

Investigation of Kinetic Parameters of Dehydrated Ulexite Mineral in Boric Acide Solution

Mehmet Harbi ÇALIMLI¹, Mehmet TUNÇ²

ABSTRACT: Ulexite used in the production of boron compounds is an important mineral. In this work, the kinetic parameters of dehydrated ulexite mineral and orginal ulexite in boric acid solution were investigated. According to the DTA diagram, it was seen that the mineral did not change the structure until around 170 °C. It was observed that the dissolution kinetics increased to this temperature. In the SEM images, it was observed that the number of pores in the mineral was increased until 170 °C and afterwards number of pores was decreased. The kinetic parameters of the original ulexite were evaluated. Study indicates that the dissolution kinetics model in the boric acide was found as below;

$$1-(1-X)^{-1} = [2.02(Rp)^{-1.013}[CA]_0^{0.4579}(S.L^{-1})^{-0.650}(M.S)^{0.0545}e^{-2649.12T^{-1}}].t$$

Keywords: Boric acide, dissolution rate, ulexite, kinetic parameters



Hidrate Edilmiş Uleksit Mineralinin Borik Asit Çözeltisindeki Kinetik Parametrelerinin İncelenmesi

ÖZET: Bor bileşiklerinin üretiminde kullanılan Uleksit çok önemli bir bor mineralidir. Bu çalışmada hidrate edilmiş uleksit minerali ve orginal mineralinin borik asit çözeltisindeki kinetik parametreleri incelenmiştir. DTA diyagramına göre 170 °C'ye kadar mineral yapısında değişim olmadığı görülmüştür. Bu sıcaklık aralığında çözünme kinetiğinin arttığı gözlemlendi. SEM görüntülerinden 170 °C'ye kadar mineral gözeneklerinde açılmaların arttığı, bu sıcaklıktan sonra ise azaldığı gözlemlendi. Orijinal uleksite ait kinetik parametreler değerlendirildi. Mineralin borik asitteki çözünme kinetiği aşağıda ki gibi bulundu;

$$1-(1-X)^{-1} = [2.02(Rp)^{-1.013}[CA]_0^{0.4579}(S.L^{-1})^{-0.650}(M.S)^{0.0545}e^{-2649.12T^{-1}}].t$$

Anahtar Kelimeler: Borik asit, çözünme kinetiği, uleksit, kinetik parametreler

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INTRODUCTION

Boron compounds now have a wide range of applications in the area of new technology and industry. This situation increases the importance of boron and boron compounds day by day. There are many boron minerals in nature. Colemanite, borax, kernite and ulexite tincal and ulexite are a few of the minerals with commercial importance. Boron minerals contain water in the form of hydrates. Some of the important boron compounds formulas are $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ (borax), $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}$ (kernite), $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 16\text{H}_2\text{O}$ (ulexite). Turkey is a very rich country in terms of boron ores. Boron minerals are found in the cities of Balıkesir and Eskişehir in the west of Turkey. Boron compounds obtained from boron minerals are boric acid, sodium perborate and boron oxides and these are commercially valuable compounds. Boron compounds with commercial importance such as boric acid and the like are obtained from ulexite mineral (Tunç et al., 1999).

Kinetic studies on boron minerals are generally related to dissolution rates in various parameters and acids. These parameters are particle size, acid concentration, temperature effect. In a study, the dissolution kinetics model was investigated using some methods such as Taguchi. It was found that the most effective parameter is pH and temperature in a study using ulexite mineral in the removal of SO_2 gas (Çopur et al., 2017).

Much work has been done on thermal degradation and kinetics of ulexite and about the other boron minerals. Some of which can be summarized as follows. In an study (Karagöz et al., 2017) KH_2PO_4 was used as a solvent for colemanite. In this study, the activation energy was calculated and tried to determine effective parameters. The activation energy was calculated to be $41.88 \text{ kJ mol}^{-1}$. When kinetic models were determined, homogeneous and heterogeneous reaction models were used. Thermal decomposition kinetics of ulexite was investigated (Tunç et al., 1997).

Recently, there are some kinetic studies about another minerals such as magnesite minerals. In the study of magnesite, the increasing temperature and grain size parameters, the dissolution kinetics were found to increase. The rate of dissolution was increased up to a certain value of acid concentration, and after this value the speed was decreased. It has been determined that the speed does not change with the mixing speed (Bakan et al., 2016).

In an study it was investigated dissolution of ulexite in perchloric acid solution. Kinetic model was found Avrami model and the activation energy was calculated as $19.12 \text{ kJ mol}^{-1}$ (Demirkıran et al., 2007). In the other study it was investigated dissolution of ulexite in oxalic acid solutions and it was found kinetic model First order Pseudo Homogeneous Model. Activation energy was calculated as $30.69 \text{ kJ mol}^{-1}$ (Alkan et al., 2004). Mergen and Demirhan investigated dissolution kinetics of probertite in boric acid solution. Kinetic model was found first order pseudo homogeneous reaction and the activation energy was calculated as $28.25 \text{ kJ mol}^{-1}$ K (Mergen et al., 2009).

The literature include some studies about the dissolution of colemanite. For example Kum et al. examined calcined colemanite in ammonium chloride solution and they found activation energy as 89 kJ mol^{-1} (Kum et al., 1994). Yartaşı et al. studied colemanite in boric acid solutions and they found activation energy as $28.60 \text{ kJ mol}^{-1}$ (Yartaşı et al 1997), Kocakerim and Alkan studied it in SO_2 saturated water solution and they found activation energy as $53.97 \text{ kJ mol}^{-1}$ (Kocakerim et al., 1988). Temur et al. examined it in phosphoric acid solution and they found activation energy as $53.91 \text{ kJ mol}^{-1}$ (Temur et al., 2000). Okur et al. examined its effect of ultrasound on kinetic in sulphuric acid solution and they found activation energy as 30 kJ mol^{-1} (Okur et al., 2002).

In addition these studies, the literature contain some studies about the dissolution of other boron minerals. For example Alkan et al. examined inyoite and inderite in water saturated with CO_2 solution and they found activation energy in turn in order $58.50 \text{ kJ mol}^{-1}$ (Alkan et al., 1991), Abali et al. studied tincal in oxalic acid they found activation energy $35.14 \text{ kJ mol}^{-1}$ (Abali et al., 2006).

When minerals which contain hydrate water are heated, their weight are decreased, losing H_2O , known as dehydration. Dehydration operation can be applied for economical and technological reasons: to decrease the weight of a material for reducing the transportation cost in the case where it includes hydrated water in large amounts, it may be a necessary step of the chemical process or to obtain a porous solid for increasing the reaction rate of a solid-fluid reaction (Künkül et al., 1997).

The aim of this study of ulexite in this study is to investigate the kinetic parameters with boric acid

solution from dehydrated mineral compared to original mineral. There is no single study reported in literature regarding the dissolution of dehydrated ulexite in boric acid solution. So the aim of our study was to control the the dissolution of calcined ulexite in boric acid solutions and to determine the kinetic parameters in boric acid solution.

MATERIAL AND METHOD

The sample used in the study was obtained from Balıkesit-Bigadiç. The sample was cleaned from apparent impurities, crumbled and sieved to obtain the desired grain size. The crystal water depleted sample was used in the study. An ash oven was used for this.

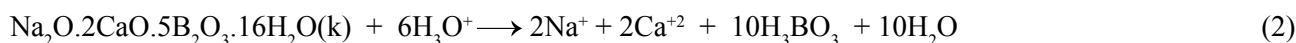
The sample at room temperature was weighed first. In the experiments a small ceramic pot was used. Each trial took 1 g of the sample. The sample, which was placed in the ash oven brought to the temperature, was

exposed to heat for 3 hours in the oven. At the end of this period, the sample removed from the oven was brought to room temperature. The sample brought to room temperature was weighed again and the lost water mass was calculated. The sample which lost the crystal water, DTA and x-ray analyzes were made.

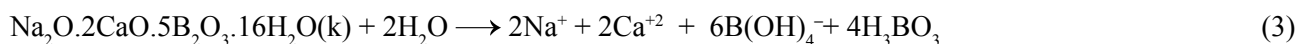
Boric acid in the appropriate concentration was put into 100 ml balloon. It was waited for 15 minutes to arrive at the thermal balance. 1 g was taken from the hydrated sample and placed in the balloon. The experiment was started. At the end of the period 10 ml of the mixture was taken and filtered and 5 ml of the filtrate was titrated. So the amount of dissolved sample was calculated.

When the process was completed, the content of reaction glass vessel was strained then Ca^{2+} in the solution was established by compleximetric method(Scott et, 1963).

The reactions between ulexite and boric acid;



and the total reaction is



RESULT AND DISCUSSION

Hydrated water containing ulexite was removed using an ash oven. Crystal water is removed from the mineral with the warmth of the mineral and causes to decrease the weight in the mineral. The water removed from the mineral is shown in Figure 1. Crystal water

loss starts at 87 °C, reaches maximum at 230 °C and disappears completely at 439 °C. It is possible to interpret structural changes in the mineral from Figure 2. Crystal water loss begins at 87 °C, the crystal structure begins to change after 170 °C, we can see a small peak at about 165 °C and then a bigger peak at about 170-184 °C

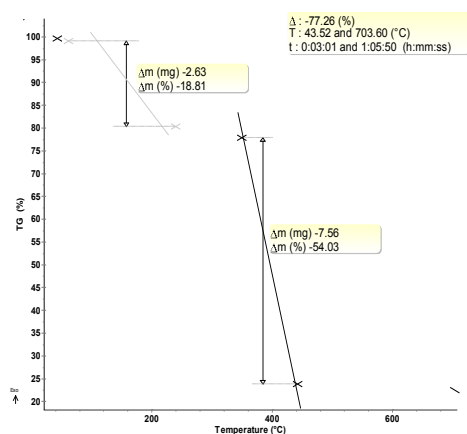


Figure 1. Mass loss of ulexite with temperature

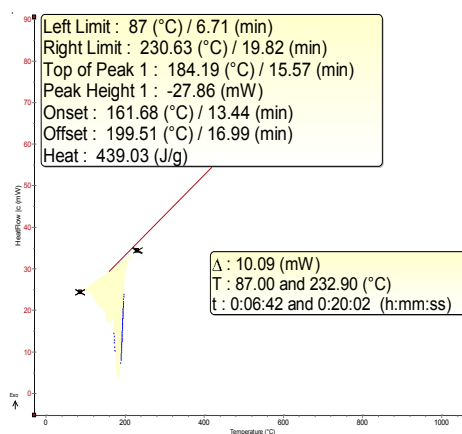


Figure 2. DTA diagram of ulexite

The change in mineral surface is seen from Figure 3. Up to 150 °C, mineral crystal water is lost and this loss reaches maximum at 170 °C. After 170 °C, the crystal water pores disappearing and the mineral reaches a static structure(Künkül et al., 1997). Together with the disappearing crystal water molecules, leads

to an increase in the number of porosity of the surface area and increasing surface area will also increase dissolution kinetics.

In the kinetic studies of the dehydrated samples, the maximum dissolution kinetics at 170 °C confirms this situation.

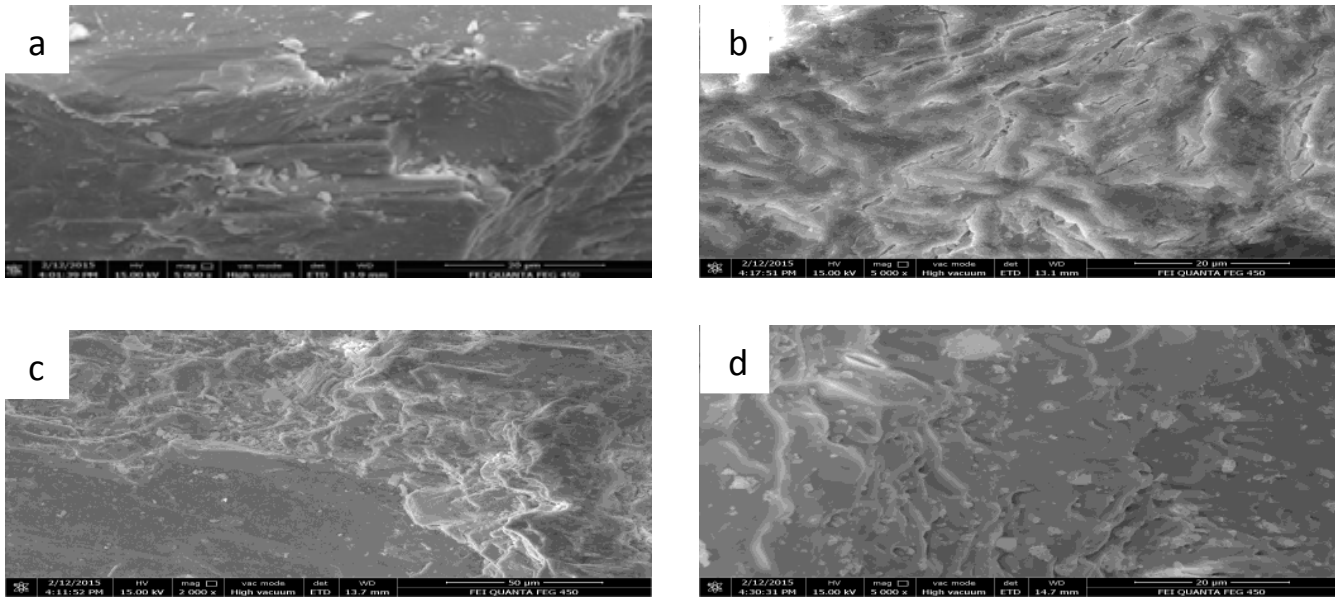


Figure 3. SEM images of the dehydrated samples: (a) dehydrated ulexite at 150 °C, (b) dehydrated ulexite at 170 °C, (c) dehydrated ulexite at 350 °C, (d) dehydrated ulexite at 650 °C

The results of the dissolution kinetics of the dehydrated sample are shown in Figure 4. As can be seen in the graphic, the maximum dissolution kinetics were at 170 degrees. This result is consistent with

SEM images. 15 °C, 20 °C, 30 °C and 40 °C kinetics experiments were carried out with the hydrated sample at 170 °C. The results of $X_{B_{2O_3}}$ ratios at different temperatures are Figure 5.

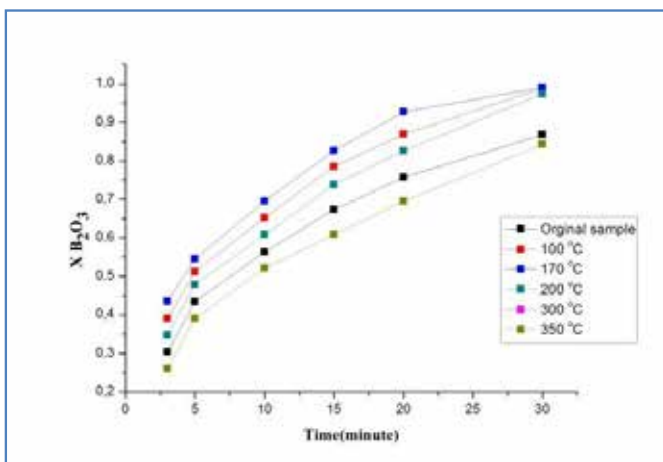


Figure 4. $X_{B_{2O_3}}$ ratio versus the time of crystal water flowed sample

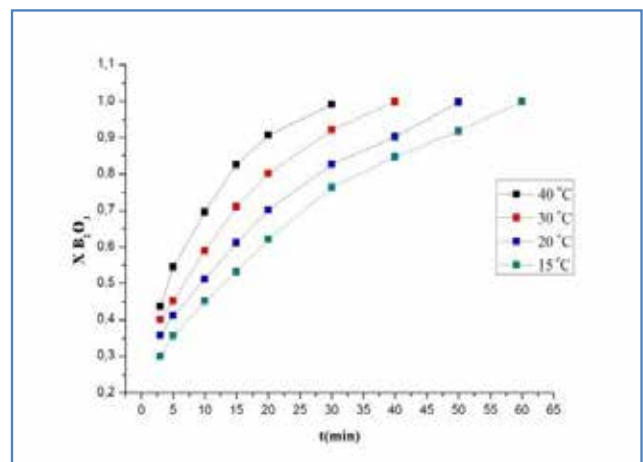
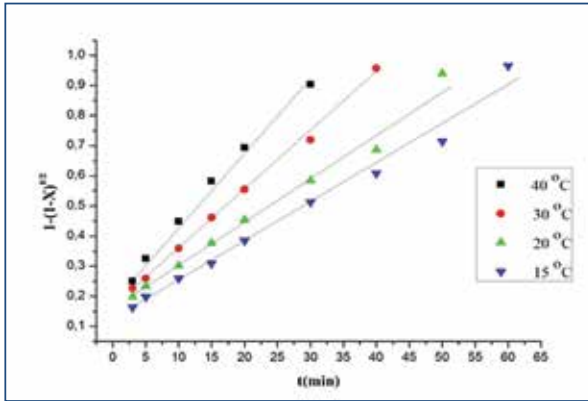


Figure 5. $X_{B_{2O_3}}$ ratios at different temperatures of the sample in which the crystal water was blown at 170 °C



Grain size: -60 + 80 mesh
 Acid concentration: % 6
 Temperature: 40 °C
 Mixing speed: 400 rpm
 Solid liquid ratio: 1.10-2 g.mL-1

Figure 6. The 1 - (1-X)^{1/2} time chart at different temperatures of the sample with the crystal water at 170 °C.

Table 1. For particle sizes, Rp, lnRp, k, lnk values

Rp	lnRp	k	ln k	a
0.485	-0.72361	0.0049	-5.31852	
0.357	-1.03002	0.0063	-5.05910	
0.282	-1.26585	0.0083	-4.79150	-0.9412
0.215	-1.53712	0.0101	-4.59522	
0.180	-1.71480	0.0126	-4.37406	

The experimental results was found and particle size, concentration, solid/liquid ratio, the data of temperature and stirring speed parameters are investigated respectively. Calculations of Rp, lnRp, k,

lnk and a are given Table 1 . Using the formula below, the velocity of this equation is found by the slope of the plot ln (k) ln (Rp).

$$k = k_1 (Rp)^a$$

Rp : Grain size

$$k_1 = k_0 [CA]_0^b (S.L^{-1})^c (MS)^d e^{-E/RT}$$

[CA] : Acid concentration

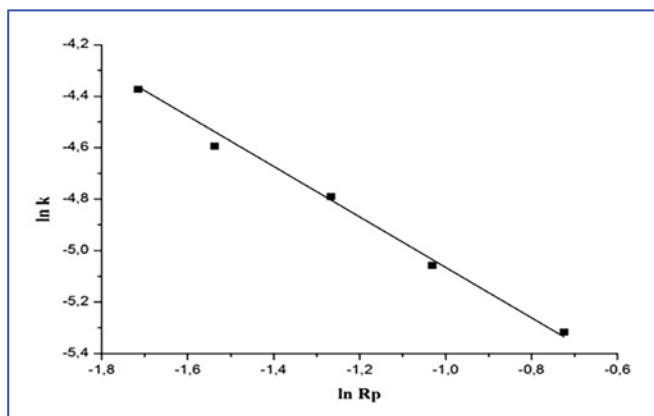
$$k_1 = \text{constant}$$

SL⁻¹ : Solid-liquid ratio

$$\ln k = \ln k_1 + a \ln Rp$$

MS : Mixing speed

$$k = k_1 (Rp)^{-0.9412}$$



Grain size: -60 + 80 mesh
 Acid concentration: % 6
 Temperature: 40 °C
 Mixing speed: 400 rpm
 Solid liquid ratio: 1.10-2 g.mL-1

Figure 7. Exchange of lnk with lnRp

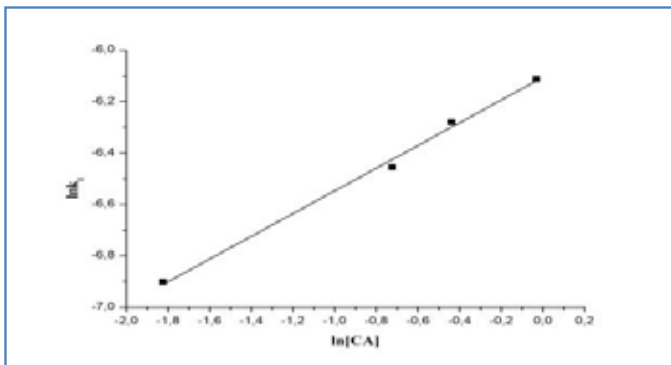
Table 2. For different Acid Concentrations ($[CA]_0$), $\ln [CA]_0$, k and $\ln k_1$ values

$[CA]_0$	$\ln [CA]_0$	k	$k_1=k/(Rp)^a$	$\ln k_1$	b
0.1617	-1.82201	0.0048	1.011×10^{-3}	-6.9027	
0.4852	-0.72319	0.0066	1.570×10^{-3}	-6.4566	
0.6458	-0.43727	0.0079	1.873×10^{-3}	-6.2801	0.4420
0.9704	-0.03005	0.0105	2.212×10^{-3}	-6.1134	

Using the data in Table 2, the value of b is calculated from the slope of the graph below.

$$k_1 = k_2 [CA]_0^b$$

$$k_1 = k_2 (Rp)^{-0.9412} [CA]_0^{0.4420}$$



Grain size: -60 + 80 mesh
 Acid concentration: % 6
 Temperature: 40 °C
 Mixing speed: 400 rpm
 Solid liquid ratio: 1.10-2 g.mL-1

Figure 8. Change graph of $\ln k_1$ against $\ln [CA]_0$

Table 3. k , k_2 , $\ln k_2$ and $\ln (S.L^{-1})$ Values for Different Solid / Liquid Ratios

$S.L^{-1}$	$\ln S.L^{-1}$	k	$k_2=k/(Rp)^a [CA]_0^b$	$\ln k_2$	c
0.005	-5.29832	0.0108	0.002307	-6.0715	
0.01	-4.60517	0.0068	0.001636	-6.4151	
0.02	-3.91202	0.0050	0.000960	-6.9416	-0.6450
0.04	-3.21888	0.0029	0.006196	-7.3863	

Using the data in Table 3, the value of c is calculated from the slope of the graph below.

$$k_2 = k_3 (S.L^{-1})^c$$

$$c = -0.64501$$

$$k_2 = k_3 (Rp)^{-0.9412} [CA]_0^{0.4420} (S.L^{-1})^{-0.6450}$$

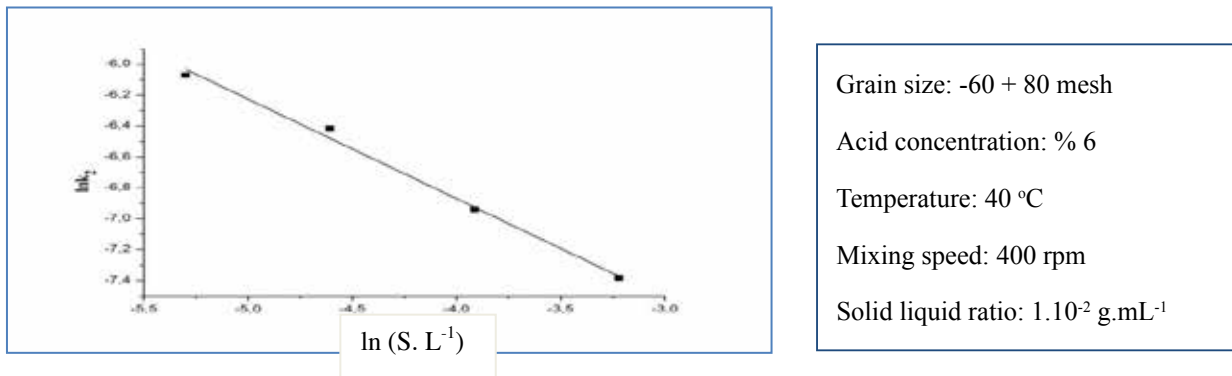
Table 4. k , k_3 , and $\ln MS$ Value for Mixing speed

Speed(rad.sec. ⁻¹)	$\ln M.S$	k	$k_3=k/(Rp)^a[CA]^b(S.L^{-1})^c$	$\ln k_3$	d
20.9439	3.041847	0.0101	0.00108	-6.8307	
31.4159	3.447314	0.0899	0.00110	-6.8054	
41.8879	3.734997	0.0918	0.00112	-6.7912	0.05809
52.3598	3.958139	0.0107	0.00114	-6.7767	

Using the data in Table 4, the value of d is calculated from the slope of the graph below.

$$k_3 = k_4(MS)^d$$

$$k_3 = k_4(Rp)^{-0.9412}[CA]_0^{0.4420}(S.L^{-1})^{-0.6450}(MS)^{0.05809}$$


Figure 9. Change graph of $\ln k_3$ against $\ln (S.L^{-1})$
Table 5. k , k_4 , $\ln k_4$, T and $1.T^{-1}$ Values for Different Reaction Temperatures

$T(K)$	$1.T^{-1}(K)$	k	$k_4=k/(Rp)^a[CA]_0^b(S.L^{-1})^c(MS)^d$	$\ln k_4$	$-E.R^{-1}$
303	0.00330	0.0068	$6.6954.10^{-5}$	-9.6115	
313	0.003195	0.0105	$1.0337.10^{-5}$	-9.1772	
323	0.003096	0.0124	$1.2208.10^{-4}$	-9.0108	-2649.12
333	0.003003	0.0170	$1.6737.10^{-4}$	-8.6953	
343	0.002915	0.0190	$1.8706.10^{-4}$	-8.5840	

Using the data in Table 5, the value of $-E.R^{-1}$ is calculated from the slope of the graph below.

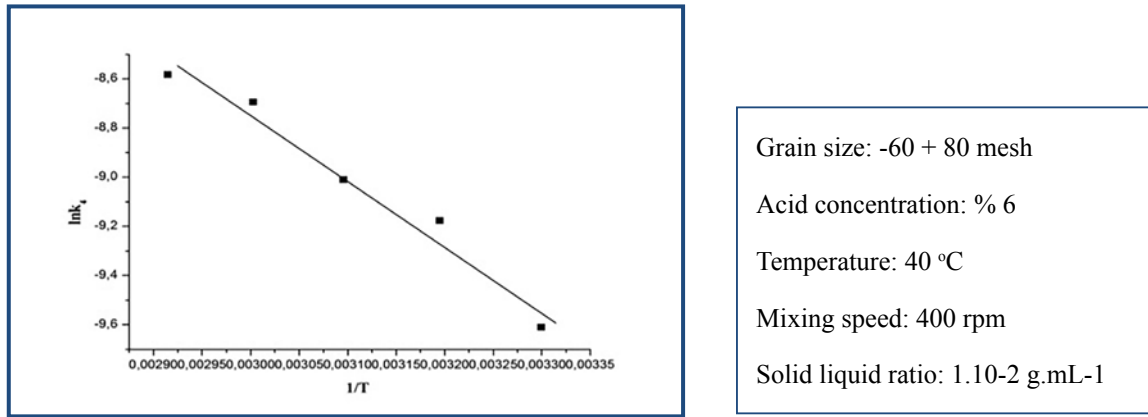


Figure 10. Change graph of $\ln k_t$ against $\ln(1/T)$

Common values of the parameters used in the experiments; particle size of -60 + 80 mesh, boric acid concentration of 6 %, stirring speed of 400 rev. min⁻¹,

the solid. liquid⁻¹ ratio of 1.10⁻¹ g.mL⁻¹, the reaction temperature 40 °C The equation expressing the effect on reaction rate of parameters,

$$1 - (1-x)^{1/2} = kt$$

$$k = k^0 (Rp)^a [CA]_0^b (S.L^{-1})^c (MS)$$

a, b, c, d and -E .R⁻¹ values, which are influenced by the parameters, can be expressed as; -1.013, 0.4579, -0.650, 0.0545, -2649.12 were found. By substituting

these values, the velocity expression representing the transformation of the ulexite ore into boric acid solutions is

$$1-(1-X)^{-1} = [2.02(Rp)^{-1.013} [CA]_0^{0.4579} (S.L^{-1})^{-0.650} (M.S)^{0.0545} e^{-2649.12T^{-1}}].t$$

CONCLUSION

During the calcination process, the ulexite ore loses its hydrated water content due to the dehydration temperature. As seen from the TGA chart, it is observed that at temperatures between 161 °C and 199 °C, where the mineral starts to lose its hydrated water content around 87 °C, most of the hydrated water is lost and the weight loss continues with increasing temperature. The TGA diagram confirms the findings of mass loss measurements. Structural changes in the mineral began after 100 °C. Structural changes in the ore have begun to become more pronounced with a distinctive peak at 160-170 °C, as seen in the TGA diagram. SEM images of the original sample showed that the pores were opened up to 170 °C and the number of pores decreased after this temperature. This situation gives the impression

that a porous structure in the crystal starts to form up to this temprature. Sintering is a mechanism that occurs by heating solid materials and sticking one of the solid particles under melting temperatures. This phenomenon is observed to be fixed at a level of 170 °C. The phenomenon of sintering is over this temperature. Sintering affects the surface area and porous structure of the ore, making the dissolution process difficult. It was observed that the dissolution rate increased up to 170 degrees. After this temperature was observed in the kinetics data and graphs that dissolution rate gradually decreased with in the decreased pores of the sample. It seems that the dissolution rate at temperatures of 300 °C and above is less than the original. This can be explained by the presence of sintering and the closing of the pores affecting the rate of dissolution. The

number of pores in the original sample is less than the heated sample. With heating, the number of pores starts to increase. The increase in dissolution rate up to about 170 °C indicates that the number of pores increases. When this temperature is exceeded, sintering is caused by the shrinkage of the pore structure, which causes

the dissolution rate to decrease due to the difficulty of penetrating the aside into the ore.

The studies about like these compliance with these models, the model tests and the experimental results, were found to match the chemical reaction control $[1-(1-X)^{1/2}]$ and this was calculated as blow;

$$1-(1-X)^{-1} = [2.02(Rp)^{-1.013}[CA]_0^{0.4579}(S.L^{-1})^{-0.650}(M.S)^{0.0545}e^{-2649.12T^{-1}}].t$$

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