

## Optimization of Dissolution of Ulexite in Disodium Hydrogen Phosphate

B. Ö. Kaya<sup>1</sup>, S. Kuşlu<sup>1</sup>, T. Çalban<sup>2</sup>

<sup>1</sup>Atatürk University, Engineering Faculty, Department of Chemical Engineering, 25240, Erzurum, Turkey

<sup>2</sup>Final Education Institutions, Erzurum, Turkey

**E-mail address:** skuslu@atauni.edu.tr

### Abstract

The study aimed to investigate the optimization of the dissolution of ulexite minerals in disodium hydrogen phosphate solutions by using a factorial experimental design. The study used the solid-liquid ratio, reaction temperature, the concentration of disodium hydrogen phosphate solutions and reaction time as parameters. 2<sup>n</sup> factorial experimental design and orthogonal central composite experimental design methods were used. The optimum conditions for maximum ulexite dissolution were: Solid-liquid ratio of 1/8 g mL<sup>-1</sup>, a reaction temperature of 65 °C, a concentration of disodium hydrogen phosphate of 2 M, and a reaction time of 4 hours. Under these optimum conditions, the dissolute B<sub>2</sub>O<sub>3</sub> was 98.16 % in disodium hydrogen phosphate solutions. The complete model, including all parameters, was obtained using the 2. degree variables of the model experiment and internal interactions was found to be as follows.

**Ŷk.model = 80,45 + 11,31X<sub>1</sub> + 5,70X<sub>2</sub> – 1,10X<sub>3</sub> – 7,29X<sub>4</sub> – 11,27X<sub>1</sub><sup>2</sup> - 1,34X<sub>2</sub><sup>2</sup> + 2,37X<sub>3</sub><sup>2</sup> – 4,33X<sub>4</sub><sup>2</sup> + 3,25 X<sub>1</sub>X<sub>2</sub> – 7,45 X<sub>1</sub>X<sub>3</sub> + 14,00 X<sub>1</sub>X<sub>4</sub> + 4,30 X<sub>2</sub>X<sub>3</sub> - 7,80X<sub>2</sub>X<sub>4</sub> + 7,17X<sub>3</sub>X<sub>4</sub>**

**Keywords:** Optimization, ulexite, disodium hydrogen phosphate, Orthogonal central composite experimental design

### 1. INTRODUCTION

Boron is a semiconductor element between metal and nonmetal. Boron's atomic number is 5. Its atomic weight is 10.82, melting temperature is 2190 °C, the boiling temperature is 2250 °C and density is 2.84 g.cm<sup>-3</sup>. It occurs in the composition of more than 230 minerals in the form of mineral salts, soils, rocks, and waters [1]; while not available freely in nature. Today, boron is used in nuclear fuel technology, motor vehicle fuels, hydrogen production, ceramics, pharmaceuticals, detergents, textile and glass industries, high-temperature transistors, and superconductors [2-4]. Turkey is the most crucial country in the World in terms of boron mineral reserves and production. Turkey's boron reserves are 851 million tons in total, 227 million tons visible, and 624 million tons are probable. Turkey's share in the World's total boron reserves is 72.2% [5-6]. The ones with commercial value are borax (tincal) (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O), kernite (razorite) (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.4H<sub>2</sub>O), colemanite (2CaO.3B<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O), ulexite (Na<sub>2</sub>O.2CaO.5B<sub>2</sub>O<sub>3</sub>.16H<sub>2</sub>O), proberite (NaCaB<sub>5</sub>O<sub>9</sub>.5H<sub>2</sub>O), pandermite (Ca<sub>4</sub>B<sub>10</sub>O<sub>19</sub>.7H<sub>2</sub>O) and borasite (CaMgB<sub>6</sub>O<sub>11</sub>.6H<sub>2</sub>O). Ulexite is found in nature in the form of massive, cauliflower, fibrous and columnar. The pure one is in shades of white color. There are also silk-sheen ones. It generally occurs together with colemanite, hydroboraxite, and proberite. B<sub>2</sub>O<sub>3</sub> content is 43%. It is located in Turkey's Kırka, Bigadiç, and Emet regions and Argentina in the World [7].

Experimental design is a commonly used method to elucidate the effects of parameters in many processes. Experimental design is needed to reduce the number of experiments and the amount of material used. It is a method used to minimize experimental errors and efficiently perform analysis based on results. 2<sup>n</sup> Factorial design is the most widely used practical design method today. In this method, the following basic steps were considered for experiments response variables were determined, factor levels were selected, and statistical analysis of experimental data was performed. In the last stage of the study, a statistical regression model is obtained [8-12].

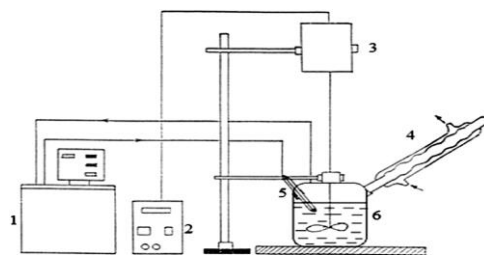
Many studies in the literature are connected with the optimization of the dissolution of ulexite in different aqueous solutions. Optimization of the dissolution of ulexite in perchloric acid solutions by the Taguchi method was investigated by Aycan *et al.*. Solid-to-liquid ratio, reaction time, particle size, and acid concentration were chosen as parameters for the optimization process. The stirring speed as 500 rpm and the reaction temperature at 30 °C in the experiments was taken as constant. The boric acid extraction from ulexite was reached a value of 99 % under these conditions [13]. The optimum conditions for the dissolution of ulexite in NH<sub>4</sub>Cl solutions using the Taguchi method were studied by Küçük. Reaction temperature (50-87 °C), solid-to-liquid ratio (0.05-0.20 g mL<sup>-1</sup>), NH<sub>4</sub>Cl concentration (1-4 M), reaction time (5-25 min.), particle size ((-850 + 600)-(-90 μm)) was chosen as parameters. 87 °C, 0.05 g mL<sup>-1</sup>, 4 M, (-300 + 212) μm and 18 min, respectively, was found as experimental parameters. The dissolution percentage of ulexite in NH<sub>4</sub>Cl solution was found as %98.37 under the optimum conditions [14]. The optimum conditions for the dissolution of ulexite in ammonium sulphate solutions with Taguchi method was investigated by Küçük *et al.*. Reaction temperature (60-88 °C), solid-to-liquid ratio (0.05-0.15 g mL<sup>-1</sup>), reaction time (5-20 min.), and particle size ((-850 + 600)-(-90 μm)) was chosen as parameters and ranges. The optimum conditions were found as 88 °C, 0.1 g mL<sup>-1</sup>, -90 μm and 20 min.. Under the optimum conditions, experimental dissolution percentages of ulexite in ammonium sulphate solutions were found as 98.36 [15]. As a new process, optimum conditions for the dissolution of ulexite in water saturated with SO<sub>2</sub> to produce monosodium pentaborate (NaB<sub>5</sub>O<sub>8</sub>) used the Taguchi method was studied by Küçük and Kocakerim [16]. The optimum precipitation conditions of Chevreul's salt using leach solutions contained copper by SO<sub>2</sub> with statistical modeling was investigated by Çalban *et al.*. pH of 3, the temperature of 62 °C, stirring speed of 600 rpm, reaction time of 12 min, SO<sub>2</sub> flow rate 358 L h<sup>-1</sup> and concentration of CuSO<sub>4</sub> solution 7.38 gCu L<sup>-1</sup> was found as optimum conditions [17]. The

Chevreur's salt from mixture of  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_3$  solutions was precipitated by Yesilyurt and Çalban. Reaction temperature  $60\text{ }^\circ\text{C}$ , pH 3,  $[\text{SO}_3^{2-}]/[\text{Cu}^{2+}]$  ratio 1.6, stirring speed 500 rpm and reaction time 20 min was found as optimum conditions [18]. The optimization of the removal of silver from anode slime in ammonium thiosulfate solutions by microwave using statistical design methods by studied by Kuslu *et al.* [19]. The optimization of the removal of lead from anode slime in triethanolamine solutions by the microwave effect using statistical design methods was investigated by Çalban *et al.* [20]. The optimization of the removal of calcium from soda liquid waste containing calcium chloride was investigated by Çalban and Kavci [21]. The optimum conditions on colemanite dissolution in  $\text{H}_3\text{PO}_4$  solutions were investigated by Yesilyurt *et al.* [22].

This work focuses obtain to optimization conditions of the dissolution of ulexite minerals in disodium hydrogen phosphate solutions in a mechanical agitation system. There is no study reported in the literature about such a procedure. In the study, solid-liquid ratio, reaction temperature, concentration of disodium hydrogen phosphate solutions and reaction time were chosen as parameters.  $2^n$  factorial experimental design and orthogonal central composite design methods were used. A model was obtained by using Matlab computer software and analyzing variance among the selected parameters in the study.

## 2. METHODS AND MATERIALS

Atmospheric pressure conditions were conducted for studying optimization experiments. Analytical grade chemicals (Merck) and distilled water were used in all the experiments. To obtain of the mixture in the spherical and jacketed glass reactor at a constant temperature, a fixed temperature water circulator combination with the reactor was used throughout the experiments. The reactor is a 600 mL reactor and the all experiments were carried out in it. To prevent evaporation during heating, a reflux condenser equipped with the reactor was used. To obtain a homogeneous suspension in the reactor, a mechanical stirrer with speed control tachometer was used. The experimental setup for the dissolution process can be seen in Fig.1.



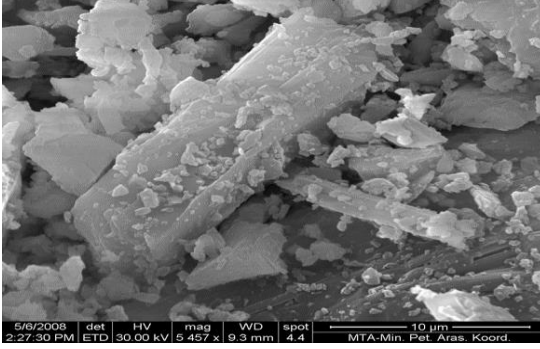
**Figure 1** - Experimental setup used for the dissolution process

1-Fixed temperature circulator, 2-Speed control tachometer, 3-Mechanical stirrer, 4-Reflux condenser, 5-Thermometer, 6-Jacketed glass reactor.

A typical experiment conducted was as follows: 600 mL of disodium hydrogen phosphate solution was poured into the reactor. The solution was heated to the desired temperature. The experiments were carried out -60 +70 mesh (231  $\mu\text{m}$ ) size fractions. After this, large quantities of solid ulexite were added to the solutions. Stirring of the solution was started immediately thereafter. The duration of the treatment depended on the experimental conditions. At definite time intervals, 1 mL samples of the reacted solution were taken for the assay of  $\text{B}_2\text{O}_3$  and analyzed by potentiometric and titrimetric methods [23,24]. Based on the  $\text{B}_2\text{O}_3$  estimated, the degree of dissolution of ulexite was determined as a function of time. Ulexite samples used in the experiments were obtained from Bandırma Borax Corporation, Turkey. The ulexite ore samples were crushed, dried under vacuum and sieved with ASTM standard sieves. The chemical analyses of original ulexite minerals used in the experiments is shown in Table 1 and the SEM photography of original ulexite minerals can be shown in Fig. 2.

**Table 1** - The chemical analysis of original ulexite minerals used in the experiments

| Component | CaO   | $\text{B}_2\text{O}_3$ | $\text{Na}_2\text{O}$ | MgO  | $\text{Al}_2\text{O}_3$ | $\text{SiO}_2$ | $\text{Fe}_2\text{O}_3$ | SrO  | $\text{H}_2\text{O}$ |
|-----------|-------|------------------------|-----------------------|------|-------------------------|----------------|-------------------------|------|----------------------|
| % (w/w)   | 17.85 | 36.37                  | 6.10                  | 1.78 | < 0.01                  | 4.13           | < 0.01                  | 1.43 | 33.47                |



**Figure 2** - The SEM photography of original ulexite minerals used in the experiments

Two-level experimental design requires  $2^n$  studies. Each factor has 2 levels. +1 for high level and -1 for low level. The central coordinates between the factor levels are zero. This value is the origin of the coordinates. While using this method, a variance analysis table (ANOVA) is prepared in order to decide on the effect of each factor on the results. This table shows the mutual and all interactions of the variables. The half values obtained from the Yates algorithm are also the main effects and interactions [10,11].

By the following statistical term, the effects of pure quadratic terms can be checked:

$$LOF_{curvature} = \frac{m_0 \cdot F \cdot (Y_1 - Y_0)^2}{m_0 + F} \quad (1)$$

Second-order effects cannot be predicted in  $2^n$  factorial designs. If the analysis of variance shows that the quadratic effects are significant, ancillary experiments are performed. Orthogonal central composite design is the most popular of the second order designs. In this case, two new factor levels emerge and it is necessary to work with them. These two new factor levels are  $-\alpha$  and  $+\alpha$ .  $\alpha$  is calculated by the following relation [9-11,17-22, 25-30].

$$\alpha = \left(\frac{QF}{4}\right)^{1/4} \quad (2)$$

$$Q = [N^{1/2} - F^{1/2}]^2 \quad (3)$$

$$N = F + 2n + m_0 \quad (4)$$

In the planning of experimental designs, coded values are usually used instead of absolute values of the variables. The relationship between coded value (X) and absolute value (Z) is as follows [9-11,17-22, 25-31] :

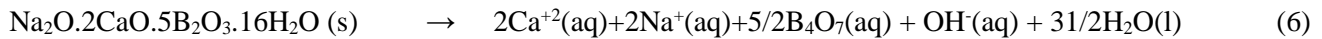
$$X = \frac{2(Z - Z_0)}{(Z_2 - Z_1)} \quad (5)$$

Each experiment was repeated twice, and the arithmetic average of the results of the two experiments was used in the analysis.

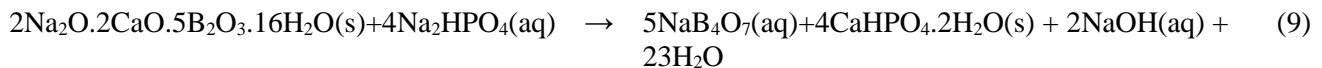
### 3. RESULTS AND DISCUSSION

#### 3.1 Dissolution Reactions

The reactions taking place in the reactor can be written as follows [23,24]:



When ulexite is added to the disodium hydrogen phosphate solutions, the reaction taking place in the solution can be written as follows:



#### 3.2 Effects of Parameters

For the optimization studies, using the  $2^n$  factorial experimental design method, four parameters that are thought to affect the dissolution of ulexite in disodium hydrogen phosphate solutions and which were determined as a result of preliminary experiments were determined. Three center point replicate experiments were performed to determine the standard deviation. The lower and upper limits of the parameters were determined with the help of literature information and preliminary experiments. The effects of the parameters on ulexite dissolution were investigated for parameters using

the values given in Table 2 and Table 3. Factor levels for first-order model and second-order model is given in Table 2 and Table 3, respectively.

**Table 2 - Factor Levels for First-Order Model**

| Parameter  | Low level (-) | High level (+) | Medium level (0) |
|--|---------------|----------------|------------------|
| <b>X<sub>1</sub></b> : solid/liquid ratio (g /mL)                            | 0.100         | 0.125          | 0.115            |
| <b>X<sub>2</sub></b> : reaction temperature (°C )                            | 65            | 75             | 70               |
| <b>X<sub>3</sub></b> : concentration of Na <sub>2</sub> HPO <sub>4</sub> (M) | 1.50          | 2.00           | 1.75             |
| <b>X<sub>4</sub></b> : reaction time (h)                                     | 3.0           | 4.0            | 3.5              |

**Table 3 - Factor Levels for Second-Order Model**

| Parameter  | Low level (-) | High level (+) | Medium level (0) |
|--|---------------|----------------|------------------|
| <b>X<sub>1</sub></b> : solid/liquid ratio (g /mL)                            | 0.092         | 0.130          | 0.113            |
| <b>X<sub>2</sub></b> : reaction temperature (°C )                            | 62            | 78             | 75               |
| <b>X<sub>3</sub></b> : concentration of Na <sub>2</sub> HPO <sub>4</sub> (M) | 1.35          | 2.15           | 1.75             |
| <b>X<sub>4</sub></b> : reaction time (h)                                     | 2.7           | 4.3            | 3.5              |

Experimental design matrix and ulexite dissolution percentage results are given in Table 4. According to Table 4, in the first series of trials; the highest yield was obtained at the upper level of solid/liquid ratio, concentration of disodium hydrogen phosphate, reaction time and lower temperature value as 100.00% in the 3rd experiment.

**Table 4 - Experimental Design Matrix and Ulexite Dissolution Percentage**

| Exp. No        | X <sub>1</sub> | X <sub>2</sub> | X <sub>3</sub> | X <sub>4</sub> | Y <sub>i</sub> | $\hat{Y}_i$  | $e_i = (Y_i - \hat{Y}_i) / S$ |
|----------------|----------------|----------------|----------------|----------------|----------------|--------------|-------------------------------|
| 1              | +              | +              | +              | +              | 97.60          | 110.14       | -27.45                        |
| 2              | -              | +              | +              | +              | 94.70          | 86.76        | 17.38                         |
| <b>3</b>       | +              | -              | +              | +              | <b>100.00</b>  | <b>99.90</b> | <b>0.23</b>                   |
| 4              | -              | -              | -              | +              | 85.26          | 88.01        | -6.02                         |
| 5              | +              | +              | -              | -              | 99.30          | 93.52        | 12.65                         |
| 6              | -              | +              | -              | -              | 96.80          | 101.12       | -9.48                         |
| 7              | +              | -              | +              | -              | 35.39          | 40.30        | -10.74                        |
| 8              | -              | -              | +              | -              | 67.72          | 59.40        | 18.20                         |
| 9              | +              | +              | -              | +              | 79.58          | 81.61        | -4.45                         |
| 10             | -              | +              | -              | +              | 96.72          | 98.91        | -4.80                         |
| 11             | +              | -              | -              | +              | 51.09          | 57.29        | -13.57                        |
| 12             | -              | -              | +              | +              | 72.62          | 72.02        | 1.30                          |
| 13             | +              | +              | +              | -              | 94.46          | 85.22        | 20.21                         |
| 14             | -              | +              | +              | -              | 96.04          | 93.60        | 5.33                          |
| <b>15</b>      | +              | -              | -              | -              | <b>25.06</b>   | <b>21.00</b> | <b>8.90</b>                   |
| 16             | -              | -              | -              | -              | 36.35          | 44.65        | -18.15                        |
| 1 <sup>0</sup> | 0              | 0              | 0              | 0              | 90.36          | 91.67        | -2.86                         |

|                |   |   |   |   |       |       |       |
|----------------|---|---|---|---|-------|-------|-------|
| 2 <sup>0</sup> | 0 | 0 | 0 | 0 | 91.12 | 91.67 | -1.19 |
| 3 <sup>0</sup> | 0 | 0 | 0 | 0 | 90.30 | 91.67 | -2.99 |

The lowest dissolution efficiency was found as 25.06 % in the 15th experiment. In order to decide on the efficiency of the parameters in the experiments, the "Anova Table" which is variance analysis table was prepared. Table of Variance Analysis is given in Table 5. In order to decide on the efficiency values of the parameters, the 99% confidence level was taken into account. The extended design matrix is created in Table 6.

As can be seen from the Tables 4-6, the dissolution percentages for disodium hydrogen phosphate solutions decreased with increasing the solid-to-liquid ratio. The obtained B<sub>2</sub>O<sub>3</sub> amounts for disodium hydrogen phosphate solutions which are using central values of the other parameters for 0.092, 0.113 and 0.130 g/mL were 45.83, 90.59 (the mean value of three central replications) and 85.56%, respectively.

**Table 5** - Table of Variance Analysis

| Source of Variation | Sum of squares | df | Mean squares | F <sub>ratio</sub> | Decision ( $\alpha = 0,01$ ) |
|---------------------|----------------|----|--------------|--------------------|------------------------------|
| X <sub>1</sub>      | 2660           | 1  | 2660         | 12666.66           | Effective                    |
| X <sub>2</sub>      | 680            | 1  | 680          | 3238.10            | Effective                    |
| X <sub>3</sub>      | 20             | 1  | 20           | 95.24              | Effective                    |
| X <sub>4</sub>      | 1100           | 1  | 100          | 476.19             | Effective                    |
| Lack of fit         | 481.11         | 1  | 481.11       | 2291               | Effective                    |
| Experimental error  | 0.42           | 2  | 0.21         |                    |                              |
| Model mismatch      | 8258.47        | 11 | 750.77       | 3575.10            | Effective                    |
| Total               | 13200          | 18 |              |                    |                              |

$$F_{0,95;1;2}=18.51 \quad F_{0,95;11;2}=19.4$$

**Table 6** - Extended design matrix

| Exp. No | X <sub>1</sub> | X <sub>2</sub> | X <sub>3</sub> | X <sub>4</sub> | X <sub>1</sub> X <sub>2</sub> | X <sub>1</sub> X <sub>3</sub> | X <sub>1</sub> X <sub>4</sub> | X <sub>2</sub> X <sub>3</sub> | X <sub>2</sub> X <sub>4</sub> | X <sub>3</sub> X <sub>4</sub> | % B <sub>2</sub> O <sub>3</sub> |
|---------|----------------|----------------|----------------|----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|
| 1       | +              | +              | +              | +              | +                             | +                             | +                             | +                             | +                             | +                             | 97.60                           |
| 2       | -              | +              | +              | +              | -                             | -                             | -                             | +                             | +                             | +                             | 94.70                           |
| 3       | +              | -              | +              | +              | -                             | +                             | +                             | -                             | -                             | +                             | 100.00                          |
| 4       | -              | -              | -              | +              | +                             | +                             | -                             | +                             | -                             | -                             | 85.26                           |
| 5       | +              | +              | -              | -              | +                             | -                             | -                             | -                             | -                             | +                             | 99.30                           |
| 6       | -              | +              | -              | -              | -                             | -                             | +                             | -                             | -                             | +                             | 96.80                           |
| 7       | +              | -              | +              | -              | -                             | +                             | -                             | -                             | +                             | -                             | 35.39                           |
| 8       | -              | -              | +              | -              | +                             | -                             | +                             | -                             | +                             | -                             | 67.72                           |
| 9       | +              | +              | -              | +              | +                             | -                             | +                             | -                             | +                             | -                             | 79.58                           |
| 10      | -              | +              | -              | +              | -                             | +                             | -                             | -                             | +                             | -                             | 96.72                           |

|                |   |   |   |   |   |   |   |   |   |   |       |
|----------------|---|---|---|---|---|---|---|---|---|---|-------|
| 11             | + | - | - | + | - | - | + | + | - | - | 51.09 |
| 12             | - | - | + | + | + | - | - | - | - | + | 72.62 |
| 13             | + | + | + | - | + | + | - | + | - | - | 94.46 |
| 14             | - | + | + | - | - | - | + | + | - | - | 96.04 |
| 15             | + | - | - | - | - | - | - | + | + | + | 25.06 |
| 16             | - | - | - | - | + | + | + | + | + | + | 36.35 |
| 1 <sup>0</sup> | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 90.36 |
| 2 <sup>0</sup> | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 91.12 |
| 3 <sup>0</sup> | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 90.30 |

### 3.3 Effect of the solid-to-liquid ratio

The effect of the solid-to-liquid ratio was researched in the ranges of 0.092–0.130 g.mL<sup>-1</sup>. In all experiments, the reaction temperature, the concentration of disodium hydrogen phosphate solutions and reaction time (the mean value of four central replications) were meticulously controlled during the reaction.

### 3.4 Effect of the reaction temperature

The effect of the temperature was investigated in the range of 62–78°C. In all experiments, the solid-to-liquid ratio, the concentration of disodium hydrogen phosphate solutions and the reaction time (the mean value of four central replications) were meticulously controlled during the reaction. As can be seen from the tables 4-6, the dissolution percentages decreased with increasing the reaction temperature. The obtained B<sub>2</sub>O<sub>3</sub> amounts for disodium hydrogen phosphate solutions which are using central values of the other parameters for 62, 75 and 78 °C were 78.93, 90.59 and (the mean value of three central replications) and 100.00%, respectively.

### 3.5 Effect of the concentration of disodium hydrogen phosphate solutions

The effect of the concentration of disodium hydrogen phosphate solutions was investigated in the range of 1.35–2.15 M. In all experiments, the solid-to-liquid ratio, the reaction temperature, and the reaction time (the mean value of four central replications) were meticulously controlled during the reaction. As can be seen from the Tables 4-6, the dissolution percentages increased with increasing the concentration of disodium hydrogen phosphate solutions. The obtained B<sub>2</sub>O<sub>3</sub> amounts for disodium hydrogen phosphate solutions which are using central values of the other parameters for 1.35, 1.75 and 2.15 M were 97.05, 90.59 (the mean value of three central replications) and 99.60%, respectively.

### 3.6 Effect of reaction time

The effect of reaction time was researched in the range of 2.7–4.3 hours. In all experiments, the solid-to-liquid ratio, the reaction temperature, and the concentration of disodium hydrogen phosphate solutions (the mean value of four central replications) were meticulously controlled during the reaction. As can be seen from the Tables 4-6, The obtained B<sub>2</sub>O<sub>3</sub> amounts for disodium hydrogen phosphate solutions which are using central values of the other parameters for 2.7, 3.5 and 4.3 hours were 70.22, 90.59 (the mean value of three central replications) and 94.40%, respectively.

**Table 7** - Analysis of variance for the internal interactive mode results

| parameter                     | sum of squares | df | mean squares | F <sub>ratio</sub> | decision ( $\alpha = 0,01$ ) |
|-------------------------------|----------------|----|--------------|--------------------|------------------------------|
| X <sub>1</sub>                | 2660           | 1  | 2660         | 12.67              | Ineffective                  |
| X <sub>2</sub>                | 680            | 1  | 680          | 3238.10            | Effective                    |
| X <sub>3</sub>                | 20             | 1  | 20           | 95.24              | Effective                    |
| X <sub>4</sub>                | 1100           | 1  | 1100         | 5238.10            | Effective                    |
| X <sub>1</sub> X <sub>2</sub> | 170            | 1  | 170          | 809.52             | Effective                    |
| X <sub>1</sub> X <sub>3</sub> | 960            | 1  | 960          | 4571.43            | Effective                    |
| X <sub>1</sub> X <sub>4</sub> | 3130           | 1  | 3130         | 14904.76           | Effective                    |

|                               |         |    |         |         |           |
|-------------------------------|---------|----|---------|---------|-----------|
| X <sub>2</sub> X <sub>3</sub> | 300     | 1  | 300     | 1428.57 | Effective |
| X <sub>2</sub> X <sub>4</sub> | 970     | 1  | 970     | 4619.05 | Effective |
| X <sub>3</sub> X <sub>4</sub> | 820     | 1  | 820     | 3904.76 | Effective |
| Lack of fit                   | 481.11  | 1  | 481.11  | 2291.00 | Effective |
| Model Mismatch                | 9258.47 | 5  | 1851.69 | 8817.57 | Effective |
| Experimental error            | 0,42    | 2  | 0,21    |         |           |
| Total                         | 13200   | 18 |         |         |           |

$F_{0,95;1,2}=18.51$   $F_{0,95;5,2}=19.3$

As can be seen from the 1st order linear models obtained above, three parameters (X<sub>1</sub>, X<sub>3</sub>, X<sub>4</sub>) are active in the selected ranges. In addition, it has been observed that the solid/liquid ratio, which is effective in the 1st order model, is effective in its internal interaction with concentration and reaction time. In the complete model, X<sub>1</sub> (solid/liquid ratio), X<sub>2</sub> (reaction temperature) had a negative effect on the dissolution reaction, while X<sub>3</sub> (concentration of disodium hydrogen phosphate) and X<sub>4</sub> (reaction time) had a positive effect on the dissolution reaction. Because it is thought that, there may be internal interactions between the parameters. Analysis of variance was performed to see the effect of internal interactions in the expanded design matrix. Analysis of variance for the internal interactive mode results are given in Table 7.

**Table 8** - 2nd order experiment design and results

| Exp.No | X <sub>1</sub> | X <sub>2</sub> | X <sub>3</sub> | X <sub>4</sub> | Dissolution yield (%) |
|--------|----------------|----------------|----------------|----------------|-----------------------|
| 17     | -1.607         | 0              | 0              | 0              | 45.83                 |
| 18     | +1.607         | 0              | 0              | 0              | 85.56                 |
| 19     | 0              | -1.607         | 0              | 0              | 78.93                 |
| 20     | 0              | +1.607         | 0              | 0              | 100.00                |
| 21     | 0              | 0              | -1.607         | 0              | 97.05                 |
| 22     | 0              | 0              | +1.607         | 0              | 99.60                 |
| 23     | 0              | 0              | 0              | -1.607         | 94.40                 |
| 24     | 0              | 0              | 0              | +1.607         | 70.22                 |

**Table 9** - Variance analysis table for the 2nd order model

| parameter                      | sum of squares | df | mean squares | F <sub>ratio</sub> | decision (α = 0,01) |
|--------------------------------|----------------|----|--------------|--------------------|---------------------|
| X <sub>1</sub>                 | 2660           | 1  | 2660         | 12.67              | Ineffective         |
| X <sub>2</sub>                 | 680            | 1  | 680          | 3238.10            | Effective           |
| X <sub>3</sub>                 | 20             | 1  | 20           | 95.24              | Effective           |
| X <sub>4</sub>                 | 1100           | 1  | 1100         | 5238.10            | Effective           |
| X <sub>1</sub> <sup>2</sup>    | 1450           | 1  | 1450         | 6904.76            | Effective           |
| X <sub>2</sub> <sup>2</sup>    | 20             | 1  | 20           | 95.24              | Effective           |
| X <sub>3</sub> <sup>2</sup>    | 60             | 1  | 60           | 285.71             | Effective           |
| X <sub>4</sub> <sup>2</sup>    | 210            | 1  | 210          | 1.00               | Ineffective         |
| X <sub>1</sub> .X <sub>2</sub> | 170            | 1  | 170          | 809.52             | Effective           |
| X <sub>1</sub> .X <sub>3</sub> | 960            | 1  | 960          | 4571.43            | Effective           |
| X <sub>1</sub> .X <sub>4</sub> | 3130           | 1  | 3130         | 14904.76           | Effective           |
| X <sub>2</sub> .X <sub>3</sub> | 300            | 1  | 300          | 1428.57            | Effective           |
| X <sub>2</sub> .X <sub>4</sub> | 970            | 1  | 970          | 4619.05            | Effective           |
| X <sub>3</sub> .X <sub>4</sub> | 820            | 1  | 820          | 3904.76            | Effective           |

|                    |        |    |       |        |           |
|--------------------|--------|----|-------|--------|-----------|
| Model Mismatch     | 649.58 | 10 | 64.96 | 309.33 | Effective |
| Experimental error | 0.42   | 2  | 0.21  |        |           |
| Total              | 13200  | 26 |       |        |           |

$$F_{0,95;1;2} = 18.51 \quad F_{0,95;10;2} = 19.40$$

That is, increasing  $X_1$ ,  $X_2$  and  $X_3$ ,  $X_4$  within the optimization limits causes a decrease in efficiency. When the Anova table is examined, although the terms LOF<sub>curve</sub> and Model Mismatch are not effective according to the 1st order design results, in order to express the test results more safely and more effectively based on the obtained values, the 2nd order experiment design method, which is initially an orthogonal central resultant experiment design method is used. For this purpose, a centered junction design matrix was designed and  $\alpha$  (star point experiments) values were determined in order to be orthogonal in the design. In the four-parameter design with 16 experiments, the number of additional experiments to be done is 8. Factor levels determined by using star points in this experimental group are given below. Some variable levels have been rounded to take into account the precision measuring conditions of the devices. 2nd order experiment design and results can be shown in Table 8 and Variance analysis table for the 2nd order model can be shown in Table 9. The second-order factor levels of each parameter were calculated with the internal interactions in the matrix. Since values close to the complete model were obtained when the 95% confidence level was studied, the 95% confidence level was preferred in the experiments.

### 3.7 Statistical analysis

Dissolutions tests of ulexite mineral in disodium hydrogen phosphate solutions were carried out. The collected data was analyzed by ANOVA using the MATLAB computer software package for the evaluation of the effect of each parameter on the optimization criteria. The factors such as the solid-to-liquid ratio, the reaction temperature, the concentration of disodium hydrogen phosphate solutions and the reaction time were chosen as independent variables and their high and low levels were decided as shown in Table 2 and Table 3. With four factors,  $2^4$  full factorial design requires 16 runs. Furthermore, four central replications were added to the experimental plan in order to estimate pure experimental error. The results are given in Table 5. To test the significance of the factor effects, an analysis of variance was conducted at 95 % confidence intervals. The results are shown in Table 6. At both confidence intervals, the solid-to-liquid ratio ( $X_1$ ), the reaction temperature ( $X_2$ ), concentration of disodium hydrogen phosphate solutions ( $X_3$ ) and the reaction time ( $X_4$ ) range have been found to be effective. As seen from Table 5 and Table 6, results of variance analysis showed a curvature effect in 95 % confidence interval. The complete model was obtained as a model that includes all parameters by using all the variables and internal interactions of the first-order model trials. According to these results, the regression model was obtained as follows.

$$\hat{Y}_c = 80,45 + 11,31X_1 + 5,70X_2 - 1,10X_3 - 7,29X_4 + 3,25X_1X_2 - 7,75X_1X_3 + 14,00X_1X_4 + 4,30X_2X_3 - 7,80X_2X_4 + 7,17X_3X_4$$

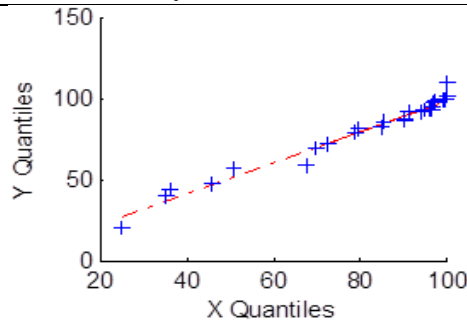
(complete model)

According to the results of variance analysis, quadratic terms are effective. Therefore, the orthogonal central composite design was planned to estimate quadratic terms. With  $F = 16$ ,  $m_0 = 4$ ,  $n = 4$ ,  $b$  is calculated as 1.607 according to eqn. 2. The Anova of obtained results shows that all of the variables studied and their combinations affect the dissolution of ulexite mineral from disodium hydrogen phosphate solutions. As seen from Table 6 and Table 7, the solid-to-liquid ratio, the reaction temperature, concentration of disodium hydrogen phosphate solutions, the reaction time and interactions of the concentration of disodium hydrogen phosphate solutions with the reaction time are effective on dissolution of ulexite mineral. Systematic errors in a well-established model are absent. Normalized residuals depend on experimental errors and these values exhibit a normal distribution. The complete model obtained for the 2nd order model using the (b) values is given below.

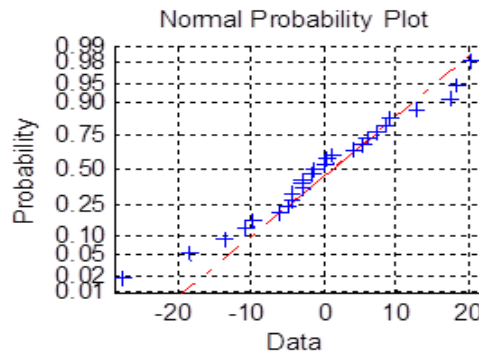
$$Y_c = 80,45 + 11,31X_1 + 5,70X_2 - 1,10X_3 - 7,29X_4 - 11,27X_1^2 - 1,34X_2^2 + 2,37X_3^2 - 4,33X_4^2 + 3,25 X_1X_2 - 7,45 X_1X_3 + 14,00 X_1X_4 + 4,30 X_2X_3 - 7,80X_2X_4 + 7,17X_3X_4$$

The values was found at the end of the experiment were compared with the values calculated from the complete model and the active model. Using these values, graphs were created to evaluate the differences between the experimental results and the model. Comparison of the test results with the complete model and compliance curve of test results and normalized residue values can be shown in Fig. 3 and Fig. 4, respectively.





**Figure 3** - Comparison of the test results with the complete model



**Figure 4** - Compliance curve of test results and normalized residue values

Compliance charts are drawn in order to test whether there are some mistakes that can be made during the experiments, systematic errors arising from the system or errors that occur as a result of chance. If there is no deviation on this graph, it can be said that the error rate in the experiments is very low. If the amount of deviation on the diagonal is high, it is necessary to investigate and correct the errors that may exist in the environment. By means of the graph given in Fig. 4, we can decide whether there is any change or system error and model mismatch that may occur in the system. If the system is working efficiently and the error rate is low, the limits on the graph will be narrower. A large residual range requires modification of the system or applied model. In the experiments, the highest efficiency was obtained at the upper level of the solid/liquid ratio, concentration, reaction time and the lower level of the temperature value. Optimum conditions; solid/liquid ratio was 1/8 g/mL, reaction temperature was 65 °C, concentration of disodium hydrogen phosphate was 2M, and time was 4h.

#### 4. CONCLUSIONS

The conclusions from the study are as follows:

1. The dissolution percentage of ulexite mineral increased with increasing in reaction temperature and the reaction time.
2. The dissolution percentage of ulexite mineral increased with decreasing in the solid/liquid ratio.
3. The dissolution extent is not affected by the stirring speed in selected experimental conditions.
4. The obtained optimum conditions on maximum dissolution of ulexite mineral were: the solid-to-liquid ratio at 0.125 g mL<sup>-1</sup> the reaction temperature 65 °C, the concentration of disodium hydrogen phosphate solutions at 2 M and reaction time at 4 hour.
5. Under these optimum conditions, the dissolved B<sub>2</sub>O<sub>3</sub> was 99.11 % .

#### Nomenclature

|                             |  |
|-----------------------------|--|
| LOF <sub>curvature</sub>    | curvature  |
| m <sub>o</sub>              | the number of trials with center point               |
| F                           | the number of experiments in factorial design        |
| Y <sub>0</sub>              | average of experiments at the central point          |
| Y <sub>1</sub>              | the dimensions of factorial experiments              |
| - $\alpha$ and + $\alpha$ . | two new factor levels emerge, star point experiments |
| N                           | total number of experiments                          |
| Z                           | absolute value                                       |
| X                           | relationship between coded value                     |

|                |                                  |
|----------------|----------------------------------|
| Z <sub>1</sub> | the low level of the variable    |
| Z <sub>2</sub> | the high level of the variable   |
| Z <sub>0</sub> | the medium level of the variable |
| b              | the main effects of the factors  |

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