oxalic acid solutions fits the product or ash layer diffusion control model. This kinetics model is also confirmed by the fact that the dissolution rate increases with increasing stirring speed from 250 to 450 rpm.

3.4. Activation energy

The activation energy of the leaching was calculated from the Arrhenius equation

$$k = k_o \exp(-E/RT), \quad (6)$$

because ln$k$ versus $1/T$ gives a straight line of slope $-E/R$. From the slope of the straight line in Fig. 8, the activation energy (E) of dissolution rate of ulexite in oxalic acid can be determined.

The reaction control model of ulexite in oxalic acid solution was determined as $1-3(1-X)^{2/3}+2(1-X)$. In this study, the activation energy of dissolution rate of ulexite in oxalic acid solutions was calculated as 24 kJ/mol. Similar results were reported by researchers who reported that the activation energies of ulexite in dissolution reagents solutions is 46.00 kJ/mol in sulfuric acid, 58.20 kJ/mol in ammonium nitrate, 55.70 kJ/mol in ammonium acetate, 83.50 kJ/mol in ammonium sulphate, 19.12 kJ/mol in perchloric acid, 30.24 kJ/mol in oxalic acid, 30.69 kJ/mol in acetic acid (Kunkul et al., 1997; Demirkiran, 2009; Demirkiran, 2008; Kunkul et al., 2003; Demirkiran et al., 2007; Alkan et al., 2004b; Tunc et al., 1999, respectively).

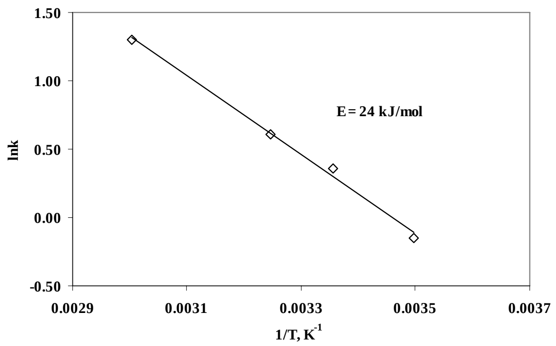

Fig. 8. Arrhenius plot for the dissolution of ulexite

4. Conclusions

The leaching kinetics of ulexite in oxalic acid solutions was investigated in a batch reactor. The results showed that the dissolution rate increases with increasing reaction temperature, acid concentration, stirring speed and decreasing with solid-to-liquid ratio and particle size. The most influential parameter on the dissolution rate was found to be temperature of ulexite while the least influential was acid concentration. Boric acid, sodium oxalate and calcium oxalate were formed in the course of dissolution of ulexite in oxalic acid. The formed boric acid and sodium oxalate which go into the filtrate. The calcium oxalate and undissolved ulexite remained as solids. Ulexite dissolution kinetics was best described by formula $1-3(1-X)^{2/3}+2(1-X)$. The activation energy of ulexite in oxalic acid solution is 24 kJ/mol.

References

ABALI, Y., BAYCA, S. U., MISTINCIK, E. (2006). Kinetics of oxalic acid leaching of tincal, *Chemical Engineering Journal*, 123, 25–30.

ABALI, Y., BAYCA, S. U., GULER, A. E. (2007). The dissolution kinetics of tincal in phosphoric acid solutions, *International Journal of Chemical Reactor Engineering*, 5, 1–10.

ALKAN, M., DOGAN, M. (2004a). Dissolution kinetics of colemanite in oxalic acid solutions, *Chemical Engineering and Processing,* 43, 867–872.

ALKAN, M, DOGAN M, NAMLI, H. (2004b). Dissolution kinetics and mechanism of ulexite in oxalic acid solutions, *Ind. Eng. Chem. Res*., 43, 1591–1598.

BAYCA, S. U. (2009). Effects of the addition of ulexite to the sintering behavior of a ceramic body, *Journal of Ceramic Processing Research*, 10, 162–166.
BROTHERTON, R. J. (1995). *Encyclopedia of Inorganic Chemistry*, Wiley, New York, USA.
CAVUS, F., KUSLU, S. (2005). Dissolution kinetics of colemanite in citric acid solutions assisted by mechanical agitation and microwaves, *Ind. Eng. Chem. Res.*, 44, 8164–8170.
DEMIRBAS, A.¸ H., YUKSEK, I., CAKMAK, M., M., KUCUK, CENGIZ M., ALKAN, M. (2000). *Resources, Conservation and Recycling*, 28, 135–146.
DEMIRKIRAN, N., KUNKUL, A., 2007, Dissolution kinetics of ulexite in perchloric acid solutions, *International Journal of Mineral Processing*, 83, 76–80.
DEMIRKIRAN, N. (2008). A study on dissolution of ulexite in ammonium acetate solutions, *Chemical Engineering Journal*, 141, 180–186.
DEMIRKIRAN, N. (2009). Dissolution kinetics of ulexite in ammonium nitrate solutions, *Hydrometallurgy*, 95, 198–202.
EKMEKYAPAR A., DEMIRKIRAN N., KUNKUL, A. (2008). *Chemical Engineering Research and Design*, 86, 1011–1016.
GERHARTZ, W. (1985). *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, Germany.
KUNKUL,A., YAPICI, S., KOCAKERIM, M., M., COPUR, M. (1997a). The dissolution kinetics of ulexite in ammonia solutions saturated with CO_2, *Hydrometallurgy*, 44, 135–145.
KUNKUL, A., TUNC, M., YAPICI, S., ERSAHAN, H., KOCAKERIM, M. M. (1997b). Dissolution of thermally dehydrated ulexite in sulphuric acid solution, *Ind. Eng. Chem. Res.*, 36, 4847–4851.
KUNKUL, A., DEMIRKIRAN, N., and BAYSAR, A., 2003, Dissolution kinetics of ulexite in ammonium sulphate solutions, *Ind. Eng. Chem. Res.*, 42, 982–986.
LEVENSPIEL, O. (1972). *Chemical Reaction Engineering*, 2nd edition, Wiley, New York.
OZMETIN, C., KOCAKERIM, M. M., YAPICI, S and YARTASI, A. (1996). A semi empirical kinetic model for dissolution of colemanite in aqueous acetic acid solutions, *Ind.Eng. Chem. Res.* 35, 2355–2359.
SCOTT, W. W. (1963). *Standard Methods of Chemical Analysis*, D. Van Nostrand, New York.
TEMUR, H., YARTAŞI, A., COPUR, M., KOCAKERIM, M. (2000). The kinetics of dissolution of colemanite in phosphoric acid solutions, *Ind. Eng. Chem. Res.*, 39, 4114.
TUNC, M., KOCAKERIM, M. M., GUR, A., YARTASI, A. (1999). A semi empirical kinetic model for dissolution of ulexite in aqueous acetic acid solutions, *Energy, Education, Science and Technology*, 3, 1–10.

List of symbols

k	reaction rate constant (min^{-1})
t	reaction time (min),
T	temperature, K
E	activation energy, J/mol
R	universal gas constant, J/mol.K
τ	time for complete reaction of a particle (min)
X	fraction of extracted B_2O_3