Optimization of Dissolution of Ulexite in Phosphate Acid Solutions

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Summary: The Taguchi optimization method was used to determine optimum conditions for the dissolution of ulexite in phosphate acid solutions. Reaction temperature, solid-to-liquid ratio, phosphate acid concentration, reaction time, particle size and stirring speed were chosen as parameters. The optimum conditions for these parameters were found to be 60°C, 0.15g.mL^{-1}, 0.70M, (-850+452) μm, 30 minutes and 200rpm, respectively. Under these conditions, the dissolution percentage of ulexite in phosphate acid solution was 100. Reaction products were found to be boric acid, sodium dihydrogen phosphate and calcium dihydrogen phosphate.

Keywords: Ulexite ore, Taguchi optimization, Phosphate acid.

Introduction

Boron consists of complex chemical compounds. Its compounds are used in many fields such as detergents, disinfectants, cosmetics, in the production of medicines and in the industries of glass, dye and plating, polymer, refractory materials, steel, etc. In addition, they are used in some production industries as catalysts, in rockets as fuel and in nuclear technology as a radiation trapper [1, 2]. Ulexite is found large deposits in Turkey and is a sodium calcium borate hydrate mineral ($Na_2O.2CaO.5B_2O_3.16H_2O$). Boron compounds as raw materials have a very important place in industry. Because they are used in many technical applications [3].

Some studies on the dissolution kinetic of boron minerals in various solutions have been made. The dissolution kinetics of ulexite in acetic acid solutions [4] were examined, and found that the dissolution rate of ulexite increased with increasing solution concentration and temperature and decreasing particle size and solid-to-liquid ratio. The activation energy for the process was 55.8 kj.mol^{-1}. Dissolution kinetics of ulexite in ammonia solutions saturated with CO_2 [5] and tincal in phosphoric acid solutions [6] were investigated and the dissolution rates were found to be based on the first order pseudo homogeneous reaction model. The dissolution kinetics of ulexite in perchloric acid solutions was investigated and the activation energy was found to be 19.12 kj mol^{-1} [7]. Leaching kinetics of ulexite in phosphoric acid [8] and colemanite in potassium hydrogen sulphate [9] were studied and the leaching processes were determined to be diffusion controlled. In a study [10], the dissolution of colemanite in $(NH_4)_2SO_4$ solutions was studied and the activation energy was found as 40.46 kj mol^{-1}. The dissolution kinetics of ulexite in borax pentahydrate solutions saturated with carbon dioxide [11] and colemanite in phosphoric acid solutions [12] were studied. It was determined that the dissolution rates were controlled by surface chemical reaction. In another study [13] the dissolution of ulexite in H_2SO_4, H_3PO_4, HNO_3 and HCl solutions was studied and this process was found to be controlled by diffusion.

For industrial processes, the optimization of dissolution conditions of the ores has an important place. Therefore, many researchers have been made studies on these subjects using various methods such as Taguchi, the factorial experiment design, the orthogonal central composite design and response surface methodology. In a study, dissolution of magnesite in citric acid solutions was optimized using Taguchi technique and the optimum conditions were found to be 2M acid concentration, 120 min. reaction period, 75°C reaction temperature, 0.125 g/mL solid-liquid ratio and -319 μm particle size [14]. The optimization of the boric acid extraction from colemanite ore was examined by the fractional factorial design and central composite design techniques, and found that the effectiveness of this process at the optimum conditions was about 99.9% [15]. In another study [3] the optimization of production of H_3BO_3 from ulexite was investigated by using the 2^n factorial design method. It was found that the highest dissolution, approximately 100%, was reached at the conditions of 80°C, 140 minute, 500rpm and the solid/liquid ratio of 1 /4.

One of the optimization techniques is Taguchi Orthogonal Array (OA) analysis. It is used to find the optimum parameters of process by making the minimum number of experiments. Taguchi technique has many advantages. One of the main advantages of this technique relative to other statistical techniques, the parameters affecting an experiment can be studied as controlling and not controlling. Another advantage, the technique can be

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applied to experimental design containing a great number of design factors [16].

In this study, ulexite ore was dissolved in phosphate acid solutions using the experimental parameters of particle size, solid-to-liquid ratio, reaction temperature, phosphate acid concentration, stirring speed and reaction time. The optimum dissolution conditions were determined by Taguchi method. Reaction products were found to be boric acid, sodium dihydrogen phosphate and calcium dihydrogen phosphate. These reaction products have wide application areas in industry [8].

Results and Discussion

Dissolution Reactions

During the experiments, the pH was measured and found in the range of 1.5-2.5. Dihydrogen phosphates occur at these pH values [17]. Therefore, the dissolution reactions are follows:

$$H_3PO_4 + H_2O \Leftrightarrow H_2PO_4^- + H_3O^+ \quad (1)$$

$$Na_2O.2CaO.5B_2O_3.16H_2O_{(s)} + 6H_3O^+ \rightarrow Na^+_{(aq)} + 2Ca^{+2}_{(aq)} + 10H_3BO_{3(aq)} + 10H_2O \quad (2)$$

The total reaction is:

$$Na_2O.2CaO.5B_2O_3.16H_2O_{(s)} + 6H_3PO_{4\,(aq)} \rightarrow 2Na^+_{(aq)} + 2Ca^{+2}_{(aq)} + 6H_2PO_4^- + 10H_3BO_{3(aq)} + 4H_2O \quad (3)$$

Statistical Analysis

Taguchi method is used for optimizing a process with one or multiple performance characteristics. The application of this method involves eight steps, which make up a Robust Design cycle view of planning and carrying out the experiments and analyzing and verifying the experimental results [18]

Three different performance characteristics are used as the optimization criteria. They are the larger-the-better, the smaller the better and the nominal-the-best. In this study, larger-the-better was used. Performance characteristic (S/N) was calculated using Eq. (4) [18]:

$$S/N = -10 \log_{10}\left(\frac{1}{n_r}\sum_{i=1}^{n_r}\frac{1}{Y_i^2}\right) \quad (4)$$

The levels of parameters that maximize the S/N are optimum values. But the experiment corresponding to optimum working conditions might not have been made in the Taguchi method. In such cases the performance value can be estimated by utilizing the balanced characteristic of OA using Eq. (5) [19]:

$$Y_i = \mu + X_i + e_i \quad (5)$$

Equation 5 is a point estimate calculated by using experimental data. It is used to decide whether results of the confirmation experiments are meaningful or not. Therefore the confidence intervals for prediction error must be evaluated [18]. The confidence intervals can be calculated using Eq. (6):

$$Se = \pm 2\sqrt{\left[\frac{1}{n_0}\right]\sigma_e^2 + \left[\frac{1}{n_r}\right]\sigma_e^2} \quad (6)$$

$$\frac{1}{n_o} = \frac{1}{n} + \left[\frac{1}{n_{Ai}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Bi}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Ci}} - \frac{1}{n}\right].. \quad (7)$$

Experimental parameters and their levels were given in Table-1. The Orthogonal Array (OA) experimental design was selected and experimental plan consists of six parameters of each five levels (L_{25} or 5^6) was prepared. Experiments were repeated twice in the same conditions at different times. In this way, uncontrolled factors influencing this process were detected (Table-2).

Minitab-13 computer software package was used to analyze the results of experiments. A statistical analysis of variance (ANOVA) was performed to determine the effective parameters and their confidence levels on the dissolution process. The ANOVA accounts values known as sums of squares, degrees of freedom, etc. and presents them in a standard table form (Table 3).

Table-1: Experimental parameters and their values

	Parameters	Levels				
		1	2	3	4	5
A	Reaction temperature (^oC)	50	60	70	80	90
B	Particle size (µm)	-1000+850	-850+452	-300+212	-212+150	-50+125
C	Stirring speed (rpm)	200	300	400	500	600
D	Solid-to-liquid ratio ($g.mL^{-1}$)	0.05	0.10	0.15	0.20	0.25
E	Acid concentration (M)	0.25	0.30	0.70	1.0	1.5
F	Reaction time (min)	5	15	30	45	60

Table-2: L_{25} (5^6) experimental plan table and results of experiments.

Experiment	Parameters and their levels						Conversion fraction of B_2O_3			S/N ratio
no	A	B	C	D	E	F	Experiment (I) B_2O_3 %	Experiment (II)B_2O_3 %	Average B_2O_3 %	
1	1	1	1	1	1	1	51,98	55,14	53,56	34,5655
2	1	2	2	2	2	2	45,78	42,03	43,91	32,8265
3	1	3	3	3	3	3	76,85	78,36	77,61	37,7966
4	1	4	4	4	4	4	66,69	63,39	65,04	36,2552
5	1	5	5	5	5	5	48,98	48,53	48,76	33,7601
6	2	1	2	3	4	5	75,22	75,69	75,46	37,5536
7	2	2	3	4	5	1	78,55	79,97	79,26	37,9800
8	2	3	4	5	1	2	38,88	37,96	38,42	31,6893
9	2	4	5	1	2	3	84,44	80,55	82,50	38,3213
10	2	5	1	2	3	4	89,72	86,54	88,13	38,8982
11	3	1	3	5	2	4	20,59	17,42	19,01	25,4866
12	3	2	4	1	3	5	99,99	99,99	99,99	39,9991
13	3	3	5	2	4	1	84,61	85,03	84,82	38,5699
14	3	4	1	3	5	2	83,02	83,02	83,02	38,3837
15	3	5	2	4	1	3	54,81	54,14	54,48	34,7235
16	4	1	4	2	5	3	83,79	87,42	85,61	38,6441
17	4	2	5	3	1	4	61,29	62,29	61,79	35,8175
18	4	3	1	4	2	5	37,79	39,80	38,80	31,7668
19	4	4	2	5	3	1	76,09	73,55	74,82	37,4766
20	4	5	3	1	4	2	96,67	92,92	94,80	39,5306
21	5	1	5	4	3	2	76,51	72,55	74,53	37,4374
22	5	2	1	5	4	3	81,89	86,46	84,18	38,4941
23	5	3	2	1	5	4	99,99	98,03	99,01	39,9123
24	5	4	3	2	1	5	67,11	61,91	64,51	36,1714
25	5	5	4	3	2	1	75,70	77,67	76,69	37,6921

Table-3: The ANOVA table

		Sum of squares	Degrees of freedom	Mean of squares	*F*	Percentage of the contribution (%)
A	Reaction temperature (^oC)	2571,11	4	642,78	172,34	12,46
B	Particle size (μm)	1122,21	4	280,55	75,22	5,44
C	Stirring speed (rpm)	193,48	4	48,37	12,97	0,94
D	Solid-to-liquid ratio($g.mL^{-1}$)	6359,41	4	1589,85	426,27	30,81
E	Acid concentration (M)	9269,56	4	2317,39	621,34	44,91
F	Reaction time (min)	1030,87	4	257,72	69,10	4,99
	Error	93,24	25	3,73		
	Total	20639,88	49			

Figure 1 shows the degree of the effects of parameters on the performance characteristics. The highest S/N value is the optimal level of a process parameter. Fig. 1C shows the change of performance characteristics with stirring speed. Level 1 for C parameter (stirring speed) is 200 rpm. The experiments for level 1 of C parameter are experiments numbered as 1, 10, 14, 18 and 22. Therefore, S/N value for level 1 of C parameter is the average of those obtained from experiments numbers 1, 10, 14, 18 and 22. All values in Figure 1 were calculated in the same way. The highest value in each graph is the optimum value for that parameter [2]. When the Figure 1 is examined, it can be seen that A5 (90^oC), B4 (-212+150μm), C4 (500rpm), D1 ($0.05gmL^{-1}$), E3 (0.70M) and F3 (30 minutes) are the optimum conditions. However, when the design parameters are analyzed in detail and paid attention to industrial applications, it was thought that there might be other options in which one can get more economical results as well as 100% percent dissolution. Selecting a larger particular size can reduce crushing and grinding costs. Because of ineffectiveness of the stirring speed 200 rpm can be used instead of 500 rpm in order to save energy. To increase the efficiency of industrial-scale applications, the high proportion of the solid-liquid is promoted. Considering all these conditions, new experiments were done in the laboratory. Then, new conditions were determined. The dissolution percentage of ulexite in phosphate acid solutions was 100 % under the following conditions: A2 (60^oC), B2 (-850+452μm), C1 (200rpm), D3 ($0.15gmL^{-1}$), E3 (0.70M) and F3 (30minutes). Therefore, for this process, conditions of A2, B2, C1, D3, E3 and F3 were taken as optimum dissolution conditions. According to these results, the acid concentration and solid-to-liquid ratio were the most effective parameters for this process.

As shown in Table-2 the experiment in optimum dissolution conditions (A2, B2, C1, D3, E3 and F3) was not in experimental plan table. Therefore, it was performed later.

Table 4 includes predicted and observed dissolved quantities for the same conditions and confidence limits of prediction. Predicted and observed dissolved quantities were calculated from Eq.5 and Eq. 6-7, respectively. It can be said that the dissolution percentages from confirmation experiments are within %95 confidence limits. This situation refers to the predicted values are compatible with the experimental values, and the interactive effects between the parameters can be neglected. According to these results it can be said that the

Taguchi method to this dissolution process can be applied successfully.

Experimental

The ulexite ore used in the study was provided from a region of Bigadiç, Balıkesir, Turkey. The ore was cleaned manually from visible impurities, it was ground and sieved by ASTM standard sieves to obtain the nominal particle size fractions of -1000+850, -850+425, -300+212, -212+150 and -150+125μm in diameter. The chemical composition of the original sample was found as follows: 41.27%B_2O_3, 13.34%CaO, 6.83%Na_2O, 34.09%H_2O, 3.22%MgO, 0.034%SiO_2 and 1.22% others. X-ray diffractogram of ulexite ore was given in Fig. 2.

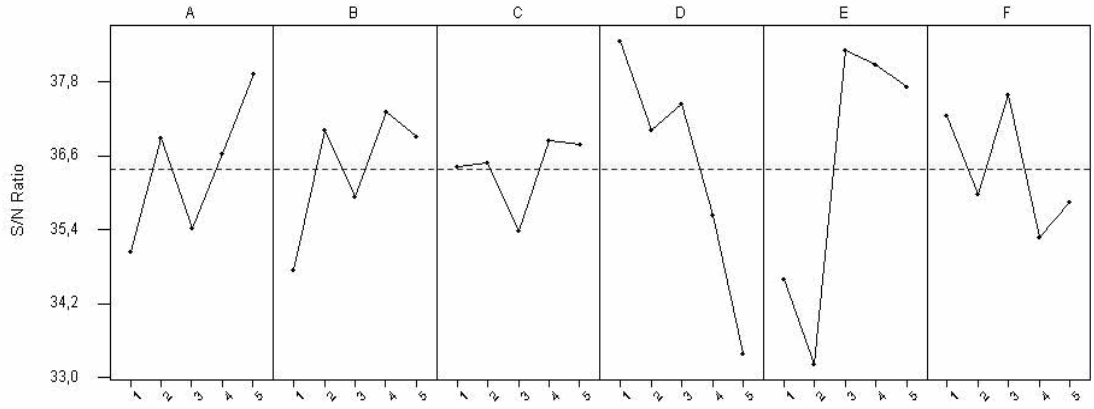

Fig. 1: The average effects plot for S/N ratios.

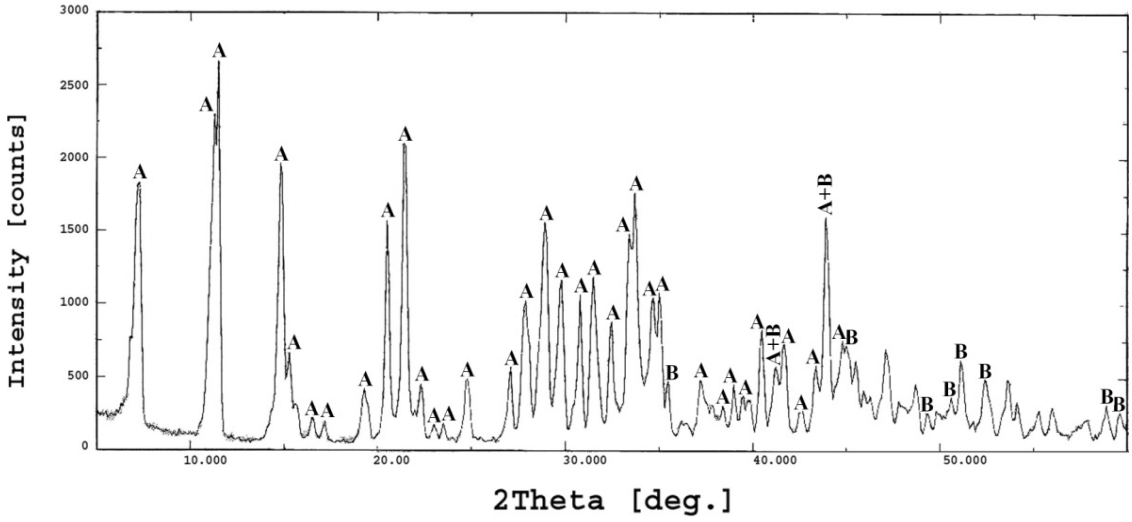

Fig. 2: X-ray diffractogram of the ulexite ore; (A) Ulexite; (B) Dolomite.

Table-4: Optimum dissolution conditions observed and predicted dissolved quantities of the ulexite.

Parameters	Value	Level
Reaction temperature (°C)	60	2
Particle size (μm)	-850+452	2
Stirring speed (rpm)	200	1
Solid-to-liquid ratio (g.mL^{-1})	0,15	3
Acid concentration (M)	0,70	3
Reaction time (min)	30	3
Observed dissolved quantity for B_2O_3 (%)	100	
Predicted dissolved quantity for B_2O_3 (%)	100	
Confidence limits of prediction for B_2O_3 (%)	95,27-100	

Dissolution experiments were performed in a 250mL jacketed glass reactor. Reactor was provided with a mechanical stirrer, thermostat and a cooler. Firstly, phosphoric acid solution at a certain concentration was put into the reactor. Then, the temperature of reactor was increased to a desirable point, and a certain amount of the ore was added into the reactor while stirring was continued. As soon as the process finished, the contents were filtered and the B_2O_3 in the solution was analyzed according to volumetric method with mannitol [20].

The Taguchi method was used to determine optimum conditions for the dissolution of ulexite in phosphate acid solutions. The results of the dissolution experiments were analyzed using the MİNİTAB-13 statistical package.

Conclusions

The significant results obtained for this study are as follows:

1. The effective parameters on the dissolution of ulexite ore in phosphate acid solutions were acid concentration, solid-to-liquid ratio, reaction temperature, particle size, reaction time, and stirring speed, respectively.
2. The optimum conditions were 60°C for reaction temperature, 0.15g.mL^{-1} for solid-to-liquid ratio, 30 minutes for reaction time, 0.70M for acid concentration, -850+452µm for particle size, and 200rpm stirring speed. Under these conditions, dissolution percentage of ulexite in phosphate acid solution was 100 (Table-4).
3. The predicted and observed dissolution values were very close to each other. This means that the Taguchi method can be applied to this dissolution process successfully.
4. In the Taguchi method, the optimum conditions obtained in a laboratory environment can be applied in real production environments. Therefore, the results of this study will be useful in industrial scale.

It was thought that boric acid, sodium dihydrogen phosphate and calcium dihydrogen phosphate could be produced by this process. Dissolution of ulexite ore in H_3PO_4 solutions will be useful in solving problems encountered in the production of boric acid such as decreasing reaction yield and filtration, etc.

Nomenclature

e_i	the random error i^{th} experiment
n	the number of rows in the matrix experiment
n_{Ai}, n_{Bi}, n_{Ci}, …	the replication number for the parameter level A_i, B_i, C_i,
n_r	the number of repetition for confirmation experiment or experimental combination
Se	the two-standard-deviation confidence limit
SN_L	performance characteristics for Larger-the-better
X_i	the fixed effect of the parameter level combination used in i^{th} experiment
Y_i	performance value of i^{th} experiment
σ_e^2	sum of squares due to error / degrees of freedom for error
μ	The overall mean of the performance value

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