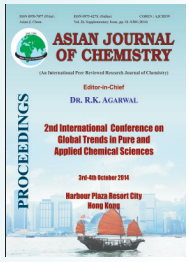
Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S183-S188

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19041



Optimization of Dissolution of Ulexite Mineral at High Temperature in Aqueous and Borax Pentahydrate Solutions Saturated with Carbon Dioxide

FEYZA ÇAVUS DISLI, SONER KUSLU, TURAN ÇALBAN* and SABRI ÇOLAK

Department of Chemical Engineering, Atatürk University, TR-25240,Erzurum, Turkey

Corresponding author: E-mail: turancalpan@atauni.edu.tr

Published online: 24 December 2014; AJC-16467

In this study, it was investigated the optimization of ulexite in both aqueous and borax pentahydrate solutions saturated with carbon dioxide. The effects of parameters such as solid-to-liquid ratio, reaction temperature, particle size and reaction time were investigated on dissolution of ulexite mineral. 2^n factorial experimental design and orthogonal central composite design methods in the dissolution experiments were used. It was observed that the most effective parameters on the dissolution of ulexite were the solid-to-liquid ratio, the particle size and the reaction time in aqueous and borax pentahydrate solutions. The optimum conditions on maximum ulexite dissolution were as: the reaction temperature 85 °C, the solid-to-liquid ratio at 0.125 g mL^{-1}, the particle size was 50 mesh and 90 min for reaction time. The chosen stationary parameters at the initial stage of the reaction were stirring speed 600 rpm and CO_2 gas flow rate 514 mL min^{-1}. Under these optimum conditions, the dissoluted B_2O_3 was 99.11 % in aqueous solutions and 99.02 % in borax pentahydrate solutions.

Keywords: Boron, Leaching, Orthogonal central composite experimental design, Borax pentahydrate solutions.

INTRODUCTION

Dissolution of inorganic compounds in aqueous solutions is considered as chemical process. Dissolution of boron minerals in aqueous solutions is one of special importance in hydrometallurgical processes. Boron is known as an element and attracts due to its strategic importance and having industrial importance. Boron minerals are important resources of Turkey. The dissolution of boron minerals is a key stage in hydrometallurgical processes and very important in aqueous systems. They are found in the form of borates (oxides) in nature. The main boron minerals are ulexite ($Na_2O{\cdot}_2CaO{\cdot}\ 5B_2O_3{\cdot}16H_2O$), colemanite ($Ca_2B_6O_{11}{\cdot}5H_2O$), tincal ($Na_2B_4O_7{\cdot}10H_2O$), kernite ($Na_2B_4O_7{\cdot}4H_2O$), datolite ($Ca_2B_2O_5{\cdot}Si_2\ O_5{\cdot}H_2O$) and hydroboracid ($CaMgB_6O_{11}{\cdot}6H_2O$). They can be employed as raw materials in some industries[1-4]. One of the most important minerals is ulexite, a hydrated calcium-sodium borate. It is a type of hydrated calcium borate with a monoclinic crystal structure and contains many clay minerals. It is used to produce boric acid[5,6]. Boric acid is the most common product of the boron minerals. It is used as starting material in the preparation of many boron chemicals[4-7].

There are many studies in the literature connected with optimization of the dissolution of ulexite and other chemicals in different aqueous solutions. Aycan *et al.*[8] used the Taguchi method to determine optimum conditions for the dissolution of ulexite in perchloric acid solutions. They chose parameters such as solid-to-liquid ratio, reaction time, particle size and acid concentration for optimization process. They took as constant the stirring speed and the reaction temperature in the experiments. They determinated 0.1 g/mL for solid to liquid ratio; 215 µm for particle size; 24 min for reaction time; 500 rpm for stirring speed; 30 °C for reaction temperature and 2 mol/dm^3 for acid concentration the optimum conditions. Under these conditions, the boric acid extraction from ulexite was reached a value of 99 %. Küçük[9] used the Taguchi method to determine optimum conditions for the dissolution of ulexite in NH_4Cl solutions. He chose 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 ranges of experimental parameters found to be 87 °C, 0.05 g mL^{-1}, 4 M, (-300 + 212) µm and 18 min, respectively. Under these optimum conditions, the dissolution percentage of ulexite in NH_4Cl solution was 98.37. Küçük *et al.*[10] used the Taguchi method to determine the optimum conditions for the dissolution of ulexite in ammonium sulphate solutions. The reaction maintained between 60-88 °C for reaction temperature, 0.05-0.15 g mL^{-1} for solid to liquid ratio, 5-20 min, for reaction time and (-850 + 600)-(-90) µm for particle size the ranges of experimental parameters. They identified to be 88 °C, 0.1 g mL^{-1}, -90 µm and 20 min, respectively. Under these conditions, the predicted

and experimental dissolution percentages of ulexite in ammonium sulphate solutions were 98.60 and 98.36, respectively.

Küçük and Kocakerim[11] used the Taguchi method to determine optimum conditions for the dissolution of ulexite in water saturated with SO_2 to produce monosodium pentaborate (NaB_5O_8) in a new process. In other studies related to optimization, Çalban *et al.*[12] researched statistical modelling of Chevreul's salt recovery from leach solutions contained copper. They determined the optimum precipitation conditions of Chevreul's salt using leach solutions. They found as pH 3, temperature 62 °C, stirring speed 600 rpm, reaction time 12 min, SO_2 flow rate 358 L h^{-1} and concentration of $CuSO_4$ solution 7.383 gCu L^{-1}.

Yesilyurt and Çalban[13] precipitated the Chevreul's salt from mixture of $CuSO_4$ and Na_2SO_3 solutions. They determined the optimum precipitation conditions as temperature 60 °C, $[SO_3^{-2}]/[Cu^{+2}]$ ratio 1.6, pH 3, stirring speed 500 rpm and reaction time 20 min. Kuslu *et al.*[14] investigated the optimization of removal of silver from anode slime in ammonium thiosulfate solutions by microwave using statistical design methods. Çalban *et al.*[15] studied the optimization of removal of lead from anode slime in triethanolamine solutions by the microwave effect using statistical design methods. Çalban and Kavcl[16] optimized the removal of calcium from soda liquid waste containing calcium chlorine. Yesilyurt *et al.*[17] determined the optimum conditions on colemanite dissolution in H_3PO_4 solutions.

The aim of our study was to investigate the optimum dissolution of ulexite mineral at high temperature in aqueous and borax pentahydrate solutions saturated with CO_2 in a mechanical agitation system. In our study, we researched the effects of parameters such as solid-to-liquid ratio, reaction temperature, particle size and reaction time on optimumdissolution of ulexite mineral. 2^n factorial experimental design and orthogonal central composite design methods in the dissolution experiments were used.

EXPERIMENTAL

Experimental design is widely used for controlling the effects of parameters in many processes. Its usage decreases the number of experiments, using time and the quantity of materials used. Furthermore, analysis based on the results is easily carried out and experimental errors are minimized. Statistical methods measure the effects of change in operating variables and their interactions on the process through factorial experimental designs. Today, the most widely used experimental design to estimate main effects, intercalarily interaction effects is the 2^n factorial design. According to the 2^n factorial experimental design method, the principal steps of experiments are designed: determination of response variables, choice of factor levels and statistical analysis of the data. Consequently, the final step of the work is to obtain a statistical regression model[18]. A factor is any aspect of experimental conditions affecting the results of experiments. A two-level experimental design requires 2^n runs for two levels of each factor. Coded values of variables are high level = +1 and low level = -1. The centre coordinates are zero between factor levels and this value coincides with the origin of coordinates.

The variance analysis Tables (ANOVA) show the effects of all variables and their mutual interactions[19,20]. Experimental data based on the design is fitted to a second-order polynomial equation as follows.

$$\hat{Y} = b_o + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii}(X_i^2 - \bar{X}_i^2) + \sum_{i=1}^{n}\sum_{j=1}^{n} b_{ij} X_i X_j \quad (1)$$

where, the coefficient b_i shows the main effects of the factors X_i; b_{ii} and b_{ij} coefficients represent second-order interaction terms. The independent term b_0 represents the response at the zero level of every factor ($X_1 = X_2 = X_3 = X_i = 0$).

The main effects and interactions obtained from regression model are entirely half values obtained from the Yates algoritm. This is because of the response over two levels of each independent variable (from -1 to +1)[21,22].

Second-order effects cannot be estimated by 2^n factorial designs. If the variance analysis indicates that second-order effects are significant, auxiliary experiments are carried out. Among various second-order designs, the orthogonal central composite design is the most popular which requires 2^n auxiliary runs conducted at two new factor levels, $-\beta$, $+\beta$. They are calculated by the following relation:

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

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

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

where F is the number of experiments in the factorial design, N is the total number of experiments and m_0 is the number of central replicates.

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:

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

where Z_1 is the low level, Z_2 is the high level and Z_0 is the medium level of the variable[19,20,23,24].

Optimization experiments were conducted under atmospheric pressure conditions. All reagents used in the experiments were prepared from analytical grade chemicals (Merck) and distilled water. A constant temperature water circulator was used in combination with the reactor to maintain the mixture in the reactor at a constant temperature. The experiments were carried out in a 500 mL spherical glass reactor. The reactor was equipped with a reflux condenser to prevent evaporation during heating and a mechanical stirrer to obtain a homogeneous suspension in the reactor. The mechanical agitation experimental system is fairly common, so no illustration of it appears in this paper.

A typical experiment conducted was as follows: 400 mL of distilled water was poured into the flask. The solution was heated to the desired temperature. Borax pentahydrate was added to the distilled water. The CO_2 gas (97 %) was supplied to the reactor from a CO_2 cylinder tank. CO_2 gas was continuously fed to the reactor during dissolution to maintain

TABLE-1
CHEMICAL ANALYSES OF ULEXITE MINERAL

Component	CaO	B_2O_3	Na_2O	MgO	Al_2O_3	SiO_2	Fe_2O_3	SrO	H_2O
Percentages	14.69	41.12	7.48	1.78	< 0.01	4.13	< 0.01	1.43	29.35

saturation conditions. The flow rates of CO_2 were maintained at 514 mL/min in all experiments. The gas was bubbled from the bottom of the reactor by means of a disk-type gas dispenser. CO_2 feed to the reactor for 20-25 min was to obtain a saturated aqueous solution and borax pentahydrate solution. After this, large qualities 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. The stirring continued during the reaction time. At the end of the reaction period, the solution was immediately filtered through a Filtrak 389 and was washed with deionized water. The reacted solution were taken for the assay of B_2O_3 and analyzed by potentiometric and titrimetric methods[25,26].

Ulexite samples used in the experiments were obtained from Bandirma Borax Corporation, Turkey. The ulexite mineral samples were crushed, dried under vacuum and sieved with ASTM standard sieves to give fractions of average sizes -10, -30, -40 and -50 mesh for dissolution experiments. The chemical analyses of original ulexite samples and the B_2O_3 content in the particle sizes used in the experiments are shown in Tables 1 and 2, respectively. Further, SEM photography of the original ulexite minerals is shown in Fig. 1.

TABLE-2
PARTICLE SIZES OF B_2O_3 UTILIZED

Particle size (mesh)	-10	-20	-40	-50
B_2O_3 (%)	41.79	41.21	41.71	40.25

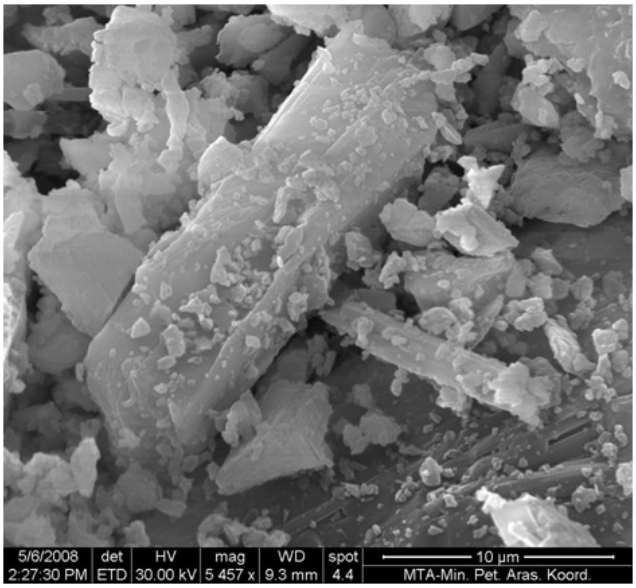


Fig. 1. SEM photograph of ulexite mineral

RESULTS AND DISCUSSION

Dissolution of ulexite mineral: Dissolution of ulexite in aqueous and borax pentahydrate solutions, the reactions taking place in the medium can be written as follows:

$$Na_2B_4O_7{\cdot}5H_2O_{(s)} + 2H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + 4H_3BO_{3(aq)} \quad (6)$$

$$10CO_{2(g)} \rightarrow 10CO_{2(aq)} \quad (7)$$

$$10CO_{2(aq)} + 10H_2O_{(l)} \rightarrow 10H_2CO_{3(aq)} \quad (8)$$

$$10H_2CO_{3(aq)} + 10H_2O_{(l)} \rightarrow 10H_3O^+_{(aq)} + 10HCO_3^-{}_{(aq)} \quad (9)$$

$$2H_3O^+_{(aq)} + 2OH^-_{(aq)} \rightarrow 4H_2O_{(l)} \quad (10)$$

Hence, the overall reaction is follows:

$$Na_2B_4O_7{\cdot}5H_2O_{(s)} + 18H_2O_{(l)} + 10CO_{2(g)} \rightarrow 2Na^+_{(aq)} + 10HCO_3^-{}_{(aq)} + 4H_3BO_{3(aq)} + 8H_3O^+_{(aq)} \quad (11)$$

when ulexite is added to the borax pentahydrate solutions, the reaction taking place in the solution can be written as follows:

$$2(Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O)_{(s)} + 4H_2O_{(l)} \rightarrow 4Na^+_{(aq)} + 4Ca^{+2}_{(aq)} + 12OH^-_{(aq)} + 20H_3BO_{3(aq)} \quad (12)$$

$$8H_3O^+_{(aq)} + 8OH^-_{(aq)} \rightarrow 16H_2O_{(l)} \quad (13)$$

$$4HCO_3^-{}_{(aq)} + 4OH^-_{(aq)} \rightarrow 4CO_3^{-2}{}_{(aq)} + 4H_2O_{(l)} \quad (14)$$

$$4Ca^{+2}_{(aq)} + 4CO_3^{-2}{}_{(aq)} \rightarrow 4CaCO_{3(s)} \quad (15)$$

The overall net reaction is:

$$Na_2B_4O_7{\cdot}5H_2O_{(s)} + 10CO_{2(g)} + 2(Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O)_{(s)} + 2H_2O_{(l)} \rightarrow 6Na^+_{(aq)} + 6HCO_3^-{}_{(aq)} + 24\ H_3BO_{3(aq)} + 4CaCO_{3(s)} \quad (16)$$

Effects of parameters on the dissolution of ulexite: The effects of the parameters on ulexite dissolution were investigated for parameters using the values given in Tables 3 and 4. The effect of the temperature was investigated in the range of 65-85 °C. In all experiments, the solid-to-liquid ratio, the particle size, the reaction time (the mean value of four central replications), the stirring speed and the CO_2 gas flow rate were meticulously controlled during the reaction. All the results are given in Tables 5 and 6. As seen from the Tables, the dissolution percentages increased with increasing the reaction temperature. The dissolution percentage was high for the chosen high temperature ranges in aqueous solutions. In borax

TABLE-3
FACTOR LEVELS FOR FIRST-ORDER MODEL

Factors	Low level (-)	High level (+)	Medium level (0)
X_1: Temperature (°C)	65	85	75
X_2: Solid-to-liquid ratio (g/mL)	0.125	0.25	0.1875
X_3: Particle size (mesh)	-50	-10	-30
X_4: Reaction time (min)	30	90	60

* While the effect of one parameter was studied, the values of the other parameters were kept constant

TABLE-4
FACTOR LEVELS FOR SECOND-ORDER MODEL

Factors	Low level (-)	High level (+)	Medium level (0)
X_1: Temperature (°C)	63	87	75
X_2: Solid-to-liquid ratio (g/mL)	0.087	0.288	0.1875
X_3: Particle size (mesh)	-40	-20	-30
X_4: Reaction time (min)	12	108	60

* While the effect of one parameter was studied, the values of the other parameters were kept constant

TABLE-5
EXPERIMENTAL DESIGN MATRIX AND ULEXITE DISSOLUTION PERCENTAGE

Exp. No.	X_1	X_2	X_3	X_4	BP* Solutions		Aqueous Solutions	
					$Y_{B2O3(b)}$	$Y_{teoretical}$	$Y_{B2O3(a)}$	$Y_{teoretical}$
1	+	+	+	+	69.97	68.75	77.21	82.30
2	-	+	+	+	49.35	51.73	73.62	76.27
3	+	-	+	+	89.12	89.25	90.00	93.36
4	-	-	-	+	87.36	87.60	93.28	94.28
5	+	+	-	-	60.39	55.39	69.99	68.76
6	-	+	-	-	50.30	47.45	63.57	60.15
7	+	-	+	-	66.65	70.66	71.98	71.03
8	-	-	+	-	58.95	57.68	56.60	59.91
9	+	+	-	+	78.47	77.01	85.36	81.99
10	-	+	-	+	71.10	65.31	76.42	77.81
11	+	-	-	+	95.83	99.02	96.05	99.11
12	-	-	+	+	69.29	72.51	85.00	86.67
13	+	+	+	-	43.41	40.44	55.21	54.15
14	-	+	+	-	32.16	27.19	46.29	43.68
15	+	-	-	-	92.21	87.11	94.42	91.71
16	-	-	-	-	80.00	79.45	87.09	82.44
17	-1.607	0	0	0	57.66	61.21	73.48	74.71
18	+1.607	0	0	0	78.22	81.04	87.55	87.01
19	0	-1,607	0	0	86.11	81.68	98.42	96.70
20	0	+1,607	0	0	16.30	39.49	67.47	69.89
21	0	0	-1,607	0	81.12	89.88	92.09	96.84
22	0	0	+1,607	0	67.34	65.75	87.55	78.99
23	0	0	0	-1,607	32.28	50.31	44.33	53.44
24	0	0	0	+1,607	71.69	79.61	93.98	85.56
25*	0	0	0	0	76.55	71.01	88.50	87.25
26*	0	0	0	0	73.90	71.01	86.77	87.25
27*	0	0	0	0	71.14	71.01	87.63	87.25
28*	0	0	0	0	72.29	71.01	85.25	87.25

*Borax Pentahidrate

TABLE-6
TABLE OF VARIANCE ANALYSIS (ANOVA) FOR BORAX PENTAHYDRATE SOLUTIONS

Source of variation	Sum of squares	df	Mean squares	Fratio	Decision ($\alpha = 0,01$)	Decision ($\alpha = 0,05$)
X_1	594.6282	1	594.6282	108.173	Effective	Effective
X_2	2121.984	1	2121.984	386.025	Effective	Effective
X_3	1168.956	1	1168.956	212.653	Effective	Effective
X_4	998.876	1	998.876	181.712	Effective	Effective
$LOF_{curvature}$	81.9315	1	81.9315	14.904	Ineffective	Effective
Model lack of fit	255.062	11	23.187	4.218	Ineffective	Ineffective
Experimental error	16.4926	3	5.497			
Total	5237.931	19				

$F_{0.99;\,1;\,3} = 34.116 F_{0.95;\,1;\,3} = 10.128 F_{0.99;\,11;\,3} = 27.13 F_{0.95;\,11;\,3} = 8.725$

pentahydrate solutions, the dissolution percentage was low. In borax pentahydrate solutions, the increase in the dissolution percentage was lower. The reason for this, B_2O_3 pre-dissolved in borax pentahydrate solutions was available. In this case, the percentage of soluble B_2O_3 decreased and the dissolution rate slowe down.

The effect of the solid-to-liquid ratio was studied in the ranges of 0.087-0.288 g/mL. The obtained B_2O_3 amounts in borax pentahydrate solutions which are using central values of the other parameters for 0.087, 0.1875 and 0.288 g/mL solid-to-liquid ratios were 86.11, 73.47 (the mean value of four central replications) and 16.11 %, respectively. The obtained B_2O_3 amounts in aqueous solutions for 0.087, 0.1875 and 0.288 g/mL solid-to-liquid ratios were 98.42, 87.04 (the mean value of four central replications) and 67.47 %, respectively. The results obtained from experiments are presented in Tables 4-6. As seen from the Tables, the dissolution percentages for aqueous and borax pentahydrates solutions decreased with increasing the solid-to-liquid ratio.

The effect of the particle size was investigated in the ranges of (-20)-(-40) mesh. The obtained B_2O_3 amounts in borax pentahydrate solutions which are using central values of the other parameters for -20, -30 and -40 mesh particle sizes were 81.12, 73.47 (the mean value of four central replications) and 67.34 %, respectively. The obtained B_2O_3 amounts in aqueous solutions for -20, -30 and -40 mesh particle sizes were 92.09, 87.04 (the mean value of four central replications) and 87.55 %, respectively. The results obtained from experiments are presented in Tables 4-6. As seen from the Tables, the dissolution percentages for aqueous and borax pentahydrates solutions decreased with increasing the particles size. As mean particle size decreased the dissolution rate increased due to increasing surface area.

The effect of reaction time was studied in the range of 12-108 min. The obtained B_2O_3 amounts for borax pentahydrate solutions which are using central values of the other parameters for 12, 60 and 108 min were 32.28, 73.47 (the mean value of three central replications) and 71.69 %, respectively. The obtained B_2O_3 amounts for aqueous solutions for 12, 60 and 108 min were 44.33, 87.04 (the mean value of three central replications) and 93.98 %, respectively. The obtained results from experiments were given in Tables 4-6. As seen from the Tables, the dissolution percentages increased with increasing the reaction times.

Statistical analysis of ulexite mineral dissolution: Dissolutions tests of ulexite mineral in aqueous and borax pentahydrate solutions saturated with carbon dioxide 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. In light of kinetic experiments, the stirring speed and CO_2 flow rate were maintained as constant parameters. Other factors such as the reaction temperature, the solid-to-liquid ratio, the particle size and the reaction time were chosen as independent variables and their high and low levels were decided as shown in Tables 3 and 4.

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 and 99 % confidence intervals. The results are shown in Tables 6 and 7. At both confidence intervals, the reaction temperature (X_1), the solid-to-liquid ratio (X_2), the particle size (X_3) and the reaction time (X_4) range have been found to be effective. Furthermore, the effects of pure quadratic terms were controlled by means of the following statistic:

$$LOF_{curv.} = \frac{m_o F(\bar{Y}_1 - \bar{Y}_0)^2}{m_o + F} \quad (17)$$

where m_o is the number of central point experiments, F is the number of factorial experiments, $\bar{Y}_1$ is the mean of factorial experiments and $\bar{Y}_0$ is the mean of central replicates.

As seen from Tables 6 and 7, results of variance analysis showed a curvature effect in 95 % confidence interval. According to these results, the regression model was obtained as follows.

B_2O_3 obtained from aqueous and borax pentahydrate solutions (%):

$$Y_{B2O3(a)} = 79.1636 + 3.8251\,X_1 - 8.3385\,X_2 - 5.5545\,X_3 + 9.9965\,X_4 - 2.7304\,X_{11} - 1.7897\,X_{22} - 7.1284\,X_{44} - 0.1631\,X_1 \cdot X_2 - 1\cdot1094\,X_1 \cdot X_4 - 1.5156\,X_2 \cdot X_3 + 1.4569\,X_2 \cdot X_4 + 3.7319\,X_3 \cdot X_4 \text{ (for aqueous solutions)} \quad (18)$$

$$Y_{B2O3(b)} = 72.240 + 6.1695\,X_1 - 13.1262\,X_2 - 7.5076 - X_3 + 9.1141\,X_4 - 4.0803\,X_{22} + 2.5903\,X_{33} - 2.3865\,X_{44} + 2.4275 X_2 X_4 \text{ (for borax pentahydrate)} \quad (19)$$

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, $m_0 = 4$ and n = 4, β is calculated as 1.607 according to eqn. 2. Factor levels for second-order model are given in Table-4. Also, the second-order model is defined as in eqns. 1 and 20:

$$\bar{X}_i^2 = \frac{1}{N}\sum_i^N X_i^2 = \frac{F + 2\beta^2}{N} \quad (20)$$

The ANOVA of obtained results shows that all of the variables studied and their combinations affect the dissolution of ulexite mineral from aqueous and borax pentahydrate solutions. As seen from Tables 6 and 7, the reaction temperature, the solid-to-liquid ratio, the particle size, the reaction time and interactions of the particle size 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 tests'graphs are shown in Figs. 2 and 3.

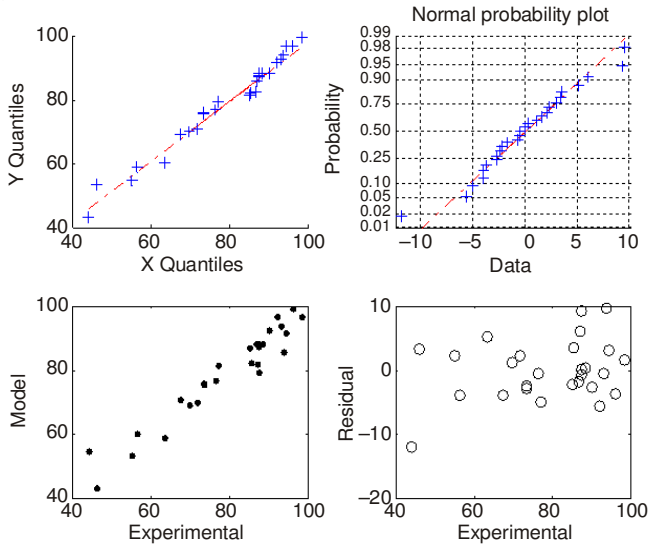


Fig. 2. Statistical test graphics for aqueous solutions

TABLE-7
TABLE OF VARIANCE ANALYSIS (ANOVA) FOR AQUEOUS SOLUTIONS

Source of variation	Sum of squares	df	Mean squares	Fratio	Decision (α = 0,01)	Decision (α = 0,05)
X_1	212.7952	1	212.7952	110.894	Effective	Effective
X_2	1004.098	1	1004.098	523.267	Effective	Effective
X_3	759.9671	1	759.9671	396.043	Effective	Effective
X_4	1085.538	1	1085.538	565.708	Effective	Effective
$LOF_{curvature}$	363.4208	1	363.4208	189.390	Ineffective	Effective
Model lack of fit	368.1378	11	33.4670	17.440	Ineffective	Effective
Experimental error	5.7567	3	1.9189			
Total	3799.713	19				

$F_{0.99;\,1;\,3} = 34.116 F_{0.95;\,1;\,3} = 10.128 F_{0.99;\,11;\,3} = 27.13 F_{0.95;\,11;\,3} = 8.725$

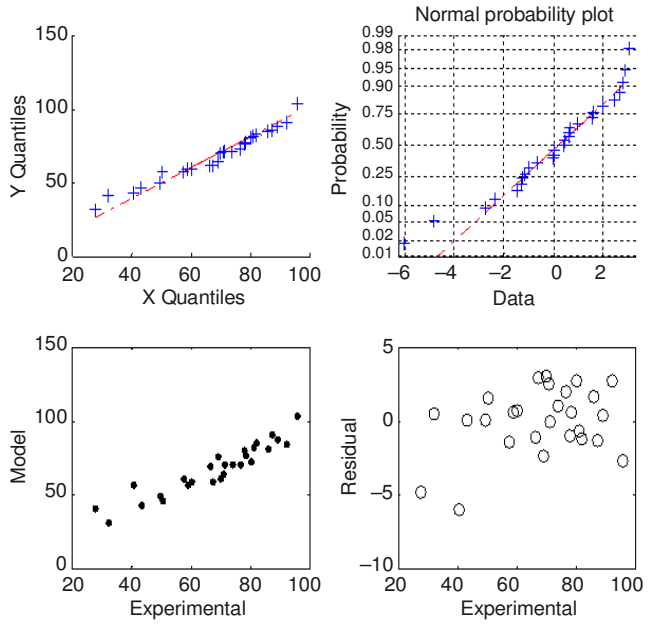


Fig. 3. Statistical test graphics for borax pentahydrate solutions

Conclusions

- The solubility of ulexite mineral can be increased by addition of CO_2.
- The dissolution percentage of ulexite mineral increased with increasing in reaction temperature and the reaction time in aqueous and borax pentahydrate solutions.
- The dissolution percentage of ulexite mineral increased with decreasing in the solid/liquid ratio and the particle size in aqueous and borax pentahydrate solutions.
- The dissolution extent is not affected by the stirring speed in selected experimental conditions.
- The obtained optimum conditions on maximum dissolution of ulexite mineral were: the reaction temperature 85 °C, the solid-to-liquid ratio at 0.125 g mL^{-1}, the particle size was at -50 mesh and 90 min for reaction time both aqueous and borax pentahydrate solutions.
- The chosen stationary parameters at the initial stage of the reaction were stirring speed 600 rpm and CO_2 gaz flow rate 514 mL min^{-1}.
- Under these optimum conditions, the dissoluted B_2O_3 was 99.11 % in aqueous solutions and 99.02 % in borax pentahydrate solutions.
- The use of CO_2 gas as reactive in the process facilitates the dissolution of solutions containing boron.
- Boric acid can be obtainedas product with crystallization of solution filtrated.
- Using of the carbon dioxide gas in this process is important for environmental protection.
- Interactions of the particle size with the reaction time are effective on dissolution of ulexite mineral.
- After final solution obtained from borax pentahydrate solutions is filtrated, the calcium carbonate precipitate can be used in the construction industry.
- The dissolution percentage of ulexite in aqueous solutions are higher than borax pentahydrate solutions. The reason for this, B_2O_3 pre-dissolved in borax pentahydrate solutions is available. In this case, the soluble B_2O_3 amount in borax pentahydrate solutions decreases.

ACKNOWLEDGEMENTS

The Atatürk University Research Council financially supported this study (Project No. 2007/149). The authors highly appreciate the Council's support of this project.

REFERENCES

1. T.W. Davies, S. Colak and R.M. Hooper, *Powder Technol.*, **65**, 433 (1991).
2. H.P. Kemp, The Chemistry of Borates: Part I, Borax Consolidated Ltd., London (1956).
3. D.E. Garret, Borates, Academic Press Ltd., New York (1998).
4. C. Ozmetin, M.M. Kocakerim, S. Yapici and A.Yartasi, *Ind. Eng. Chem. Res.*, **35**, 2355 (1996).
5. Ö. Küçük, M.M. Kocakerim, A.Yartasi and M. Çopur, *Ind. Eng. Chem. Res.*, **41**, 2853 (2002).
6. H.Temur, A.Yartasi, M. Copur and M.M. Kocakerim, *Ind. Eng. Chem. Res.*, **39**, 4114 (2000).
7. M. Alkan and M. Muhtar Kocakerim, *J. Chem. Technol. Biotechnol.*, **40**, 215 (1987).
8. G. Aycan, A. Yildiz, H. Çelik and A. Selçuk, *Asian J. Chem.*, **20**, 2929 (2008).
9. Ö. Küçük, *Korean J. Chem. Eng.*, **23**, 21 (2006).
10. Ö. Küçük, M.M. Kocakerim, M. Çopur and A.Yartasi, *Can. Metall. Quar.*, **44**, 53 (2005).
11. Ö. Küçük and M.M. Kocakerim, *Process Intensification*, **44**, 1005 (2005).
12. T. Çalban, S. Çolak and M. Yesilyurt, *Chem. Eng. Process.*, **45**, 168 (2006).
13. M. Yesilyurt and T. Çalban, *Chem. Process Eng.*, **28**, 85 (2007).
14. D. Tokkan, S. Kuslu, T. Çalban and S. Çolak, *Ind. Eng. Chem. Res.*, **52**, 9719 (2013).
15. D. Tokkan, T. Çalban, S. Kuslu, S. Çolak and B. Dönmez, *Ind. Eng. Chem. Res.*, **51**, 3903 (2012).
16. T. Çalban and E. Kavci, *Energy Sources A*, **32**, 407 (2010).
17. M. Yesilyurt, S. Çolak, T. Çalban and Y. Genel, *Ind. Eng. Chem. Res.*, **44**, 3761 (2005).
18. D.C. Montgomery, Design and Analysis of Experiments, John Wiley, New York (1976).
19. T. Çalban, S. Çolak and M. Yesilyurt, *Chem. Eng. Commun.*, **192**, 1515 (2005).
20. A.G. Gonzalez, *Anal. Chim. Acta*, **360**, 227 (1998).
21. A. Martŷinez-L, A. Uribe S, F.R. Carrillo P, J. Coreño A and J.C. Ortiz, *Int. J. Miner. Process.*, **70**, 83 (2003).
22. F. Yates, Farnham Royal: Commonweath Agricultural Bureaux (1959).
23. E. Sayan and M. Bayramoglu, *Hydrometallurgy*, **57**, 181 (2000).
24. T. Çalban, Ph. D. Thesis, Atatürk University, Erzurum, Turkey (2002) (In Turkish).
25. A.A. Nemodruk and Z.K. Karalova, *Israel Program for Scientific Translations, Jerusalem*, **1**, 33 (1965).
26. D.A. Sookg, D.W. West, F.J. Holler, Fundamentals of Analytical Chemistry, Saunders College Publishing, edn. 7 (1996).