

Leaching Optimization of Sarcheshmeh Copper Concentrate by Application of Taguchi Experimental Design Method

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ABSTRACT: Taguchi Method is used as a statistical approach to optimize the process parameters and improve the quality of components that are produced. The present study aimed to illustrate the leaching optimization of Sarcheshmeh copper concentrate using Taguchi's experimental design. Various operating parameters such as acid concentration (C_A), temperature (T), solid percentage (%S), O_2 flow rate (O_2), extra oxidizing agent (OxA), NaCl concentration (C_{NaCl}), and contact time (t), each at three levels, were selected and their effect on the copper extraction ($R\%$) was analyzed. L_{27} Orthogonal Array (OA) was employed as the experimental design and the results were analyzed using analysis of variance (ANOVA) and analysis of mean (ANOM). The experiment results indicated that (T) variable was the most significant parameter with 81% contribution to the response. It is also observed that the interactions between (C_A and OxA), (C_A and C_{NaCl}) had no significant effect on the copper dissolution process. Furthermore, (T), (%S), (O_2), (C_{NaCl}) and (t) parameters were found to be statistically significant at 95% confidence level for the desired response. The study showed that Taguchi's method was suitable to optimize the experiments for increasing leaching efficiency.

KEYWORDS: Sarcheshmeh copper complex; Leaching; Chalcopyrite; Taguchi.

INTRODUCTION

Sarcheshmeh Copper Mine is considered as one of the largest complexes of mining industry in the world and is a major copper producer in Iran. The archeological reserve of this mine is over 1,200 billion tons of sulfide ore with an average grade of 0.7% [1]. Chalcopyrite is the most common and important sulfide ore which is extracted from this mine. This mineral is concentrated by the froth

flotation and processed by pyrometallurgical techniques including smelting and converting [1].

However, in recent years, there has been an interest in hydrometallurgical processes due to their unique environmental features, lower energy demands and less emission of gases such as SO_2 [2-4]. Therefore, much effort has been directed toward the development of copper

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extraction by using hydrometallurgical techniques including various leach agents and oxidants like oxygen, ferric sulfate, ferric chloride, cupric chloride and etc [3, 5, 6]. Unfortunately, these methods have not had much success due to very slow reaction kinetics, as well as, economic and technical reasons. Thus, studies have been conducted to increase the reaction rate and, several techniques have been used to increase the reactivity of chalcopyrite, such as, organic extracting addition, sulfidic activation, mechanical activation, the use of ozone as an oxidant, temperature change and the use of promoters (silver ions, surfactants, carbon particles, iron powder or hematite) [7, 8].

In a study, investigating the effect of Fe^{2+} and temperature on chalcopyrite leaching rate showed that the copper dissolution in sulfate media reached 94% after 11 days when the temperature was 60°C and pH value adjusted on 0.7. However, when 1.8g/l Fe^{2+} was added, the copper extraction reached 93% after 5 days in the same pH [9]. In another research, the effects of reagent (Cl^- , Fe^{3+} and Cu^{2+}) concentrations and temperature (70°C to 90°C) on the copper leaching were determined. The results showed that chalcopyrite leaching was faster with Cu^{2+} than Fe^{3+} . Moreover, copper dissolution was also higher (50%) with Cu^{2+} in 90°C [10]. The effects of some variables such as temperature, solids content, initial acid concentration, iron concentration, redox potential and pyrite on copper extraction of sulfide minerals were studied in the same research. A copper recovery of higher than 80% in 24 h was achieved at 85°C temperature, a solid percentage of 7.8% (w/v), an initial acid concentration of 15 g/L, 5 g/L of iron concentration, redox potential of 410 mV vs Ag, AgCl and pyrite to copper sulfide minerals mass ratio 2:1 [11].

Furthermore, in another research, experimental results on the chalcopyrite concentrate leaching in H_2SO_4 -NaCl solutions and in presence of oxygen at ambient pressure were investigated by taking into account the evolution of the solution redox potential and the concentration of ferric ions during leaching. Results indicated that concentrate leaching in sulfate-chloride solutions were rapid. Over 90% copper was dissolved at 100°C in 180 min. The results also showed that, in comparison to leaching without chloride, chloride ions (0.5 M) had a significant effect on leaching rate. Addition of 3 g/L of Fe^{3+} ions to the leaching solution caused

an increase in the solution potential which decreased the leaching rate of chalcopyrite. However the concentrate leaching in H_2SO_4 -NaCl O_2 media depends largely on the temperature [12].

As mentioned in above, although the effect of some controlling parameters like acid concentration (C_A), temperature (T), solid percentage (%S), extra oxidizing agent (OxA), NaCl concentration (C_{NaCl}) and contact time (t) are investigated [3, 12-14], but there is no systematic study on these parameters and their effects on copper extraction. This paper uses Taguchi's experimental design method to screen significant factors which would have a considerable effect on the multi-component leaching efficiency of the chalcopyrite concentrate of Sarcheshmeh Copper Complex. In other words, leaching efficiency of copper concentrate (R%) is investigated by optimizing various parameters. The effects of these individual parameters and their interactions on R% will be examined by employing the standard procedure suggested by the Taguchi design.

EXPERIMENTAL SECTION

Preparation of Sample

High-grade sulfide concentrate of Sarcheshmeh copper complex was considered as raw material in the experiments. The samples of concentrate were sieved into $d_{80} < 45$ micron. The chemical and mineralogical analysis are presented in Table 1.

All chemicals used in this study were purchased from Merck® and were in laboratory grade. The conventional acid leaching experiments were carried out in a 2L double chambered glass reactor which was equipped with a condenser and was set at the desired temperature by circulating hot water in the outer chamber. So, 1L of a mixed solution with a designed H_2SO_4 concentration containing 0.2M extra oxidizing agent and designed NaCl concentration were prepared and then injected using O_2 gas with a specified flow rate. Then the temperature of the solutions was adjusted at the preferred value designed by Taguchi method. Afterward, the sample was added into the solution to adjust the determined solid percentage. The pulp was stirred for defined hours at 300 rpm, and Sampling was performed at the end of the leaching operation to determine the copper concentration. The condition of all operating parameters are mentioned in next section.

Table 1: Chemical and mineralogical analysis of samples.

Chemical analysis		Mineralogical analysis	
Element	%	Mineral	%
S	36.64	CuFeS ₂	60
Fe	31.22	FeS ₂	17
Cu	20.93	Cu ₂ S	2.5
SiO ₂	4.99	CuS	1.9
Zn	0.72	Fe ₂ O ₃	1.9
K ₂ O	0.38	Fe ₃ O ₄	0.94
MgO	0.23	ZnS	0.76
TiO ₂	0.20	MoS ₂	0.13
P ₂ O ₅	0.15	None Metallic mineral	11.9
CaO	0.15		
Other	4.39	Other	2.97

Table 2: Main controlling factors and their levels.

Factors	Levels		
	1	2	3
C _A (M)	0.25	0.5	1
OxA	None	Fe ₂ (SO ₄) ₃	FeCl ₃
O ₂ (l/min)	0	0.5	1
C _{NaCl} (M)	0	1	2
T(°C)	Ambient	60	90
%S	3	5	7
t(h)	5	10	15

Design of experiments

Experiments were conducted according to the Taguchi experimental design. Taguchi approach developed rules which further simplify and standardize experiment design [15, 16]. The permissible range of the input factors and their effect on design output can be determined through complete understanding of the process. In these experiments, as shown in Table 2, seven factors in three levels were chosen as study variables. These include acid concentration (C_A), temperature (T), Solid percentage (%S), O₂ flow rate (O₂), extra oxidizing agent (OxA), NaCl Concentration (C_{NaCl}) and contact time (t).

The Taguchi orthogonal L₂₇(3¹³) array was employed in this study (Table 3). The effect of each controlling factor at a given level can be estimated using analysis of mean (ANOM) and consequently the optimum level of each factor can be determined [17, 18]. A statistical variance

analysis (ANOVA) was performed to determine the effective parameters and their confidence levels. F-test is a powerful tool to determine which parameters have significant effects in a defined condition. For this purpose, the F value of all factors was compared with the F value of the table for α : (risk) = 0.05. If the F value of a factor is greater than the F value α : (risk), then the variance of the factor is significant compared to the variance of error, and this factor has a significant effect on the response. In the next step, a verification test was performed to validate the optimized parameters [18].

Material characterization

A mineralogical analysis was first conducted by Optical microscopy to qualitatively investigate the sulfide, oxide and none metallic minerals at the Central Laboratory of the Sarcheshmeh Copper Complex. X-Ray Fluorescence (XRF)

Table 3: Experimental condition based on Taguchi $L_{27}(3^{13})$ standard orthogonal array.

Run	A	B	C	D	E	F	G	H	I	J	K	L	M
	C_A (M)	OxA	$C_A * OxA$		O_2 (l/min)	$C_A * O_2$		C_{NaCl} (M)	$C_A * C_{NaCl}$		T(°C)	%S	t(h)
1	0.25	None	1	1	0	1	1	0	1	1	Ambient	3	5
2	0.25	None	1	1	0.5	2	2	1	2	2	60	5	10
3	0.25	None	1	1	1	3	3	2	3	3	90	7	15
4	0.25	$Fe_2(SO_4)_3$	2	2	0	1	1	1	2	2	90	7	15
5	0.25	$Fe_2(SO_4)_3$	2	2	0.5	2	2	2	3	3	Ambient	3	5
6	0.25	$Fe_2(SO_4)_3$	2	2	1	3	3	0	1	1	60	5	10
7	0.25	$FeCl_3$	3	3	0	1	1	2	3	3	60	5	10
8	0.25	$FeCl_3$	3	3	0.5	2	2	0	1	1	90	7	15
9	0.25	$FeCl_3$	3	3	1	3	3	1	2	2	Ambient	3	5
10	0.5	None	2	3	0	2	3	0	2	3	Ambient	5	15
11	0.5	None	2	3	0.5	3	1	1	3	1	60	7	5
12	0.5	None	2	3	1	1	2	2	1	2	90	3	10
13	0.5	$Fe_2(SO_4)_3$	3	1	0	2	3	1	3	1	90	3	10
14	0.5	$Fe_2(SO_4)_3$	3	1	0.5	3	1	2	1	2	Ambient	5	15
15	0.5	$Fe_2(SO_4)_3$	3	1	1	1	2	0	2	3	60	7	5
16	0.5	$FeCl_3$	1	2	0	2	3	2	1	2	60	7	5
17	0.5	$FeCl_3$	1	2	0.5	3	1	0	2	3	90	3	10
18	0.5	$FeCl_3$	1	2	1	1	2	1	3	1	Ambient	5	15
19	1	None	3	2	0	3	2	0	3	2	Ambient	7	10
20	1	None	3	2	0.5	1	3	1	1	3	60	3	15
21	1	None	3	2	1	2	1	2	2	1	90	5	5
22	1	$Fe_2(SO_4)_3$	1	3	0	3	2	1	1	3	90	5	5
23	1	$Fe_2(SO_4)_3$	1	3	0.5	1	3	2	2	1	Ambient	7	10
24	1	$Fe_2(SO_4)_3$	1	3	1	2	1	0	3	2	60	3	15
25	1	$FeCl_3$	2	1	0	3	2	2	2	1	60	3	15
26	1	$FeCl_3$	2	1	0.5	1	3	0	3	2	90	5	5
27	1	$FeCl_3$	2	1	1	2	1	1	1	3	Ambient	7	10

and X-Ray Diffraction (XRD) spectroscopy were also used for chemical and mineralogical analysis of the Sarcheshmeh copper concentrate. The XRD and XRF equipment models were Philips Xpert pro X-ray diffraction system and Philips Magix Pro X-ray Fluorescence, respectively. The Inductive Coupled Plasma (ICP) optical emission spectrometry (VARIAN OES) was used to determine leachates Cu^{2+} concentrations.

RESULTS AND DISCUSSION

The results of the matrix experiment, conducted under the conditions in Table 3, are illustrated in Table 4. The copper extraction efficiency ranges from 1.24% to 52.52%.

Table 5 shows the results of variance analysis (ANOVA). In this table, the sum of squares (SS_{Factor}), degrees of freedom (df) and mean of squares

Table 4: Results of leaching efficiency for designed Experiments.

Run	R%	Run	R%	Run	R%
1	1.24	10	1.36	19	1.59
2	28.14	11	18.73	20	28.58
3	43.80	12	52.52	21	35.40
4	34.28	13	44.80	22	24.24
5	13.13	14	10.44	23	11.74
6	17.70	15	14.60	24	19.00
7	16.89	16	19.68	25	22.40
8	32.37	17	40.16	26	36.40
9	10.81	18	13.62	27	11.43

Table 5: Analysis of variance (ANOVA). $F(0.05, 2, 4) = 6.94$

Source	SS _{Factor}	d _f	V _{Factor}	Value-F	p-value
Model	5005.98	26	192.54	32.07	0.002
C _A (M)	36.93	2	18.46	2.62	-
OxA	26.23	2	13.12	2.86	-
C _A *OxA	46.03	4	11.51	1.63	-
O ₂ (l/min)	206.58	2	103.29	14.64	0.0144
C _A * O ₂	65.96	4	16.49	2.33	-
C _{NaCl} (M)	238.61	2	119.3	16.91	0.011
C _A * C _{NaCl}	28.22	4	Error Factor		
T(°C)	4050.88	2	2025.44	287.11	< 0.0001
%S	160.62	2	80.31	11.38	0.022
t(h)	145.92	2	72.96	10.34	0.026
V _{Error}	28.22	4	7.05	-	-
Total	5005.98	26	-	-	-

($V_{\text{Factor}} = SS_{\text{Factor}}/d_f$), were represented respectively. Subsequently, the F-value ($F_{\text{Factor}} = V_{\text{Factor}}/V_{\text{Error}}$), and P-value were calculated.

As illustrated in Table 5, F-value of some factors was greater than the extracted F-value of the table for ($\alpha = 0.05$). It shows that the variance of those factors is significant compared to the variance of error and all of them have a significant effect on the response. The significance of each coefficient was also determined by p-values, which are listed in this table. P-value less than 0.05 indicates that model terms are significant with 95% confidence level.

Finally, the contribution of each factor to the leaching efficiency was determined as presented in Fig. 1. This analysis reveals that the order of factors affecting the leaching efficiency is $T > C_{\text{NaCl}} > O_2 > \%S > t$, respectively.

Fig. 2, shows the effect of each parameter level on the response variable and demonstrates that the best efficiency was obtained when (T) was set at the third, (C_{NaCl}) at the third, (S%) at the first and (t) at the second levels. Briefly, the optimum level of each parameter is shown in Table 6.

Prediction of leaching efficiency at the optimized conditions was the last objective of the Taguchi statistical design and one of the most important goals of this research.

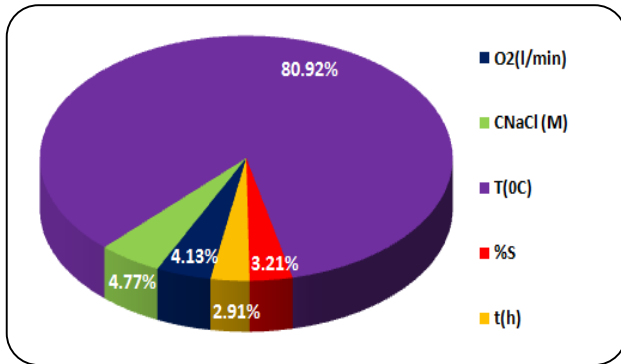


Fig. 1: Contribution of affecting factors to the response.

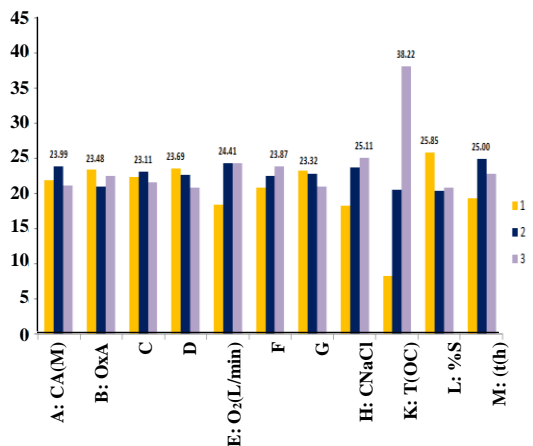


Fig. 2: Effect of each parameter level on the response variable.

By determining the optimized factors and their levels, the maximum leaching efficiency will be predicted by Equations (1) and (2) [19, 20].

$$\bar{Y} = \frac{\sum_{i=1}^n y_i}{n} = 22.40 \quad (1)$$

$$Y_{Opt} = \bar{Y} + (A_2 - \bar{Y}) + (B_1 - \bar{Y}) + (C_2 - \bar{Y}) + (D_1 - \bar{Y}) + (E_2 - \bar{Y}) + (F_3 - \bar{Y}) + (G_1 - \bar{Y}) + (H_3 - \bar{Y}) + (K_3 - \bar{Y}) + (L_1 - \bar{Y}) + (M_2 - \bar{Y}) = 55.97 \quad (2)$$

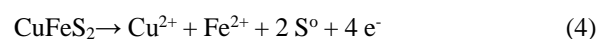
In Equation (1), \bar{Y} is the grand average of the responses and, in Equation (2), Y_{Opt} is the predicted surface area in the optimum condition. After prediction, a verification test should be conducted. This experiment was conducted under optimum conditions presented in Table 6. The leaching efficiency reached 57.19%. Therefore, the best result was achieved under optimum condition and the difference between predicted (55.97%) and the obtained values is negligible. The low error of (2.1%) confirms the predictability of the process and accuracy of the

experimental results.

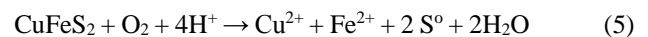
As mentioned, it is proved that the effect of temperature on the leaching efficiency of Sarcheshmeh concentrate is significant. Generally, a double increase in the reaction rates is noted for each 10°C rise in temperature [12]. In a similar research, increasing temperature from 70°C to 90°C increased the leaching efficiency from 28% to 70% after 120 min in a sulfate media including sodium nitrate[21]. This effect can be quantified by calculating the activation energies for the first 5 h of leaching (region in which the kinetics are linear) at high and low temperatures, respectively. Based on the published data, the activation energy during the initial stages of the reaction was equal to 48 kJ.mol⁻¹ at low temperature and 20 kJ.mol⁻¹ at high temperatures [22]. Therefore, the temperature effect on leaching efficiency is completely clear.

As illustrated in Fig. 2, NaCl concentration also has a positive effect on copper leaching efficiency. Indeed, the presence of chloride ions in the solution fosters the formation of a porous sulfur product that allows the diffusion of reactants through the sulfur film and reaching the reaction surface [13, 23].

O₂ flow rate is another main parameter which results in increasing copper dissolution. The main reason can be attributed to redox reaction between anodic and cathodic sites of chalcopyrite and oxygen. In this process, oxygen is reduced and chalcopyrite is oxidized according to Equations (3) and (4) respectively.



Consequently, the chalcopyrite dissolution happens by the overall Equation (5) [23].



In short it is the best result which has been reported until now since in the presented condition, the maximum leaching efficiency of 57% was achieved after 2 hours for Sarcheshmeh copper concentrate leaching at atmosphere pressure.

CONCLUSIONS

Taguchi design method with L₂₇ orthogonal array was implemented to optimize experimental conditions

Table 6: The optimum levels of each parameter.

Levels	C_A (M)	OxA	O_2 (l/min)	C_{NaCl} (M)	T($^{\circ}$ C)	%S	t(h)
Optimum	0.5	None	0.5	2	90	3	10

for copper extraction from chalcopyrite concentrate of Sarcheshmeh copper complex. Acid concentration (C_A), temperature (T), solid percentage (%S), O_2 flow rate (O_2), extra oxidizing agent (OxA), NaCl concentration (C_{NaCl}) and contact time (t) were chosen as the main parameters. ANOVA and ANOM analyses were applied to evaluate the relative importance of how effective various factors were. As a result, temperature (T) was determined as the main parameter which had a significant effect on the leaching efficiency. NaCl concentration (C_{NaCl}) and O_2 flow rate (O_2) were in the next levels of importance. By applying this optimized method, the leaching efficiency reached more than 57% after 2 hours, which is the most Competitive value ever reported among the research carried out on the chalcopyrite leaching at atmospheric pressure.

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