Application of Taguchi method in the optimization of dissolution of ulexite in NH₄Cl solutions

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Abstract—The Taguchi method was used to determine optimum conditions for the dissolution of ulexite in NH₄Cl 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 NH₄Cl 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 NH₄Cl solution was 98.37. Reaction products were found to be boric acid, ammonium tetraborates, sodium tetraborate decahydrate, calcium chloride, and sodium chloride.

Key words: NH₄Cl, 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 have applications 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 [Carrel, 1998]. Ulexite, which is a sodium-calcium borate with a chemical formula of Na₂O·2CaO·5B₂O₃·16H₂O, 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 Balıkesir-Bigadiç and Kütahya-Emet.

The dissolution of ulexite in various media is of economic interest. Imamudinova [1967] studied the dissolution of ulexite in H₂SO₄, H₂PO₄, HNO₃, and HCl solutions. The dissolution process in these acidic solutions has been determined to be diffusion controlled. Zdanovskii and Biktagirov [1967] carried out a study of the dissolution of ulexite in H₂SO₄ solutions and found that at acid concentrations of 5%, a solid film of H₂BO₃ 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 SO₃ and CO₂ solutions revealed that the dissolution process was found to be diffusion controlled in the case of CO₂, while it is chemical reaction-controlled in SO₃ solutions [Köcekerm and Altan, 1988; Gillemsoy and Köcekerm, 1978; Kocakerim et al., 1993]. Imamudinova and Abdurashinkova [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 HNO₃ solutions [Imamudinova and Vladykina, 1969]. Künkül et al. [1997] studied the dissolution of ulexite in NH₄ solutions saturated with CO₂, 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 H₃PO₄ was controlled by the diffusion of H₂O through the H₂BO₃ product layer and the by-product layer of CaSO₄ and/or Ca₃(PO₄)₂·2H₂O. Kucuk et al. [2002] studied the dissolution of Kestelek's colemantite in water saturated with SO₃ and the dissolution process was found to be chemical reaction-controlled. Telkin 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 colemantine in ammonium chloride solutions and found that the dissolution rate can be expressed in terms of a homogeneous reaction model. Özmen et al. [1996] investigated dissolution of colemantine in acetic acid solutions and determined that dissolution rate of colemantine 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] 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 [Yapıcı et al., 1990; Çopur, 2002; Yesilyurt, 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...
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 Balıkesir-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% B₂O₃, 15.22% CaO, 6.38% Na₂O, 29.67% H₂O, 5.38% MgO, and 7.5% other components containing SiO₂ 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. The orthogonal array (OA) was chosen as the most suitable to make up the experimental design, L₁₆(4⁵), 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].

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

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Reaction temperature (°C)</td>
<td>50</td>
</tr>
<tr>
<td>B Solid-to-liquid ratio (g/mL⁻¹)</td>
<td>0.05</td>
</tr>
<tr>
<td>C NH₄Cl concentration (M)</td>
<td>1</td>
</tr>
<tr>
<td>D Particle size (µm)</td>
<td>−850 + 600</td>
</tr>
<tr>
<td>E Reaction time (min)</td>
<td>5</td>
</tr>
</tbody>
</table>
Application of Taguchi method in the optimization of dissolution of ulexite in NH₄Cl solutions

1. Dissolution Reactions

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

\[
\begin{align*}
\text{Na₂O·2CaO·5BO₃·16H₂O} & \rightleftharpoons 2\text{Na}^+ + 2\text{Ca}^{2+} + 6\text{BO}^{3-} + 4\text{H}^+ + 2\text{BO}_x\text{O}_y\text{O}_z \\
\text{NaCl} & \rightleftharpoons \text{Na}^+ + \text{Cl}^- \\
\text{NH}_4\text{Cl} & \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \\
\text{NH}_4\text{BO}_x\text{O}_y\text{O}_z & \rightleftharpoons \text{NH}_4^+ + \text{H}^+ + \text{BO}_x\text{O}_y\text{O}_z
\end{align*}
\]

As a result, the overall reaction is

\[
\begin{align*}
\text{Na}_2\text{O}·2\text{CaO}·5\text{BO}_3·16\text{H}_2\text{O} + 6\text{NH}_4\text{Cl} & \rightleftharpoons 2\text{Na}^+ + 2\text{Ca}^{2+} + 6\text{BO}_x\text{O}_y\text{O}_z + 6\text{NH}_4^+ + 6\text{Cl}^- + 4\text{H}^+ + 4\text{H}_2\text{O}
\end{align*}
\]

Species such as Ca²⁺, Na⁺, NH₄⁺, Cl⁻ ions, H₂BO₃, and NH₄Cl are present in the reaction medium. When the solution is evaporated, a part of NH₄Cl passes into the gas phase depending on temperature and pH. NH₄Cl remaining in the solution forms (NH₄)₂BO₃·xH₂O. In addition to this, Na₂BO₃·10H₂O, H₂BO₃, NaCl, and CaCl₂·2H₂O precipitate, depending on their solubilities (Fig. 4).

2. Statistical Analysis

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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 B₂O₃.

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·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-

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

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean of squares</th>
<th>F</th>
<th>Cr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Reaction temperature (°C)</td>
<td>3487.9</td>
<td>3</td>
<td>1162.6</td>
<td>2326.40</td>
<td>18.86</td>
</tr>
<tr>
<td>B Solid-to-liquid ratio (g·mL⁻¹)</td>
<td>11226.8</td>
<td>3</td>
<td>3742.3</td>
<td>7488.25</td>
<td>60.72</td>
</tr>
<tr>
<td>C NH₄Cl concentration (M)</td>
<td>2735.6</td>
<td>3</td>
<td>911.9</td>
<td>1824.65</td>
<td>14.79</td>
</tr>
<tr>
<td>D Particle size (µm)</td>
<td>426.9</td>
<td>3</td>
<td>142.3</td>
<td>284.76</td>
<td>2.30</td>
</tr>
<tr>
<td>E Reaction time (min)</td>
<td>601.7</td>
<td>3</td>
<td>200.6</td>
<td>401.30</td>
<td>3.25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Error</th>
<th>8</th>
<th>16</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>18486.9</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. The effect of each parameter on the optimization criteria for B₂O₃.

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

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Case 1*</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Level</td>
</tr>
<tr>
<td>A Reaction temperature (°C)</td>
<td>87</td>
<td>4</td>
</tr>
<tr>
<td>B Solid-to-liquid ratio (g·mL⁻¹)</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>C NH₄Cl concentration (M)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>D Particle size (µm)</td>
<td>180-212</td>
<td>2</td>
</tr>
<tr>
<td>E Reaction time (min)</td>
<td>18</td>
<td>3</td>
</tr>
</tbody>
</table>

| Observed dissolved quantity for B₂O₃ (%) | 97.93 | 94.30 |
| Predicted dissolved quantity for B₂O₃ (%) | 98.37 | 94.73 |
| Confidence limits of prediction for B₂O₃ (%) | 96.31-100 | 92.67-96.79 |

*The parameter levels for maximum dissolution of B₂O₃

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·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·mL⁻¹), C4 (4M), 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 intensive 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].

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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 B₂O₃ 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 Fe³⁺ and Al³⁺ 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:

\[
\mu = \frac{\sum X}{N} = \frac{24.85 + \ldots + 19.26}{32} = 38.519
\]

Also, Xᵢ value in the same equation is calculated from \(X_i = \frac{X_{\text{ave}}}{2} \) (average of selected source level-μ). According to this, when this value is calculated for optimum conditions (Aᵢ, Bᵢ, Cᵢ, Dᵢ and Eᵢ), it is found

\[
X_i = \frac{98.81 + \ldots + 19.26}{8} = 38.519 - 12.896
\]

Using the same way for Xᵢ, Xᵢ, Xᵢ, Xᵢ, and Xᵢ, the values of 29.6035, 9.6485, 3.64, and 4.0635 were calculated respectively. So,

\[
X_i = (12.896 + \ldots + 4.0635) = 59.851
\]

From this, Yᵢ value is found as

\[
Y_i = \frac{X_i}{\mu} = \frac{59.851}{38.519} = 1.553
\]

In Table 3, it is seen that σₓ² = 0.5. From Eq. (7), (1/nᵢ) is calculated as

\[
\frac{1}{n_i} = \frac{1}{16} + \frac{1}{4} + \frac{1}{32} + \frac{1}{32} + \frac{1}{32} = \frac{1}{16} - \frac{1}{1.125}
\]

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

\[
S_n = \pm 2 \sqrt{\frac{1.125 \times 0.5 + \frac{1}{2} \times 0.5}{2}} = 1.8
\]

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

SNᵢ : performance characteristics for Larger-the-better
SNᵢ : performance characteristics for Smaller-the-better
Yᵢ : performance value of iᵗʰ experiment
μ : the overall mean of performance value
Xᵢ : the fixed effect of the parameter level combination used in iᵗʰ experiment
eᵢ : the random error in iᵗʰ experiment
Q(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,
nᵢ : the number of repetition for confirmation experiment or experimental combination
nᵢ, nᵢ, nᵢ, … : the replication number for parameter level Aᵢ, Bᵢ, Cᵢ, …

REFERENCES


