Korean J. Chem. Eng., **23**(1), 21-27 (2006)

Application of Taguchi method in the optimization of dissolution of ulexite in NH_4Cl solutions

Özkan Küçük†

Department of Chemical Engineering, Engineering Faculty, Atatürk University, Erzurum, Turkey
(*Received 20 July 2005 • accepted 28 September 2005*)

Abstract−The Taguchi method was used to determine optimum conditions for the dissolution of ulexite in NH_4Cl solutions. The ranges of experimental parameters were between 50-87 °C for reaction temperature, 0.05-0.20 g·mL^{-1} for solid-to-liquid ratio, 1-4 M for NH_4Cl concentration, 5-25 min for reaction time, and (−850+600)-(−90) μm for particle size. The optimum conditions for these parameters were found to be 87 °C, 0.05 g·mL^{-1}, 4 M, (−300+212) μm, and 18 minutes, respectively. Under these conditions, the dissolution percentage of ulexite in NH_4Cl solution was 98.37. Reaction products were found to be boric acid, ammonium tetraborates, sodium tetraborate decahydrate, calcium chloride, and sodium chloride.

Key words: NH_4Cl, Ulexite, Dissolution, Optimization, Taguchi Method

INTRODUCTION

Boron has the ability to form a large number of complex chemical compounds. Boron compounds are important raw materials in many branches of industry, and their use increases and expands continuously in the production of medicines, disinfectants, cosmetics, detergents, and in the industries of glass, polymer, dye and plating, steel, refractory materials etc. Furthermore, they have applications in nuclear technology as a radiation trapper, in rockets as fuel, and in some production industries as catalysts [Garret, 1998]. Ulexite, which is a sodium-calcium borate with a chemical formula of $Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 16H_2O$, is available in huge quantities in nature and is commercially important. It is used in the production of boron compounds, especially boric acid and boron materials such as boron glass and wool. Turkey has the largest boron resources in the world, and ulexite is available together with other borates around the regions of BalIkesir-Bigadiç and Kütahya-Emet.

The dissolution of ulexite in various media is of economic interest. Imamutdinova [1967] studied the dissolution of ulexite in H_2SO_4, H_3PO_4, HNO_3, and HCl solutions. The dissolution process in these acidic solutions has been determined to be diffusion controlled. Zdanovskii and Biktagirova [1967] carried out a study of the dissolution of ulexite in H_3PO_4 solutions and found that at acid concentrations of 5%, a solid film of H_3BO_3 formed on the ulexite crystals and the dissolution rate of this product restricted the dissolution rate of the mineral. The investigations on the dissolution of ulexite in aqueous SO_2 and CO_2 solutions revealed that the dissolution process was found to be diffusion controlled in the case of CO_2, while it is chemical reaction-controlled in SO_2 solutions [Kocakerim and Alkan, 1988; Gülensoy and Kocakerim, 1978; Kocakerim et al., 1993]. Imamutdinova and Abdrashitova [1970] investigated the dissolution of ulexite in acetic acid solutions and found that the dissolution rate was maximum at relatively low acid concentrations (10-20%), and over these concentrations the dissolution rate decreased with increasing acid concentration. The dissolution of ulexite in perchloric acid solutions was also investigated, and it was determined that the dissolution is faster than that in HNO_3 solutions [Imamutdinova and Vladykina, 1969]. Künkül et al. [1997] 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. Tunç et al. [1999] reported that the dissolution of ulexite in H_2SO_4 was controlled by the diffusion of H_3O^+ through the H_3BO_3 product layer and the by-product layer of $CaSO_4$ and/or $CaSO_4\cdot 2H_2O$. Kucuk et al. [2002] studied the dissolution of Kestelek's colemanite in water saturated with SO_2 and the dissolution process was found to be chemical reaction-controlled. Tekin et al. [1998] studied the leaching kinetics of ulexite in ammonium chloride solutions and the activation energy for the dissolution was found to be 80 kj·mol^{-1}. Kum and Alkan [1994] studied the dissolution kinetics of calcined colemanite in ammonium chloride solutions and found that the dissolution rate can be expressed in terms of a homogeneous reaction model. Özmetin et al. [1996] investigated dissolution of colemanite in acetic acid solutions and determined that dissolution rate of colemanite obeyed the first order pseudo-homogeneous reaction model in the form of $-Ln(1-X)=k.t$. 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 determined as 12.89 kJ mol^{-1}. ZareNezhad [2004] was investigated the production of boric acid through reaction of borax crystals with propionic acid in batch mode.

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 [YapIcI et al., 1990; Çopur, 2002; Yeşilyurt, 2003; Küçük et al., 2005].

As an optimization 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 Taguchi method has been used to determine optimum parameters because of its many advantages. The main advantages of the method over other statistical experimental design methods are that

†To whom correspondence should be addressed.
E-mail: okucuk@atauni.edu.tr

the parameters affecting an experiment can be investigated as controlling and not controlling, and that the method can be applied to experimental design involving a large number of design factors [Çopur, 2002].

In this study, ulexite mineral was dissolved in ammonium chloride solutions by taking into consideration the experimental parameters of particle size, solid-to-liquid ratio, reaction temperature, and reaction time, and Taguchi experimental design method was employed to determine optimum dissolution conditions.

EXPERIMENTAL

Ulexite mineral used was provided from the resources in the Ballkesir-Bigadiç region. It was crushed and then ground followed by sieving, using ASTM standard sieves, to obtain the particle size fractions of (−850+600), (−300+212), (−212+150), and −90 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 containing SiO_2 and clay minerals. X-ray diffractogram of the original sample obtained by a Rigaku DMAX 2000 series X-ray diffractometer was given in Fig. 1.

The dissolution process was carried out in a 500 mL-jacketed glass reactor at atmospheric pressure. A mechanical stirrer was used, for stirring the reactor contents and a thermostat for maintaining reaction medium at a given temperature. A cooler was attached to the reactor to inhibit boiling away the reactor content by evaporation. The parameters investigated and their ranges are given in Table 1.

In the experiments, 100 mL NH_4Cl solution was put into the reactor, and heated to a desired temperature. Subsequently, a known amount of the sample was added into the solution while the stirring was started. At the end of a given reaction period, the stirring was stopped and the contents were filtered. At the end of dissolution period, the amounts of B_2O_3 passing into the solution during the reaction were determined by a complexometric method [Gülensoy, 1984].

The application of the Taguchi Method to optimize the process by using multiple performance characteristics includes eight steps, which make up a Robust Design cycle view of planning and performing the experiments and analyzing and verifying the experimental results [Phadke, 1989].

Experimental parameters and their levels are seen in Table 1. The orthogonal array (OA) was chosen as the most suitable to make up the experimental design, $L_{16}(4^5)$, with five parameters each with four values given in Table 2. Each experiment was repeated twice under the same conditions at different times, to determine the effects of noise sources on process. Performance characteristics chosen as the optimization criteria are divided by three categories, the larger-the-better, the smaller-the-better and the nominal-the-best. The first two of them were calculated by using Eq. (1) and (2) [Phadke, 1989].

$$\text{Larger-the-better } SN_L = -10\text{Log}_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \quad (1)$$

$$\text{Smaller-the-better } SN_S = -10\text{Log}_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \quad (2)$$

In the Taguchi method, the experiment corresponding to the opti-

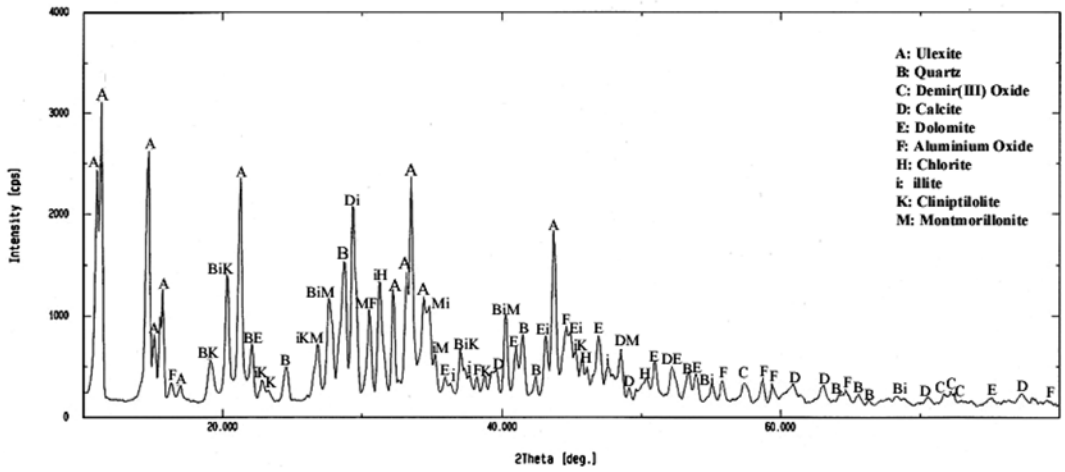

Fig. 1. X-ray diffractogram of the original ulexite mineral.

Table 1. Parameters and their values corresponding to their levels to be studied in experiments

	Parameters	Levels			
		1	2	3	4
A	Reaction temperature (°C)	50	60	74	87
B	Solid-to-liquid ratio ($g \cdot mL^{-1}$)	0.05	0.1	0.15	0.20
C	NH_4Cl concentration (M)	1	2	3	4
D	Particle size (μm)	−850+600	−300+212	−212+150	−90
E	Reaction time (min)	5	10	18	25

Table 2. L_{16} (5^4) experimental plan table

Experiment no	Quantities and their levels					B_2O_3% experiment (I)	B_2O_3% experiment (II)	B_2O_3% average
	A	B	C	D	E			
1	1	1	1	1	1	24.85	25.28	25.07
2	1	2	2	2	2	27.35	27.79	27.57
3	1	3	3	3	3	21.81	22.24	22.03
4	1	4	4	4	4	17.48	17.92	17.70
5	2	1	2	3	4	68.01	68.14	68.23
6	2	2	1	4	3	28.62	29.27	28.95
7	2	3	4	1	2	27.85	26.56	27.21
8	2	4	3	2	1	19.41	19.96	19.69
9	3	1	3	4	2	79.52	82.14	80.83
10	3	2	4	3	1	49.93	48.86	49.40
11	3	3	1	2	4	23.97	22.06	23.02
12	3	4	2	1	3	20.88	21.10	20.99
13	4	1	4	2	3	98.81	97.93	98.37
14	4	2	3	1	4	56.34	56.56	56.45
15	4	3	2	4	1	31.61	31.32	31.47
16	4	4	1	3	2	19.48	19.26	19.37

mum working conditions might not be found in a randomized experimental plan table. In such cases, the performance values for optimum conditions can be predicted by using the balanced characteristics of OA. For this purpose, an additive model can be used as follows [Phadke et al., 1983].

$$Y_i=\mu+X_i+e_i \tag{3}$$

If experimental results are in percentage (%), before evaluating Eq. (3) Ω transformation of percentage values should be applied first using Eq. (4) by which values of interest are also later determined by carrying out reverse transformation by using the same equation [Taguchi, 1987]:

$$\Omega(\text{db}) = -10\text{Log}\left(\frac{1}{\text{P}}-1\right) \tag{4}$$

Because Eq. (3) is a point estimation, which is calculated by using experimental data in order to determine whether the additive model is adequate or not, the confidence limits for the prediction error must be evaluated [Phadke, 1989]. The prediction error is the difference between the observed Y_i and the predicted Y_i. The confidence limits for the prediction error, Se, is

$$\text{Se}=\pm 2\sqrt{\left[\frac{1}{n_0}\right]\sigma_e^2+\left[\frac{1}{n_r}\right]\sigma_e^2} \tag{5}$$

$$\sigma_e^2=\frac{\text{sum of squares due to error}}{\text{degrees of freedom for error}} \tag{6}$$

$$\frac{1}{n_0}=\frac{1}{n}+\left[\frac{1}{n_{A_i}}-\frac{1}{n}\right]+\left[\frac{1}{n_{B_i}}-\frac{1}{n}\right]+\left[\frac{1}{n_{C_i}}-\frac{1}{n}\right]\cdots\cdots \tag{7}$$

If the prediction error is outside these limits, the possibility that the additive model is not adequate should be suspected. Otherwise, the additive model can be considered to be adequate.

A verification experiment is a powerful tool for detecting the presence of interactions among the control parameters. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then the interactions are probably not important and the additive model is a good approximation [Phadke, 1989].

The order of the experiments was obtained by inserting parameters into columns of OA, $L_{16}(4^5)$, which were chosen as the experimental plan given in Table 2. But the order of experiments was made random in order to avoid noise sources which had not been considered initially and which could take place during an experiment and affect results in a negative way.

RESULTS AND DISCUSSION

1. Dissolution Reactions

The following reactions take place when ulexite is dissolved in ammonium chloride solutions:

$$Na_2O\cdot 2CaO\cdot 5B_2O_3\,16H_2O_{(s)}+2H_2O \Leftrightarrow 2Na^+_{(aq)}+2Ca^{+2}_{(aq)}+6B(OH)^-_{4(aq)}+4H_3BO_{3(aq)} \tag{8}$$

$$NH_4Cl_{(aq)} \Leftrightarrow NH^+_{4(aq)}+Cl^-_{(aq)} \tag{9}$$

$$NH^+_{4(aq)}+H_2O_{(s)} \Leftrightarrow NH_{3(aq)}+H_3O^+_{(aq)} \tag{10}$$

$$B(OH)^-_4+H_3O^+ \Leftrightarrow H_3BO_3+2H_2O \tag{11}$$

As a result, the overall reaction is

$$Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 16H_2O_{(s)}+6NH^+_4+6Cl^-_{(aq)} \rightarrow 2Na^+_{(aq)}+2Ca^{+2}_{(aq)}+10H_3BO_{3(aq)}+6NH_{3(g)}+6Cl^-_{(aq)}+4H_2O \tag{12}$$

Species such as Ca^{2+}, Na^+, NH_4^+, Cl^- ions, H_3BO_3, and NH_3 are present in the reaction medium. When the solution is evaporated, a part of NH_3 passes into the gas phase depending on temperature and pH. NH_3 remaining in the solution forms $(NH_4)_2B_4O_7\cdot xH_2O$. In addition to this, $Na_2B_4O_7\cdot 10H_2O$, H_3BO_3, NaCl, and $CaCl_2\cdot 2H_2O$ precipitate, depending on their solubilities (Fig. 4).

2. Statistical Analysis

Table 3. Results of the analysis of variance for the dissolution values of ulexite

	Parameters	Sum of squares	Degrees of freedom	Mean of squares	F	Cr (%)
A	Reaction temperature (°C)	3487.9	3	1162.6	2326.40	18.86
B	Solid-to-liquid ratio ($g \cdot mL^{-1}$)	11226.8	3	3742.3	7488.25	60.72
C	NH_4Cl concentration (M)	2735.6	3	911.9	1824.65	14.79
D	Particle size (μm)	426.9	3	142.3	284.76	2.30
E	Reaction time (min)	601.7	3	200.6	401.30	3.25
	Error	8	16	0.5		
	Total	18486.9	31			

The collected data were analyzed by using the MINITAB computer software. An analysis of variance was performed to see effective parameters and their confidence levels on the dissolution process. A statistical analysis of variance (ANOVA) was performed to determine whether process parameters are statistically significant. The F test is a tool to see which process parameters have a significant effect on the dissolution value. The F value for each process parameter is simply a ratio of the mean of the squared deviations to the mean of squared error. Usually, the larger the F value, the greater the effect on the dissolution value due to the change of the process parameter. With the performance characteristics and ANOVA analyses, the optimal combination of process parameters can be predicted [Çopur, 2002]. The results of variance analysis are given in Table 3.

To obtain optimal dissolution performance, the larger-the-better performance characteristic (Eq. (1)) has been taken for dissolution of B_2O_3.

The order of graphs in Fig. 2 is according to the degrees of the influences of parameters on the performance characteristics. The optimal level of a process parameter is the level with the highest SN ratio value calculated by Eq. (1). Fig. 2B shows the variation of performance characteristics with solid-to-liquid ratio. To determine the experimental conditions for the first datum point, the B for that point is level 1 which is 0.05 $g \cdot mL^{-1}$ for this parameter. The experiments for which B level (column B) is 1 are experiments 1, 5, 9, and 13. The first datum point in Fig. 2B is the arithmetical aver-

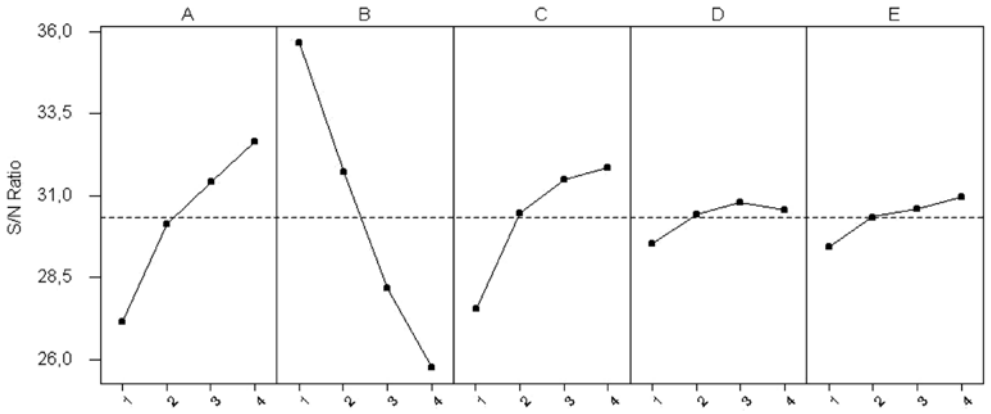

Fig. 2. The effect of each parameter on the optimization criteria for B_2O_3.

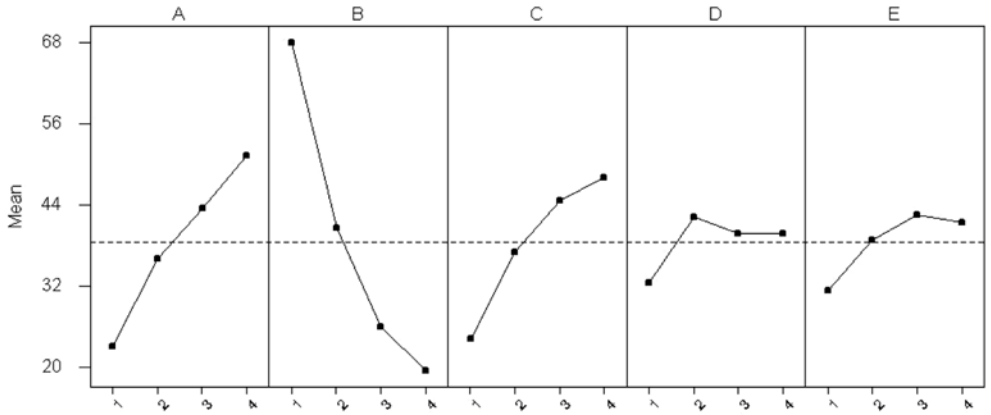

Fig. 3. The mean effects plot for means.

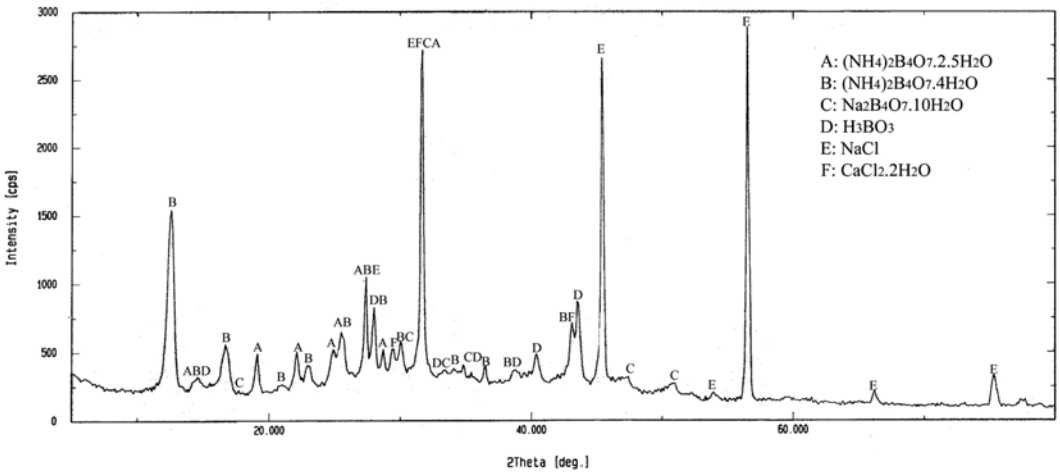

Fig. 4. X-ray diffractogram of crystals obtained.

Table 4. Optimum working conditions, predicted dissolved quantities of the ulexite

	Parameters	Case 1*		Case 2	
		Value	Level	Value	Level
A	Reaction temperature (°C)	87	4	87	4
B	Solid-to-liquid ratio ($g \cdot mL^{-1}$)	0.05	1	0.05	1
C	NH_4Cl concentration (M)	4	4	4	4
D	Particle size (μm)	−300+212	2	−212+150	3
E	Reaction time (min)	18	3	25	4
Observed dissolved quantity for B_2O_3 (%)		97.93		94.30	
Predicted dissolved quantity for B_2O_3 (%)		98.37		94.73	
Confidence limits of prediction for B_2O_3 (%)		96.31-100		92.67-96.79	

*The parameter levels for maximum dissolution of B_2O_3

age of the performance characteristics for these experiments. All the points in 2B graphs and other graphs are established by the same way. In each graph, the numerical value of a maximum point corresponds to the best value for that parameter. These values are seen to be A4 (87 °C), B1 (0.05 $g \cdot mL^{-1}$), C4 (4M), D3 (181 μm) and E4 (25 min).

Fig. 3 shows the main effect plots for means. The points in these plots are found in the same way as those obtained in Fig. 2, but, the average of experimental data corresponding are taken instead of averages of the performance characteristics. When Figs. 2 and 3 are compared, it is seen that although they are similar for other parameters, optimum conditions for the particle size and reaction time are different. Optimum condition for particle size was D3 (181 μm) in Fig. 2D, but D2 (256 μm) in Fig. 3D and reaction time E4 (25 min) in Fig. 2E, but E3 (18 min) in Fig. 3E.

Dissolution value at optimum conditions was 94.30% in Fig. 2, but 98.81% in Fig. 3. It was verified that these dissolution data were in agreement with those predicted. This case was attributed to the following reason. Normally, dissolution rate increases with decreasing the particle size, and also the dissolving amount increases with increasing of dissolving time. When the reaction rate becomes higher than the transfer rate of products to main solution, the reaction products form a film around ulexite particles, and progressively this film becomes thick, diffusion becomes difficult, and the conversion fraction of ulexite decreases. The small particle size may not always be an element of optimum conditions in a dissolution process, as well.

Therefore, for this process A4, B1, C4, D2, and E3 conditions were taken as optimum dissolution conditions and the dissolution fraction under these conditions was found to be 98.81%.

If the experimental plan given in Table 2 is studied carefully together with parameter values given as A4 (87 °C), B1 (0.05 $g \cdot mL^{-1}$), C4 (4 M), D3 (181 μm), and E4 (25 min), it can be seen that experiments corresponding to optimum conditions have not been carried out during the experimental work.

Thus, it should be noted that the dissolution percentages in Table 4 are predicted results from Eqs. (3)-(4) and observed results for same conditions. Also, the results in Table 4 are confidence limits of predictions. In order to test the predicted results, confirmation experiments were carried out twice at the same working conditions. The fact that the dissolution percentages from confirmation experiments are within the calculated confidence intervals calculated from Eqs. (5)-(7) (see Table 4) shows that the experimental results are within ±5% in error. This case states that there is a good agreement between the predicted values and experimental values, and the interactive effects of the parameters are indeed negligible. It may be concluded that the additive model is adequate for describing the dependence of this dissolution process on the various parameters [Phadke, 1989].

CONCLUSIONS

The major conclusions from the present work are:

1. The effective parameters on the dissolution of ulexite in ammonium chloride solutions are solid-to-liquid ratio, reaction temperature, ammonium chloride concentration, reaction time and particle size.
2. The optimum conditions within the selected parameter values are 87 °C for reaction temperature, 0.05 g·mL^{-1} for solid to liquid ratio, 18 min for reaction time, 4 M for ammonium chloride concentration, and 256 μm for particle size. Under these conditions, dissolution of 98.81% in terms of B_2O_3 can be achieved (Table 4).
3. The predicted and observed dissolution values are very close to each other, and it may be concluded that the additive model is adequate for describing the dependence of the dissolution process on the various parameters.
4. The small particle size may not always be an element of optimum conditions in a dissolution process.
5. Since optimum conditions determined by the Taguchi method in a laboratory environment are reproducible in real production environments as well, the findings of the present study may be very useful for processing on an industrial scale.
6. It was thought that boric acid, ammonium tetraborates and sodium tetraborate could be produced by this process. On the other hand, in the production of boric acid by sulphuric acid process, pH of reaction mixture is low (about 1-2) and the produced boric acid is contaminated with Fe^{2+} and Al^{3+} ions at this pH. However, reaction mixture does not contain these contaminants in the process proposed in this paper because pH changes from 5 to 7.

APPENDIX

The μ Value in Eq. (3) (the grand average of all experimental results) is calculated as follows:

$$\mu = \frac{\sum X}{N} = \frac{(24.85 + \ldots\ldots\ldots + 19.26)}{32} = 38.519$$

Also, X_i value in the same equation is calculated from X_i=Σ(average of selected source level-μ). According to this when this value is calculated for optimum conditions (A_4, B_1, C_4, D_2 and E_3), it is found

$$X_{A4} = \frac{(98.81 + \ldots\ldots\ldots + 19.26)}{8} - 38.519 = 12.896$$

Using the same way for X_{B1}, X_{C4}, X_{D2} and X_{E3}, the values of 29.6035, 9.6485, 3.64, and 4.0635 were calculated respectively. So,

$$X_i = (12.896 + \ldots\ldots\ldots + 4.0635) = 59.851$$

From this, Y_i value is found as

$$Y_i = \mu + \Sigma(\text{average of selected source level} - \mu) = 38.519 + 59.851 = 98.37$$

In Table 3, it is seen that σ_e^2=0.5. From Eq. (7), $(1/n_0)$ is calculated as

$$\frac{1}{n_0} = \frac{1}{32} + \left(\frac{1}{4} - \frac{1}{32}\right) + \left(\frac{1}{4} - \frac{1}{32}\right) + \left(\frac{1}{4} - \frac{1}{32}\right) + \left(\frac{1}{4} - \frac{1}{32}\right) = 1.125$$

If this value is written in Eq. (5), it is found as

$$S_e = \pm 2\sqrt{1.125 \times 0.5 + \frac{1}{2} \times 0.5} = 1.8$$

So, for this dissolution process, the confidence limit is given as 98.37±1.8 and this result corresponds to a level of 96.57% to 100%. As seen, experimental data from the present study (98.81 and 97.93) are between these limits.

NOMENCLATURE

SN_L : performance characteristics for Larger-the-better
SN_S : performance characteristics for Smaller-the-better
Y_i : performance value of i^{th} experiment
μ : the overall mean of performance value
X_i : the fixed effect of the parameter level combination used in i^{th} experiment
e_i : the random error in i^{th} experiment
Ω(db) : the decibel value of percentage value subject to omega transformation
P : the percentage of the product obtained experimentally
Se : the two-standard-deviation confidence limit
n : the number of rows in the matrix experiment,
n_r : the number of repetition for confirmation experiment or experimental combination
n_{A_i}, n_{B_i}, n_{C_i}, … : the replication number for parameter level A_i, B_i, C_i, …

REFERENCES

Çopur, M., "An optimization study of dissolution of Zn and Cu in ZnS concentrate with HNO_3 solutions," *Chem. Biochem. Eng. Q*, **15**(4), 191 (2002).

Garret, D. E., *Borates*, Academic Press Limited, USA (1998).

Gülensoy, H., *Kompleksometrinin esaslarý ve kompleksometrik titrasyonlar*, Istanbul Univ. YayInlarI, Istanbul, Turkey, pp 250 (1984).

Gülensoy, H. and Kocakerim, M. M., "Solubility of ulexite mineral in CO_2-containing water and geological formation of this mineral," *Bulletin of Mineral Research and Exploration Institute of Turkey*, **90**, 19 (1978).

Imamutdinova, V. M., "Rates of dissolution of native borates in H_3PO_4 solutions," *Zh. Prikl. Khim*., **40**, 2596 (1967).

Imamutdinova, V. M. and Abdrashidova, N., "Rates of dissolution of borates in CH_3COOH solution," *Zh. Prikl. Khim*., **43**(2), 452 (1970).

Imamutdinova, V. M. and Vladykina, A. N., "Rate of decomposition of native borates in perchloric acid solutions," *Zh. Prikl, Khim*., **42**(2), 1172 (1969).

Kocakerim, M. M. and Alkan, M., "Dissolution kinetics of colemanite in SO_2-saturated water," *Hydrometallurgy*, **19**, 385 (1988).

Kocakerim, M. M., Çolak, S., Davies, T. and Alkan, M., "Dissolution kinetics of ulexite in CO_2-saturated water," *Canadian Met. Quarterly*, **32**(4), 393 (1993).

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

Küçük, Ö., Kocakerim, M. M., YartaşI, A. and Çopur, M., "Dissolution of Kestelek's colemanite containing clay minerals in water saturated with sulphur 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).

Künkül, A., YapIcI, S., Kocakerim, M. M. and Çopur, M., "Dissolution kinetics of ulexite in ammonia solutions saturated with CO_2," *Hydrometallurgy*, **44**, 135 (1997).

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

Phadke, M. S., *Quality engineering using robust design*, Prentice Hall, New Jersey, 61-292 (1989).

Phadke, M. S., Kackar, R. N., Speeney, D. D. and Grieco, M. J., "Off-line quality control in integrated circuit fabrication using experimental design," *The Bell System Tech. J.*, **62**, 1273 (1983).

Taguchi, G., *System of experimental design. Quality resources*, New York, 108 (1987).

Tekin, G., Onganer, Y. and Alkan, M., "Dissolution kinetics of ulexite in ammonium chloride solution," *Canadian Met. Quarterly*, **37**, 91 (1998).

Tunç, M., Kocakerim, M. M. and YapIcI, S., "Dissolution mechanism of ulexite in H_2SO_4 solution," *Hydrometallurgy*, **51**, 359 (1999).

YapIcI, S., Kocakerim, M. M. and Künkül, A., "Optimization of production of H_3BO_3 from ulexite," *Tr. J. Eng. Environ. Sci.*, **18**, 91 (1990).

Yeşilyurt, M., "Determination of the optimum conditions for the boric acid extraction from colemanite ore in HNO_3 solutions," *Chem. Eng. Process*, **43**, 1189 (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).

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).

Zdanovskii, A. B. and Biktagirova, L. G., "Mechanism of decomposition of calcium borates in H_3PO_4 solutions," *Zh. Prikl. Khim.*, **40**, 2559 (1967).