Effects of Leaching Parameters on the Impurity Ion Concentrations at Ulexite Ore Leaching: An Experimental Design Approach

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ABSTRACT: *An experimental study was conducted to determine the effects of the leaching parameters on impurity ion concentrations of the liquid phase in ulexite leaching. Powdered ulexite ore was leached in an aqueous medium with sulfur dioxide. The Taguchi experimental design approach and statistical methods were used to evaluate the effects of the leaching parameters (solid/liquid ratio, temperature, pH, particle size, time) on impurity ion concentrations (concentrations of magnesium, calcium, iron ions) in the liquid phase. The average B_2O_3 leaching ratio of ulexite ore was found as 98.56 % (± 0.95). Statistically effective leaching parameters on impurity concentrations (and delta values for concentrations) were found as pH (770 ppm) for magnesium, solid/liquid ratio (372 ppm) for calcium ion concentrations. The examined parameters were not found effective for iron ion concentrations.*

KEYWORDS *Leaching; Dissolution; Impurity ion concentration; Borate; Ulexite; Mineral; Taguchi method; Design of Experiments (DoE).*

INTRODUCTION

Boron chemicals are used in the production of many different materials [1-3] such as the production of medicines [4], fire retardants [5-7], fertilizers [8-10], composite materials and glasses [11-13], fibreglass [14], fine chemicals, etc. Naturally occurring borate minerals are used in the production of boron chemicals as natural precursors [3, 15, 16]. In the industrial practice, commonly found borate minerals like tincal ($Na_2[B_4O_5(OH)_4].8H_2O$), ulexite ($NaCaB_5O_6(OH)_6.5H_2O$), colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$), razorite ($Na_2B_4O_6(OH)_2.3H_2O$) [2] are leached with water [17]; then the liquid phase is separated and crystallized in different conditions to form several borate salts [3, 17, 18]. Some of the common boron chemicals produced with this approach are boric acid (H_3BO_3), borax pentahydrate ($Na_2B_4O_7.5H_2O$), sodium pentaborate ($Na_2O.5B_2O_3.10H_2O$) and sodium metaborate ($NaBO_2$) [3, 19]. Some of the borate minerals like colemanite, ulexite have low solubility in water. Acids are used to increase the leaching rate of these borate minerals [17, 20]. However strong acids (like sulfuric acid) react with accompanying minerals (like calcite, clay) and extract metal ions like magnesium, calcium, iron. These metal ions create highly soluble salts [17, 20]. Removing these impurities from crystallite requires additional purification steps which leads to waste of time, energy, resources [20] and increase the process waste [18, 21-23].

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Leaching boron minerals with weak acid solutions can prevent this problem. There are many studies on leaching boron minerals with weak acids. Leaching colemanite with oxalic acid [24], citric acid [25], ammonium sulphate [26], ammonium nitrate [27, 28], potassium hydrogen sulphate [29], potassium dihydrogen phosphate [30] and leaching ulexite with sodium hydrogen phosphate [31], ammonium chloride [32], ammonium acetate [33], EDTA [34], citric acid [35, 36], ammonium carbonate [37], oxalic acid [38], sulphur dioxide (aq.) [39, 40] have been studied recently. The dissolution of ulexite in acidic solutions such as hydrochloric acid [41], phosphoric acid [42] and also aqueous solutions of sulfur dioxide (SO_2) [43-45] and carbon dioxide (CO_2) [46] have been examined Kinetics and the optimization of leaching process were examined in these studies The main motivation of these studies are limiting unwanted reactions and impurity concentrations with leaching borate minerals with different weak acids however in these studies researchers did not consider impurities passing to solutions, except one study where *Bulutçu et al.* [20] found the decrease of magnesium ion concentrations with using mixture of sulphuric acid and propionic acid instead of sulphuric acid solutions in the leaching process.

In this study, ulexite ore was leached in an aqueous medium with sulfur dixode. Sulfur dioxide is preferred because of its wide availability and high activity in leaching boron minerals [39, 40, 43-45]. The effects of the leaching parameters on the impurities passing into the solution (liquid phase) in ulexite leaching were analyzed by using statistical and experimental design methods. One of the most used boron chemicals, boric acid is produced by dissolving ulexite in sulfuric acid solutions, then crystalizing it from hot concentrated solution. Impurities that pass to the solution significantly affect the product quality.

Therefore, obtaining a leaching solution with a minimum of impurities is important to minimize impurities in the boric acid produced. It may be possible to reduce repetitive purification and recrystallization steps. As far as the authors' knowledge this is the first study in the literature that investigates effects of leaching parameters on concentrations of impurities passing to solution in ulexite leaching with statistical methods and experimental design methods [20].

Experimental design methods could be used to have a better understanding of chemical systems and elucidate the relationship between inputs and outputs [47]. There are several research studies in mineral leaching that uses experimental design methods [48, 49]. They are mostly focused on obtaining optimal parameter levels for maximizing the leaching rate [49-54] but experimental design methods may also be used to systematically investigate the effects of parameters on outputs as well. Using experimental design methods like Taguchi method effects parameters could be investigated systematically [55-59]. Taguchi Method is a well known method and it is widely preferred by researchers because of its simplicity and easy implementation. Taguchi Orthogonal arrays are very useful in analysing high number of parameters with least amount of experiments. In this study, Taguchi L_{16} (4^5) orthogonal array was used for experimental runs. Taguchi experimental design method and hypothesis testing were used for determining the effects of leaching parameters on impurity concentrations.

EXPERIMENTAL SECTION

Materials

Commercial grade ulexite ore was obtained from Eti Mine Corporation, Turkey. The ore includes ulexite ($Na_2O.2CaO.5B_2O_3.16H_2O$), calcite ($CaCO_3$) and clay minerals. The ore was powdered with a disk type crusher and divided into four portions. Then, each portion was sieved with one of stainless steel sieves according to the ASTM E11:13 standards. Fractions under sieve were used in studies. Chemical analysis of each fraction was done by wet chemical methods. The results of chemical analyses were given in Table 1.

Chemical analysis of the sample was found to be consistent with the manufacturer's specifications. Borate ores have similar appearance so X-ray powder diffraction analysis was carried out for the identification of crystalline structures in the crushed ore. The ore consists predominantly of ulexite crystals. Calcite is also detectable because of its relatively high amount and crystal structure. X-ray powder diffraction pattern of ulexite ore was given in Fig. 1.

Methodology

Taguchi method is an experimental design method and it is developed by *Genichi Taguchi* at 1950's [60-62]. According to Taguchi, the factors that affect the quality of the product could be divided into two groups: controllable and uncontrollable factors. Uncontrollable factors or noise factors originate from inside of the system or surroundings of the system.

Table 1: Chemical analysis of ulexite ore fractions.

Particle Size	% B_2O_3	% CaO	% Na_2O	% MgO	% Fe_2O_3	% H_2O	Others
-250 µm	39.27	17.26	5.42	1.30	0.01	32.31	4.43
-150 µm	40.49	16.60	5.59	1.33	0.02	33.32	2.65
-75 µm	36.59	17.71	4.71	2.24	0.02	30.11	8.62
-45 µm	36.94	18.70	3.50	2.50	0.04	30.40	7.92

"Particle size" denotes to the lower portion of the sieve. For example "-250 µm" denotes that all the particles are smaller than 250 µm. Particles bigger than 250 µm (the higher portion of the sieve) are discarded.

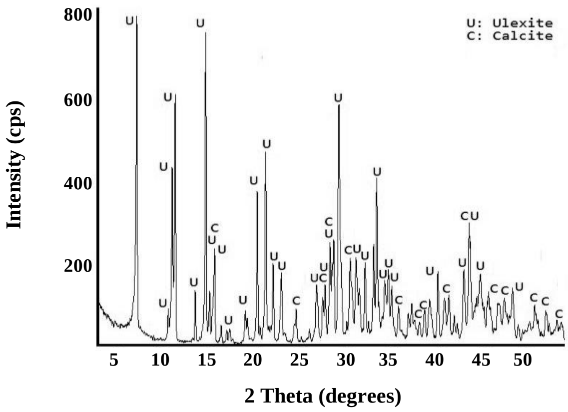

Fig. 1: X-ray powder diffraction pattern of ulexite ore.

Uncontrollable factors may be very hard or very costly to control. Sometimes it is practically impossible to alter these factors. It is possible to minimize the undesired effects of uncontrollable factors with Taguchi method. This could be achieved by comparing different levels of controllable factors on the system. Signal/noise ratio (mean/variance) is proposed in Taguchi Method in order to gather meaningful information about effects of parameters on the system [63]. Signal refers to the desired output while noise refers to the undesired outputs [64, 65].

Using Signal/Noise (S/N) ratios, "main effects plots" could be obtained. Main effects plots could be used to show variation at the output caused by the controllable inputs. If the slope of the plot is very low or almost horizontal it could be interpreted as a parameter has little or no effect on the output. On the contrary if the slope of the plot is very high or almost vertical then it could be said that parameter is highly effective on the input [66]. Hypothesis tests could be used to strengthen the findings from the main effect plots. The proposed Taguchi orthogonal arrays based methodology was given in Fig. 2.

Experimental runs were repeated at least two times according to the orthogonal experimental plan. The experimental plan used in this study L_{16} (4^5) were given in Table 2. Main effects plots were prepared with Minitab for impurity ion concentrations (iron, magnesium, calcium and sulfate ion concentrations in the solution). These plots were used for analyzing the effects of leaching parameters on impurity concentrations. It was aimed to keep the leaching rate (B_2O_3 amount in the solution/B_2O_3 amount in the ulexite ore) high (> 95%) in order to evaluate impurity ion concentrations more clearly.

Parameters

Solid/liquid ratio, temperature, pH, particle size and time after reaching the set pH were the parameters that are investigated in this study. Parameters and parameter levels were shown in Table 3. Gas flow controller for sulfur dioxide feeding in reactor enabled precise pH control and high leaching rate.

Experimental Procedure

Ulexite ore was leached with pure water with sulphur dioxde in a well stirred glass reactor. A common industrial gas, sulfur dioxide [67-69] was used for regulating the acidity in the liquid phase. Sulfur dioxide was acquired from Linde Gas and had 99.99% purity. Leaching water was purified with Merck Millipore Milli-Q Elix Essential. The reactor was heated with Polyscience water circulator. Temperature and pH inside the reactor were measured with Adwa AD4000 multimeter. Sulfur dioxide was directly fed into the liquid phase. Gas flow was manually controlled with Aalborg GFM mass flow controller to maintain desired pH. The gas flow rate was set to the 1000mL/min until the desired pH was reached. Using gas flow controller enabled precise pH control and high leaching rate. When reaction time ended, gas flow was cut. Leaching parameters were selected as solid/liquid ratio, temperature, pH, particle size of granulated the ore, time (after reaching the set pH) according to the previous studies [44]. After the leaching

Table 2: L_{16} orthogonal experimental plan.

Exp. Run No.	Solid/Liquid g/500 g	Temp (°C)	pH	Particle Size (µm)	Time (minute)
1	100	60	5.2	-45	0
2	100	70	5.6	-75	30
3	100	80	6.0	-150	60
4	100	90	6.4	-250	90
5	165	60	5.6	-150	90
6	165	70	5.2	-250	60
7	165	80	6.4	-45	30
8	165	90	6.0	-75	0
9	250	60	6.0	-250	30
10	250	70	6.4	-150	0
11	250	80	5.2	-75	90
12	250	90	5.6	-45	60
13	300	60	6.4	-75	60
14	300	70	6.0	-45	90
15	300	80	5.6	-250	0
16	300	90	5.2	-150	30

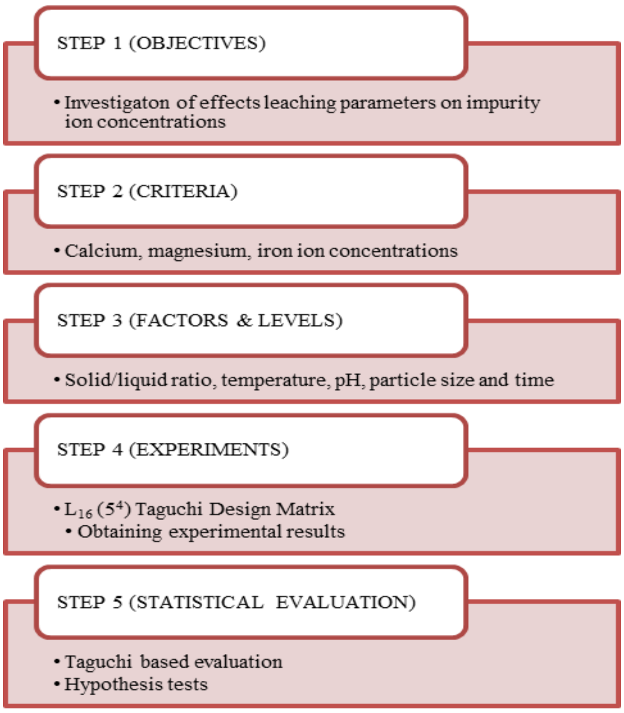

Fig. 2: Proposed Methodology [62].

Table 3: Parameters and parameter levels.

Parameters	Parameter levels			
Solid/liquid ratio, (g/500 g)	100	165	250	300
Temperature, (^{o}C)	60	70	80	90
pH	5.2	5.6	6.0	6.4
Particle Size, (µm)	-45	-75	-150	-250
Time, (minute)	0	30	60	90

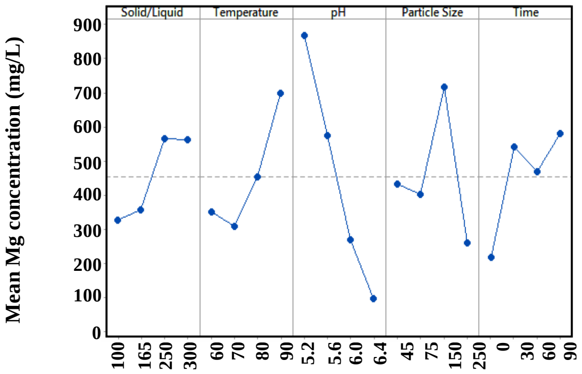

Fig. 2: Main effects plot for mean magnesium ion concentrations.

process, liquid, and solid phases were separated with a vacuum filtration apparatus. Samples were taken from liquid phase and analysed with Thermo X-Series Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to measure calcium, magnesium, iron ion concentrations. Taguchi orthogonal arrays (L_{16} 4^5) were used for experimental runs, Taguchi method and hypothesis tests were used to determine effective leaching factors on impurity concentrations. The leaching rate of ulexite was calculated from boron oxide (B_2O_3) analysis.

RESULTS AND DISCUSSION

It was observed that the average B_2O_3 leaching ratio was 98.56 % (±0.95). Impurity ion concentrations at the liquid phase were given in Table 4.

Statistical analysis of the results

S/N ratios were calculated and with these ratios, main effects plots were prepared for each impurity type with Minitab statistical software. These plots were used to analyze the effect of parameters. The difference between the minimum and maximum concentration values (delta value) was calculated and used to rank effectiveness of the parameters.

P-values were calculated and hypothesis tests were conducted for each impurity type to evaluate the statistical significance of the parameters. H_0 was marked as null hypothesis. The null hypothesis set as "change at the parameter level does not differentiate the response". H_1 was marked as alternative hypothesis and set as "change at the parameter level differentiate the response". If the calculated p-value is bigger than 0.05 at 95 % confidence interval, H_0 was accepted and the parameter was considered as statistically not effective. Similarly, if the calculated p-value was smaller than 0.05 at 95 % confidence interval, H_1 was accepted and the parameter was considered as statistically effective.

Effects of leaching parameters on magnesium ion concentrations

The main effects plot for magnesium ion concentrations were given in Fig. 2.

According to the plot, magnesium concentrations were affected antagonistically with pH and it was effected synergistically with solid/liquid ratio, temperature and time. The effect of particle size cannot be regarded as antagonistical or synergistical.

Delta values (the difference between the minimum and maximum values in the column) for solid/liquid ratio, temperature, pH, particle size and time were found as 238, 389, 770, 456, 364 ppm respectively. Effectiveness of the parameters on magnesium concentrations could be ranked as 1. pH, 2. particle size, 3. temperature, 4. time, 5. solid/liquid ratio based on delta values. It was obviously observed on the plot that pH was more effective on concentrations of magnesium than other parameters. Formation of Mg^{2+} ions from clay minerals could be represented with following reactions:

Table 4: Impurity concentrations.

Exp. No.	Magnesium ion concentrations (ppm)	Calcium ion concentrations (ppm)	Iron ion concentrations (ppb)
1	386.43	71.92	235
2	344.27	54.09	109
3	426.20	34.68	66
4	152.61	69.93	222
5	768.82	45.95	78
6	450.72	69.64	366
7	72.91	145.93	231
8	131.84	131.18	177
9	177.32	1017.09	174
10	94.06	394.18	556
11	1060.26	78.81	97
12	932.63	231.21	285
13	71.78	231.84	323
14	344.74	405.95	555
15	257.88	398.21	142
16	1574.31	73.84	120

$$SO_{2(g)} \leftrightarrow SO_{2(aq)} \quad (1)$$

$$SO_{2(aq)} + 2H_2O \leftrightarrow HSO^{-}_{3(aq)} + H_3O^{+}_{(aq)} \quad (2)$$

$$HSO^{-}_{3(aq)} + H_2O \leftrightarrow SO^{2-}_{3(aq)} + H_3O^{+}_{(aq)} \quad (3)$$

$$MgCO_{3(s)} + SO^{2-}_{3(aq)} + 2H_3O^{+}_{(aq)} \rightarrow MgSO_{3(aq)} + CO_{2(g)} + 3H_2O \quad (4)$$

$$MgSO_{3(aq)} \leftrightarrow Mg^{2+}_{(aq)} + SO^{2-}_{3(aq)} \quad (5)$$

Decreasing in Mg^{2+} concentration is expected because acidic activity decreases with at the higher pH levels

P-values for solid/liquid ratio, temperature, pH, particle size and time were found as 0.127, 0.063, 0.001, 0.515, 0.102 respectively. P-values of solid/liquid ratio, temperature, particle size and time were higher than 0.05 and these parameters were not found statistically effective at 95 % confidence interval. The only pH was found statistically effective on magnesium concentrations at 95% confidence interval.

P-value of temperature was slightly above 0.05 so it could not be considered effective at 95 % though it could be considered effective at 93.7 % and 90% confidence intervals.

Effects of leaching parameters on calcium ion concentrations

Main effects plot for calcium ion concentrations were given in Fig. 3.

According to the plot, calcium ion concentrations were affected by antagonistically with temperature and time. The antagonistical effect of temperature seems linear within the range. The effects of particle size and time cannot be considered be regarded as antagonistical nor synergistical.

Delta values (the difference between the minimum and maximum values in the column) for solid/liquid ratio, temperature, pH, particle size and time was found as 372,

Table 5: Effectve and ineffective parameters at 95% confidence interval.

Leaching parameters	Magnesium ion concentrations (ppm)	Calcium ion concentrations (ppm)	Iron ion concentrations (ppb)
Solid/liquid ratio, g/500 g	I	E	I
Temperature, °C	I	I	I
pH	E	I	I
Particle Size, μm	I	I	I
Time, min.	I	I	I

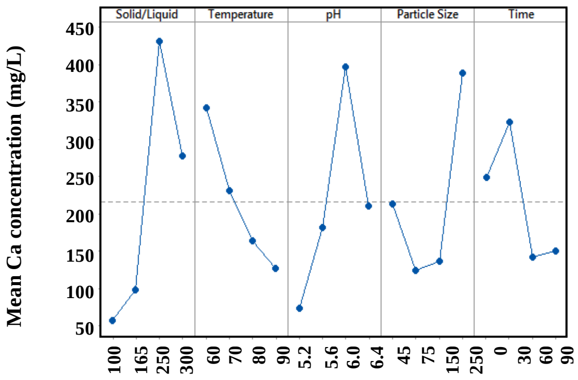

Fig. 3: Main effects plot for mean calcium ion concentrations.

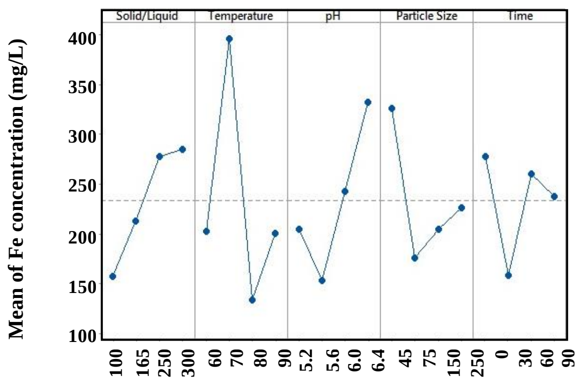

Fig. 4: Main effects plot for mean iron ion concentrations.

215, 328, 264, 180 ppm respectively. Effectiveness of parameters on calcium ion concentrations could be ranked as 1. solid/liquid ratio, 2. pH, 3. particle size, 4. temperature, 5. time based on delta values. P-values for solid/liquid ratio, temperature, pH, particle size and time were found as 0.037, 0.141, 0.190, 0.153, 0.309 respectively. P-values of temperature, particle size and time were higher than 0.05 and these parameters are considered statistically not effective at 95% confidence interval. Only the solid/liquid ratio was found statistically effective on calcium ion concentrations at 95 % confidence interval. When Fig. 3 were examined, it could be seen that Ca^{2+} concentration increases with the first three values of solid/liquid ratio, but it decreases with the last value of the solid/liquid ratio. In the experiments, the dissolutions are almost complete (over 95%). This decrease in the Ca^{2+} concentration with the highest solid/liquid ratio could be explained by the increase in the ratio of B_2O_3 passing to the solution. When the concentration of boric acid in the solution approaches to the saturation point, boric acid crystals could be formed, they could cover the undissolved clay particles and thus they could significantly limit the leaching.

Effects of leaching parameters on iron ion concentrations

The main effects plot for iron ion concentrations were given in Fig. 4.

According to the plot, iron ion concentrations were affected antagonistically with solid/liquid ratio and pH. Effects of temperature, particle size and time could not be considered to be regarded as antagonistical nor synergistical.

Delta values (the difference between the minimum and maximum values in the column) for solid/liquid ratio, temperature, pH, particle size and time were found as 127.0, 262.5, 179.5, 150.0, 118.8 respectively. Effectiveness of parameters on iron ion concentrations could be ranked as 1. temperature, 2. pH, 3. particle size, 4. solid/liquid ratio, 5. time based on delta values.

P-values for solid/liquid ratio, temperature, pH, particle size and time were found as 0221, 0.460, 0.203, 0.625, 0.961 respectively. P-values of all the parameters were found higher than 0.05 and these parameters were considered statistically not effective at 95% confidence interval. As a result leaching parameters are not effective on iron concentrations. This is an expected result since pH is not low enough to increase iron concentrations. Also, it should be noted that all of the iron concentrations at ppb level.

CONCLUSIONS

In this study, the Taguchi experimental design approach and statistical methods were used to investigate the effects of leaching factors on impurity ion concentrations. Although there are many studies in boron ore leaching with the intent of limiting unwanted impurity concentrations, there is only one prior study that investigates impurity ion concentrations in boron ore leaching. *Bulutcu et. al.* [20] investigated the replacement of sulfuric acid with propionic acid in colemanite leaching in order to limit magnesium ion concentrations. They determined that Mg^{2+} ion concentration in the solution decreases with increasing propionic acid concentration in the mixture. This is expected due to lower high strength of propionic acid compared to the sulphuric acid. Also the results were not evaluated by statistical methods.

In this study, a methodological approach was applied to ulexite leaching process to analyze unwanted impurity concentrations at the leachate and it is found that leaching parameters could be effective on impurity concentrations at the liquid phase. This may be an important finding for leaching process since it may be possible to decrease unwanted impurity concentrations with altering leaching parameters.

It is thought that preferred methodology is convenient for the purpose and this approach could be used for other borate minerals and leaching processes.

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