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OPTIMIZATION OF DOLOMITE ORE LEACHING IN HYDROCHLORIC ACID SOLUTIONS

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In this study, the Taguchi method was used to determine the optimum conditions for leaching of dolomite ore in hydrochloric acid solutions. The experimental parameters were leaching temperature, solid-to-liquid ratio, acid initial concentration, leaching time and stirring speed. The following optimum leaching parameter levels were found: temperature 50°C, solid-to-liquid ratio 2%, acid concentration 20 g/cm^3 (2 mol/dm^3), stirring speed 450 rpm, leaching time 5 min. Under the optimum process conditions, the dolomite ore leaching efficiency was about 83%.

keywords: optimization, dolomite ore, hydrochloric acid, leaching, Taguchi method

1. INTRODUCTION

Dolomite ($CaCO_3 \cdot MgCO_3$, carbonate of calcium and magnesium) is different from limestone and contains minimum 45% of $MgCO_3$. Dolomite occurs either as coarse, granular mass or in fine-grained compact form. The crystal structure of dolomite is hexagonal-rhombohedral. Dolomite is naturally white, but may, due to impurities to be creamy gray, pink, green or black (Brady et al., 1997).

Dolomite leaching has been rarely studied in the past. However, the determination of optimum conditions for leaching of dolomite in hydrochloric acid has not been studied yet. Lund et al. (1977) carried out a work on leaching of dolomite in hydrochloric acid. They reported that at 25°C the dissolution process is surface

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reaction rate limited. As the temperature is increased to 100°C, the dissolution process approaches diffusion limitation even at relatively high (500 min^{-1}) stirring speeds. The rate of reaction was found to be proportional to a temperature dependent fractional power on the hydrochloric acid concentration. Herman and White (1985) investigated leaching of dolomite in CO_2-undersaturated water. They reported that at lower temperatures the rate was lower and grain size effects were insignificant. Chou et al. (1989) investigated the dissolution of various carbonates (including calcite, magnesite and dolomite) in HCl solutions at 25°C using a continuous fluidized bed reactor and samples of relatively course particle size. Busenberg and Plummer (1989) carried out a work on the leaching of dolomite in CO_2-undersaturated water. Abali et al. (1992) reported that the activation energy for dissolution kinetics of magnesite in water saturated by SO_2 gas was 81 kJ/mol and the reaction was controlled by the surface chemical reaction. Ozbek et al. (1990) investigated the dissolution kinetics of magnesite with Cl_2 gas in water. They found that the reaction diffusion was controlled through the fluid layer. Gautlier et al. (1999) carried out a work on influence of pH on the rate of dissolution of dolomite. They reported that the rate increases from 0.63 at 25°C to 0.80 at 80°C. Harris et al. (1988) studied the production of magnesium from concentrated magnesium chloride solutions. Also, Abali et al. (2006) investigated the optimum conditions for dissolution of magnesite with H_2SO_4 solutions. They reported that the optimum conditions were found to be 65°C, 5/100 g/cm^3, 2M, 60 min and 300 rpm. Optimization for the dissolution of ores in different acidic media has been investigated by a great number of authors (Abali et al., 1997; Demirbas et al., 1999; Copur et al., 2004; Demir et al., 2003; Ata et al., 2001; Yartasi et al., 1999).

The aim of this study was to investigate the optimization of dolomite leaching in hydrochloric acid solutions. The Taguchi method was used to determine the optimum conditions. An experimental plan was used based on parameters and their levels to determine the leaching rate of dolomite in HCl solutions. *F* test was carried out to the leaching results to determine the most effective and the least effective parameters. Each of the parameter of signal-noise graphics was drawn to determine the optimum conditions. The maximum leaching performance of dolomite was predicted by calculation of the optimum conditions.

2. THEORY OF THE TAGUCHI METHOD

The use of a quantitive design in the Taguchi method in order to optimize a process with multiple performance characteristics includes the following steps: (a) identification of the performance characteristics and selection of process factors to be evaluated; (b) determination of the number of quantity levels for the process and possible interaction between the process parameters; (c) selection of the appropriate orthogonal array and assignment of process factors to the orthogonal array; (d) conduction of the experiments based on the arrangement of the orthogonal array; (e) calculation of the performance characteristics; (f) analyzing the experimental result using the performance characteristic and ANOVA; (h) selection of the optimal levels of process factors; and (i) verifying the optimal process factors through the confirmation experiment (Copur et al., 1997; Phadke, 1989).

The orthogonal array (OA) experimental design was chosen as the most suitable method to determine experimental plan, L_{25} (5^5), five parameters, each of five values (Phadke, 1989). In order to observe the effects of noise sources on the leaching process, each experiment was repeated twice under the same conditions at different times. The performance characteristics were chosen as the optimization criteria. There are three categories of performance characteristics, the larger-the-better, the smaller-the-better and the nominal-the-better. The performance statistics was evaluated using Eq. (1) (Phadke 1989; Pignatiello, 1988):

$$SN = -10\log\left(\frac{1}{n}\Sigma\frac{1}{Y_i^2}\right), \tag{1}$$

where larger-the-better *SN* is performance characteristics, *n* number of repetition done for an experimental combination, and Y_i performance value of i^{th} experiment.

In the Taguchi method the experiment corresponding to optimum working conditions might not been done during the whole period of the experimental stage. In such cases the performance value corresponding to optimum working conditions can be predicted by utilizing the balanced characteristic of OA. For this the following additive model may be used (Phadke et al., 1983):

$$Y_i = \mu + \sum X_i + \varepsilon_i \tag{2}$$

where μ is the overall mean of performance value, X_i the fixed effect of the quantity level combination used in i^{th} experiment, and ε_i the random error in i^{th} experiment. Because Eq. (2) is a point estimation, which is calculated using experimental data in order to determine whether results of the confirmation experiments are meaningful or not, the confidence interval must be evaluated. The confidence interval at chosen error level may be calculated by (Taguchi, 1987):

$$Y_i \pm \sqrt{F\alpha;1,\ dfMSe\ MSe\left(\frac{1+m}{N}+\frac{1}{n_i}\right)} \tag{3}$$

where F is the value of F table, α the error level, *dfMSe* the degrees of freedom of mean square error, m the degrees of freedom used in the prediction of Y_i, N the number of total experiments, and n_i the number of repetitions in the confirmation experiment.

If experimental data are in percent (%), before evaluating Eq. (2), transformation of percent values should be applied first, using Eq. (3) due to which values of interest are later determined by carrying out reverse transformation using the same Eq. (4) (Taguchi, 1987):

$$\Omega_i = -10 \cdot \log\left(\frac{P_i}{1 - P_i}\right) \quad (4)$$

where *Ω* is the value of percentage value subject to omega transformation and the percentage of the product obtained experimentally.

3. MATERIALS AND METHODS

The dolomite ore used in the present experiments was obtained from Kutahya Fertilizer Plant Co., Kutahya, Turkey. The dolomite ore was initially crushed with a jaw crusher. The sample was then sieved using –200 +160 µm ASTM Standard sieves. The chemical composition of the dolomite ore was determined by volumetric and gravimetric methods (Scott, 1963) and the results are given in Table 1.

Table 1. The chemical composition of dolomite ore

Component	wt %
MgO	16.93
CaO	23.68
Fe_2O_3	2.80
SiO_2	16.80
Al_2O_3	2.79
Ignition Loss	36.89

The leaching experiments were carried out in a 250 cm^3 glass reactor equipped with a mechanical stirrer having a digital controller unit and timer, thermostat and cooler. The temperature of the reaction medium could be controlled within ±0.5 °C. In the leaching process, 100 cm^3 HCl of known concentration was introduced into the reactor. After the desired leaching temperature was reached, a predetermined amount of the sample was added into the solution while the content of the vessel was stirred at a certain speed. At the end of the experiment, the content of the vessel was filtered by a filter paper of Filtrak 391 and the filtrate solution was analyzed volumetrically for Ca + Mg. The leaching ratio (in percent) *Y* was calculated from:

$$Y = \frac{M_1}{M_o} \cdot 100, \quad (5)$$

M_1 is the percent of Ca+Mg in the solution, M_o is the percent of Ca+Mg in the original sample.

A robust design method is developed for reducing cost and improving leaching dolomite ore in HCl. In the experiments, an L_{25} orthogonal array is employed to determine the effect of five process parameters on the dolomite ore leaching rate. For each factor, five levels are chosen to cover the wide region of variation.

Table 2. Parameters and their values corresponding to their levels

	Parameters	Parameter levels				
		1	2	3	4	5
A	Leaching temperature, °C	20	32	50	65	74
B	Solid-to-liquid ratio, %	0.5	1	2	5	10
C	Acid concentration, mol/dm^3	0.2	0.5	1	2	5
D	Stirring rate, min^{-1}	50	300	450	600	750
E	Leaching time, minutes	5	10	20	30	45

In this study the following parameters were selected: leaching temperature, solid-to-liquid ratio, acid initially concentration, stirring speed and leaching time. These parameters can potentially affect leaching rate of dolomite ore in HCl. Experimental factors and their levels, determined in the preliminary tests, are given in Table 2.

Since five parameters were investigated in the research, five levels of each parameter were considered. Therefore, a L_{25} orthogonal array (L_{25} 5^5) was selected for this study. The total of 25x5=125 data values were collected, which were conducted for analysis in this study.

4. RESULT AND DISCUSSION

To determine the optimum conditions for leaching of dolomite ore in hydrochloric acid solutions were investigated. The leaching reaction of dolomite ore in hydrochloric acid solutions can be described by the following equation:

$$CaCO_3 \cdot MgCO_{3(s)} + 4HCl_{(aq)} \rightarrow CaCl_{2(aq)} + MgCl_{2(aq)} + 2CO_{2(g)} + 2H_2O_{(l)}\ . \qquad (6)$$

In this study, a L_{25} orthogonal array with five columns and 25 rows was used. Each leaching parameter was assigned to a column, 25 leaching-parameter combinations being available. Therefore, only 25 experiments were required to study the entire parameter space using the L_{25} orthogonal array. The experimental layout for the five leaching parameters using the L_{25} orthogonal array is shown in Table 3.

F factors were calculated and given in Table 4. As seen from Table 4, acid concentration parameters were significant for dolomite ore leaching rate. *F* test is a tool to see which process parameters have a significant effect on the leaching. The *F*-value for each process parameters is simply a ratio of mean of the squared deviations to mean of the squared error. Usually, the larger the *F*-value, the greater effect of process parameter on leaching. With the leaching rate characteristics and ANOVA analyses, the optimum combination of process parameters can be predicted.

Table 3. Chosen $L_{25}(5^5)$ experimental plan

Experiment number	Parameters and levels					Exp. 1	Exp. 2
	A	B	C	D	E	Y_1	Y_2
1	1	1	1	1	1	22.75	27.36
2	1	2	2	2	2	45.25	43.64
3	1	3	3	3	3	66.33	70.69
4	1	4	4	4	4	80.31	74.63
5	1	5	5	5	5	85.23	78.52
6	2	1	2	4	3	85.65	86.29
7	2	2	3	5	4	84.43	70.76
8	2	3	4	1	5	90.83	83.51
9	2	4	5	2	1	77.43	69.07
10	2	5	1	3	2	07.64	08.52
11	3	1	3	2	5	88.41	98.85
12	3	2	4	3	1	89.85	75.76
13	3	3	5	4	2	86.13	76.82
14	3	4	1	5	3	15.98	17.01
15	3	5	2	1	4	20.08	17.17
16	4	1	4	5	2	84.29	78.48
17	4	2	5	1	3	87.86	96.74
18	4	3	1	2	4	31.24	27.06
19	4	4	2	3	5	41.59	34.87
20	4	5	3	4	1	42.39	41.76
21	5	1	5	3	4	77.93	79.10
22	5	2	1	4	5	78.34	85.98
23	5	3	2	5	1	81.29	70.49
24	5	4	3	1	2	85.45	71.96
25	5	5	4	2	3	69.70	72.98

To obtain optimum leaching rate, the-higher-the-better leaching rate characteristic shown in Eq. (1) has been used for leaching of Ca+Mg. The *SN* for the-larger-the-better for leaching rate were calculated. The level, which has a higher value, determines the maximum level of each factor. For example, level five for temperature has the highest *SN* value (Fig. 1).

Increasing the temperature up to 65°C does not influence the rate of dissolution. However, a rapid increase in the rate of leaching was observed between 65 and 74°C.

The effect of solid-to-liquid ratio on the performance statistics for dolomite ore is given in Figure 2. The dissolution rate increases with decreasing the solid-to-liquid ratio. As seen in Figure 3, the leaching rate rapidly increases as acid concentration increases up to 3.0 mol/dm^3 and then leaching rate slowly increases as acid concentration increases from 3.0 to 5.0 mol/dm^3. The leaching rate has not changed with the stirring speed up to 450 min^{-1}. Further on the leaching rate increases (Fig. 4). From 5 up to 30 minutes leaching time, no significant change in the leaching rate is observed. However from 45 minutes, leaching rate increased, as can be seen in Fig. 5.

Consequently, the maximum leaching conditions were determined as A_5, B_2, C_5, D_4 and E_5. Then, the maximum leaching parameter levels will be temperature: 74°C, solid-to-liquid ratio: 1.0 %, acid concentration: 5 mol/dm^3, stirring speed: 600 min^{-1}, leaching time: 45 min on leaching process. The predicted leaching rate using maximum *SN* conditions can be calculated by Eq. (3).

The selection of optimum leaching conditions for Ca+Mg production is done according to the conditions of maximum amount with minimum cost, as given in Table 5. The optimum process conditions were selected as A_2, B_3, C_4, D_4 and E_3. As a result, the optimum leaching parameter levels will be temperature: 32°C, solid-to-liquid ratio: 2 %, acid concentration: 20 g/dm^3, stirring speed: 600 min^{-1}, leaching time: 20 minutes. The predicted leaching rate using optimum *SN* conditions were also calculated by equation (3).

Table 4. The results of variance analysis (ANOVA)

	Parameters	Degree of freedom	Sum of Squares	Mean Squares	Test Statistic, F
A	Temperature	4	1433.825	358.456	1.290
B	Solid-to-liquid ratio	4	3374.577	843.644	3.035
C	Acid concentration	4	8845.756	2211.439	7.957
D	Stirring speed	4	979.757	244.939	1.220
E	Leaching time	4	1356.249	339.062	0.881
	Error	4	1111.734	277.934	
	Total	24	17101.898		

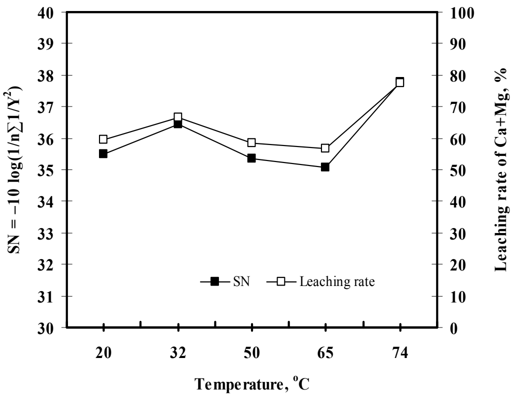

Fig. 1. The effect of leaching temperature on the performance statistics for dolomite ore

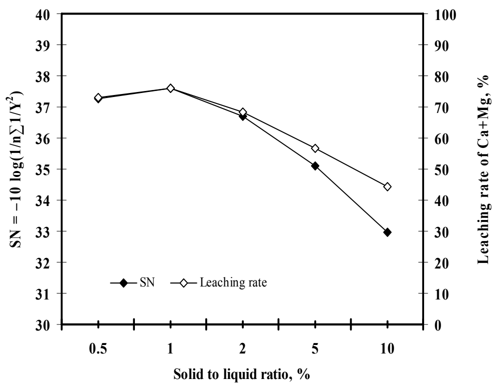

Fig. 2. The effect of solid-to-liquid ratio on the performance statistics for dolomite ore

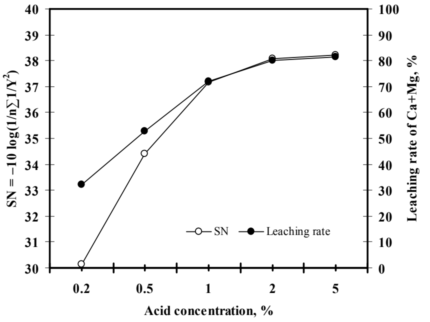

Fig. 3. The effect of acid concentration on the performance statistics for dolomite ore

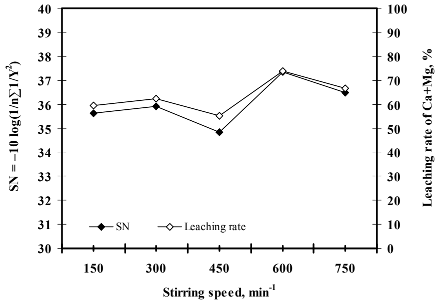

Fig. 4. The effect of stirring speed on the performance statistics for dolomite ore

Table 5. Chosen $L_{25}(5^5)$ experimental plan

	Parameters	Parameters level	Performance statistic, *SN*	Cost	Maximum *SN*	Optimum *SN*
		20	35.49	Min.		
A	Leaching temperature, °C	32	36.45	↓		
		50	35.36		A_5	A_2
		65	35.06			
		74	37.77	Max.		
		0.5	37.26	Min.		
B	Solid-to-liquid ratio, %	1	37.60	↑		
		2	36.71		B_2	B_3
		5	35.09			
		10	32.95	Max.		
		0.2	30.15	Min.		
C	Acid concentration, mol/dm^3	0.5	34.42	↓		
		1.0	37.16		C_5	C_4
		2.0	38.07			
		5.0	38.22	Max.		
		150	35.62	Min.		
D	Stirring speed, min^{-1}	300	35.90	↓		
		450	34.84		D_4	D_4
		600	37.36			
		750	36.48	Max.		
		5	35.54	Min.		
E	Leaching time, min	10	35.39	↓		
		20	36.51		E_5	E_3
		30	35.01			
		45	37.69	Max.		

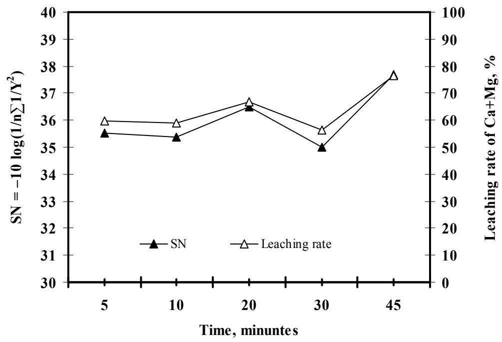

Fig. 5. The effect of dissolution time on the performance statistics for dolomite ore

3. CONCLUSION

In this study, the optimum conditions for leaching of dolomite ore in hydrochloric acid solutions were determined by the Taguchi method. The leaching rate increases with decreasing solid-to-liquid ratio and increasing acid concentration. The most significant parameter affecting leaching of dolomite ore is acid concentration.

Optimum reaction conditions were determined as 32°C leaching temperature, 2% for solid-to-liquid ratio, 20 g/dm^3 for acid concentration, 600 rpm for stirring speed and 20 minutes for leaching time. Under these optimum process conditions, the dolomite ore leaching rate in HCl solution was about 83%.

The findings of the present study may be very useful for leaching on the industrial scale since the optimum conditions determined by the Taguchi method in laboratory environment is reproducible in real production environments as well. Leaching reaction products were found to be calcium chloride and magnesium chloride.

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Wykorzystano metodę Taguchi do określenia optymalnych warunków ługowania rudy dolomitowej w roztworach kwasu solnego. Badano takie parametry jak temperatura, stosunek fazy stałej do ciekłej, początkowe stężenie kwasu, czas ługowania i prędkość mieszania. Ustalono, że optymalnymi parametrami są: stosunek fazy stałej do ciekłej 2%, początkowe stężenie kwasu 20 g/cm^3 (2 mol/dm^3), prędkość mieszania 450 rpm, czas ługowania 5 min. W tych warunkach wyługowanie dolomitu było około 83%

słowa kluczowe: optymalizacja , ruda dolomitowa, kwas solny, ługowanie, metoda Taguchi