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Determination of the Optimum Conditions for Boric Acid Extraction from Ulexite in Perchloric Acid Solutions

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In this study, Taguchi method was used to determine optimum conditions for the dissolution of ulexite in perchloric acid slutions. For optimization process; solid-to-liquid ratio, reaction time, particle size and acid concentration were chosen as parameters. In the experiment, stirring speed and reaction temperature were kept as constant. The ranges of experimental parameters were between 0.1-0.2 g/cm^3 for solid-to-liquid ratio, 1.5-2.5 M for acid concentration, 165.0-512.5 μm for particle size and 12-36 min for reaction time. In the end of the experimental sections the optimum conditions were determined as 0.1 g/mL for solid to liquid ratio; 215 μm for particle size; 24 min for reaction time; 500 rpm for stirring speed; 30 ºC for reaction temperature and 2 mol/dm^3 for acid concentration. Under these conditions, it was found that the boric acid extraction from ulexite was reached a value of 99 %.

Key Words: Ulexite, Perchloric acid, Dissolution, Taguchi method.

INTRODUCTION

Boron is available in nature mostly as sodium and calcium compounds. Boron minerals are named according to their water contents and crystal structure. For example, ulexite, which has been used in this study, is a boron mineral that contains sodium-calcium, has the formula of $Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$ and is one of the most common boron minerals and available in huge amounts in Turkey[1]. The increasing demand and new industrial uses of boron compounds have increased their importance. Borates are used commonly in many industries, such as chemical, metallurgy, nuclear engineering, *etc*. Commercially, extensively used boron minerals are borax, boric acid, borax hydrates and sodium perborates[2].

Some authors have studied dissolution of boron minerals in acidic solutions, *viz.*, in nitric acid[3], sulphuric acid[4], oxalic acid[5], hydrochloric acid[6], *etc*. Imamutdinova and Abdrashitova[7] investigated the dissolution of ulexite in acetic acid solutions and found that the dissolution rate was maximum at relatively low acid concentrations. Kum *et al.*[8] studied the dissolution

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kinetics of calcined colemanite in ammonium chloride solutions and found that the dissolution rate can be expressed in terms of a homogeneous reaction model. Künkül *et al.*[9] studied the dissolution of ulexite in NH_3 solutions saturated with CO_2 and found that the dissolution kinetics could be expressed with a pseudo-homogeneous first order reaction rate model. Yapici *et al.*[10] studied the optimum conditions for the dissolution of ulexite in water saturated with CO_2 to obtain boric acid. Tekin *et al.*[11] investigated the leaching kinetics of ulexite in ammonium chloride solutions and the activation energy for the dissolution was found to be 80 kJ/mol. Karagölge *et al.*[12] investigated the leaching kinetics of colemanite i aqueous dissodium EDTA solutions and calculated the activation energy as 50.6 kJ/mol and the pre-exponential factor as 5.14×10^7 m/s. Yesilyurt[13] investigated the optimum conditions for the boric acid extraction from colemanite ore in HNO_3 solutions and the optimum conditions were found to be particle size, 2.4 mm, acid concentration, 2.2 M, stirring speed, 500 rpm, reaction time 11 min, solid-to-liquid ratio, 0.25 g/mL and reaction temperature, 94 ºC. The optimization of leaching conditions of the ores is important in industrial processes and some researchers have been interested in these topics by using various techniques[14]. Zdanovskii and Biktagirova[15] carried out a study of the dissolution of ulexite in H_3PO_4 solutions and found that in acid concentrations of 5 %, a solid film of H_3BO_3 formed on the ulexite crystals and the dissolution rate of the mineral. Küçük[16] investigated optimization of dissolution of ulexite in water saturated with sulphur dioxide. Experiments were carried out in two stages. In the second stage, a conversion of 100 % was reached. The optimum conditions were found as 0.25 g/mL for solid-to-liquid ratio, 725 μm for particle size, 400 rpm for stirring speed and 0.5 h for reaction time at 92 ºC reaction temperature.

As a technique, Taguchi's Orthogonal Array (OA) analysis is used to produce the best parameters for the optimum design process, with the least number of experiments. In recent years, the main advantages of this method over other statistical experimental can be investigated as controlling and non-controlling and that the method can be applied to experimental design involving a large number of design factors[17].

In this study, optimum conditions for the dissolution of ulexite in perchloric acid solution were investigated. For optimization process; solid-to-liquid ratio, reaction time, particle size and acid concentration were chosen as parameters.

EXPERIMENTAL

The ulexite mineral used in the study was obtained from Bigadic, town of Balikesir Province in Turkey. The sample mineral was first broken into small pieces, grounded and sieved with ASTM standard sieves to particle

sizes of 215, 330, 225 μm. The original sample was tested for chemical composition and found to have 35.85 % B_2O_3, 15.22 % CaO, 6.38 % Na_2O, 29.67 % H_2O, 5.38 % MgO and 7.5 % other components. The X-ray diffractogram of the original sample was taken (Fig. 1).

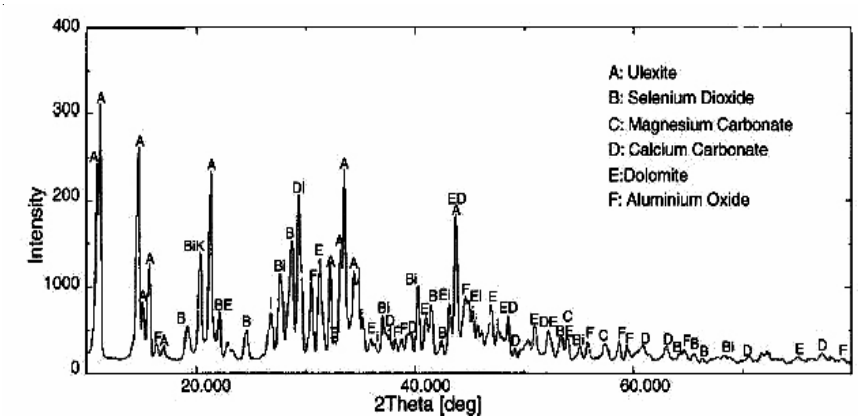

Fig. 1. X-ray diffractogram of the ulexite ore

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 contents of the vessel were 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 the present sample reacted is defined:

XB_2O_3 = The amount of dissolved B_2O_3/
The amount of B_2O_3 in original sample (1)

Experimental parameters and their levels determined in the light of preliminary tests are given in Table-1.

TABLE-1
PARAMETERS AND THEIR VALUES CORRESPONDING TO THEIR LEVELS

	Parameters	Levels		
		1	2	3
A	Solid-to-liquid ratio (g/mL)	0.1	0.15	0.2
B	Particles size (μm)	512.5	215	165
C	Acid concentration (M)	1.5	2	2.5
D	Reaction time (min)	12.0	24	36

The orthogonal array experimental design was chosen as the most suitable method to determine the experimental plan L_9 (3^4), for four parameters of each three values given in Table-2. In order to determine the effects of uncontrollable factors on this process, each experiment was repeated twice under same conditions at different times. Performance characteristics chosen the larger the better, the smaller the beter and nominal the best. When the desired characteristic for the response is the larger the better; Taguchi recommends the use of

$$\theta = -\log 10\left\{\frac{1}{n}\sum\frac{1}{y2}\right\}$$

TABLE-2
EXPERIMENTAL DESIGN USED

Experiment No.	Parameters levels				1st trial	2nd trial	3rd trial	Mean
	A	B	C	D				
1	1	1	1	1	0.29	0.32	0.33	0.31
2	1	2	2	2	0.98	1.00	0.99	0.99
3	1	3	3	3	0.99	1.00	1.00	0.99
4	2	1	2	3	0.56	0.53	0.57	0.55
5	2	2	3	1	0.60	0.62	0.61	0.61
6	2	3	1	2	0.97	0.96	0.95	0.96
7	3	1	3	2	0.47	0.49	0.48	0.48
8	3	2	1	3	0.87	0.85	0.88	0.86
9	3	3	2	1	0.68	0.66	0.67	0.67
Grand average								**0.71**

for the n observations, y in each trial. The analysis of some experimental results have indicated that the optimal settings for the studied parameters, estimation of the process's future performance under optimal conditions is usually required. This method suggest an estimation formula based on individual differences between the average of the chosen factor levels and the overall mean. The process average under the optimal levels can be estimated as;

$$\mu = Mx\beta(M) + (\overline{A}_3 - M)x\beta(A) + (\overline{B}_4 - M)x\beta(B)$$

where μ is the process average, M the grand average of all experimental results, β the coefficient of grand average (M) and each parameter (A,B) defined by $1-(1/F_{(A,B)})$, $F_{(A,B)}$ = F- ratio of each parameter, $\overline{A}_3$ = the average yield at level A_3 and β = the average yield at level B_4. μ is clearly only an estimate of the real process average under the selected conditions. To determine whether results of the confirmation experiments are meaningful or not, the confidence limits for μ must be evaluated. (100-α) % confidence limits can be obtained using the formula

$$\mu \pm \sqrt{F(1,df_e;\alpha)MMS_e n_e^{-1}}$$

where df_e, $F(1,df_e;\alpha)$ and n_e represent degrees of freedom at level of α, critical value from the F-tables and effective number of replications, respectively. General formula for the effective number of replications is as follows:

$$n_e = \frac{N}{1 + \sum(ED)}$$

where N is the size of the experiment and Σ(ED) is the total effective number of degrees of freedom.

The interactive effects of parameters were not taken into account in the theoretical analysis because confirmation experiments performed at the optimum conditions showed that they could be neglected. Always a confirmatory experiment should be run to verify predicted results. If the predicted results are confirmed, the suggested optimum working conditions will be adopted. If not, or the results are otherwise unsatisfactory, it will be concluded that the additional experiments underlying the experimental design has failed and ways need to be found to correct that problem.

RESULTS AND DISCUSSION

During the dissolution of ulexite in $HClO_4$ solutions, the reaction can be represented as

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^- \quad (2)$$

$$Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O + 6\,H_3O^+ \longrightarrow 2Na^+ + 2Ca^{2+} + 10H_3BO_3 + 10H_2O \quad (3)$$

$$Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O + HClO_4 + 5H_3O^+ \longrightarrow 2Na^+ + 2Ca^{2+} + 10H_3BO_3 + ClO_4^- + 9H_2O \quad (4)$$

The collected data were analyzed by using the Minitab computer software package program. In order to see effective parameters and their confidence levels on the dissolution process, an analysis of variance was performed. A statistical analysis of variance (Anova) was performed to see whether the process parameters are statistically significant or not. The results are given in Fig. 2.

At first sight it is difficult and complicated to deduce experimental conditions for graphs given in these figures. The optimal levels of these factors are the levels with the maximum performance statistics (θ), *i.e.*, with minimum variability. On the basis of level averages (for θ), Fig. 2. constructed for the experiments. There is evidence from performance measures (Fig. 2) and Anova analysis (Table-4). There is a significant effect on the dissolution process from the following factors: reaction time, particle

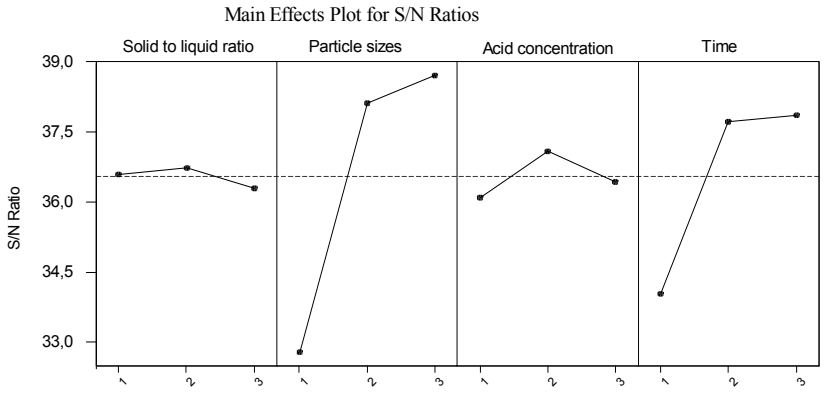

Fig. 2. Effect of each parameter on the optimization criteria

TABLE-3
LEVEL AVERAGES FOR THE DISSOLUTION PROCESS

Levels	A	B	C	D
1	76.6667	44.8889	71.3333	53.1111
2	70.7778	82.2222	73.7778	81.0000
3	67.2222	87.5556	69.5556	80.5556

TABLE-4
ANOVA ANALYSIS FOR B_2O_3 EXTRACTION

Source	df	SS	MSS	F-ratio	Cr (%)
Solid-to-liquid	2	409.6	204.8	112.84	2.73
Particle size	2	9728.0	4864.0	2680.16	65.50
Acid concentration	2	80.9	40.4	22.29	0.52
Reaction time	2	4593.6	2296.8	1265.57	30.92
Error	18	32.7	1.8	–	–
Total	26	14844.7	–	–	–

size, acid concentration and solid-to-liquid ratio, respectively. From Fig. 2, the optimal levels of these factors are 2, 2, 2 and 2 for reaction time, particle size, acid concentration and solid-to-liquid ratio, respectively.

Using Taguchi's estimation formula based on the level averages and the associated 'β coefficents' an estimate of the performance for μ under the optimal conditions is given by formula (3), which yields;

$$\mu = Mx\beta(M) + (\overline{A}_3 - M)x\beta(A) + (\overline{B}_4 - M)x\beta(B) + (C_3 - M)x\beta(C) + (D_3 -)x\beta(D)$$

We can find M (grand average) to be 71.55 with $\beta(M) = 1 - \left(\frac{1}{F_{(M)}}\right)$

where

$$F_{(M)} = \frac{C_f}{MSS_e} = \frac{(29 + ... + 67)^2 / 27}{1.8} = 101802.9 \quad \text{and so}$$

$$\beta_{(M)} = 1 - \left(\frac{1}{101802.9} \right) = 0.999 \cong 1$$

Also from Table-4,

$$\beta(A) = 1 - \frac{1}{112.84} = 0.999, \ \beta(B) = 1 - \frac{1}{2680.16} = 0.996, \ \beta(C) = 0.955, \ \beta(D) = 0.998$$

Therefore,

μ = 71.50 × 1 + (70.77-71.50) × 0.999 + (82.22-71.50) × 0.996 +
(73.77-71.50) × 0.995 + (81-71.50) × 0.998 = 93.176

The confidence limits on the above estimate can be calculated using formula (4) and (5)

$$\mu \pm \sqrt{F(1, df_e; \alpha) MMS_e n_e^{-1}}$$

where

$F(1,df_e; \alpha) = F(1.18; 5\%) = 4.41$ $MMS_e = 1.8$ and $n_e = 3$

$$\sqrt{F(1, df_e; \alpha) MMS_e n_e^{-1}} = \sqrt{4.41 x 1.8 x 3} = 4.87$$

Thus, confidence interval for dissolution process was given by 93.176 ± 4.87, it may vary from 88.3 to 98.04. To test the predicted results, confirmation experiments were carried out at optimum working conditions. From the fact that dissolution percentages obtained from confirmation experiments (mean 92 %) were acceptable within the calculated confidence interval, it could be suggested that the experimental results are within ± 5 % in error. This proves that interactive effects of parameters are negligible. But, this dissolution percentage was unsatisfactory. In the light of experimental results, while keeping the particle size, acid concentration and solid-to-liquid ratio at optimum levels (2, 2 and 2, respectively), the levels of reaction time were increased by one level (0.5 h). In the 0.5 h of process, the conversion fraction was reached a value of 99 %.

Conclusion

In this paper, Taguchi method has been used to determine the optimum working conditions for the dissolution of ulexite in $HClO_4$ solutions. The orthogonal array $OA_9(3^4)$, technique is described for experimental design. The essential conclusions from the present study are:

(a) The effective parameters on the dissolution of ulexite in $HClO_4$ solution are reaction temperature, solid-to-liquid ratio, reaction time, acid concenration and particle size, respectively, while stirring speed was kept as 500 rpm and reaction temperature was kept at 30 ºC.

(b) The optimum conditions are 0.15 g/mL for solid to liquid ratio 215 μm for particle size, 24 min for reaction temperature and 2 M for acid concentration under these conditions, it was determined that conversion fraction was reached a value of 100 %.

(c) As the optimum conditions determined by the Taguchi method in a laboratory environment is reproducible in real production environments as well, the findings of the present study may be very useful for processing on industrial scale.

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