Physicochem. Probl. Miner. Process. 52(2), 2016, 1023−1035

www.minproc.pwr.wroc.pl/journal

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received November 6, 2015; reviewed; accepted March 13, 2016

RESPONSE SURFACE METHODOLOGY (RSM) FOR OPTIMIZATION OF CHALCOPYRITE CONCENTRATE LEACHING WITH SILVER-COATED PYRITE

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Abstract: This study aims to leach copper from chalcopyrite and optimizing the leaching process, using the response surface methodology (RSM). The RSM, a D-optimal design with four factors in three levels was employed to evaluate the effect of particle size, temperature, silver-coated pyrite to chalcopyrite ratio and redox potential parameters on the copper extraction efficiency. A quadratic model was then proposed by the RSM to correlate leaching variables. The tests results indicated that the model was significant with the experimental data at a correlation coefficient (R^2) of 0.96. The most important parameters of copper extraction efficiency were particle size and silver-coated pyrite-to-chalcopyrite ratio, and also the squared term of particle size (A^2), temperature (B^2) and redox potential (D^2). In addition, the interaction between redox potential and silver-coated pyrite-to-chalcopyrite ratio (*CD*) was significant. It was shown that the finer the particle size the faster the leaching rate of copper. It was also indicated that by increasing silver-coated pyrite to chalcopyrite ratio of 6:1 copper recovery increased. The maximum recovery of copper (71%) was obtained for the particle size of -38 μm, 70 °C, 420 mV of redox potential, silver-coated pyrite-to-chalcopyrite ratio of 6 and leaching time of 8 hours.

Keywords**:** *chalcopyrite, copper extraction, silver-coated pyrite, optimization, response surface methodology*

Introduction

Chalcopyrite is the most important copper bearing mineral accounting for about 70% of the world copper reserve (Wang, 2005). Presently chalcopyrite ores are concentrated by the froth flotation and processed by pyrometallurgical techniques of smelting and converting. Although the recovery of copper in this process is quite high, but its major drawback is the emision of SO_2 into the atmosphere (Venkatachalam, 1991; Wang, 2005). For that reason extensive research in the field of hydrometallurgy

http://dx.doi.org/10.5277/ppmp160239

has been conducted to develop an efficient process to extract copper from chalcopyrite. Hydrometallurgical processes to extract copper from chalcopyrite can be categorized, according to the type of lixiviant used as chloride, sulfate, nitrate and ammonia leaching and bioleaching. Sulfate leaching is the most interesting approach, due to the simplicity of their leaching reactions, low capital and operating cost and the conventional solvent extraction and electrowinning (Nazari et al., 2011).

In spite of these benefits, slow leaching kinetics and low levels of extraction are the drawbacks of this process which have been attributed to the formation of a passive layer, that could prevent the transport of reactants and products to and from chalcopyrite. In the conventional studies, elemental sulfur, polysulfide or iron precipitates have been considered to be the passive layer formed on chalcopyrite (Cordoba et al., 2008a; Dutrizac et al., 1969; Hackel et al., 1995; Hiroyoshi et al., 2004; Stott et al., 2000). Most recently, the interest in the improvement of chalcopyrite leaching rate attributed to the galvanic effect and generated between sulfide minerals has increased (Munoz et al., 1979; Dixon et al., 2008; Koleini et al., 2011; Ahmadi et al., 2012; Nazari et al., 2012a).

Pyrite and chalcopyrite, the most common and exploitable sulfide minerals, usually occur together. Due to the association of pyrite with chalcopyrite in nature, the co-treatment of these minerals might have advantages from an economic point of view. A novel process for chalcopyrite leaching, Galvanox™, based on a galvanically-assisted leaching has been introduced (Dixon et al., 2008). In this process, pyrite provides an alternative surface for ferric reduction. Providing a larger surface area for the cathodic reaction on pyrite than for the anodic reaction on chalcopyrite, also increases the anodic dissolution rate (Tshilombo, 2004).

When pyrite is present in the leach slurry, ferric reduction increases, and this allows the system to maintain the solution potential within the active region of the mineral. Therefore, in the Galvanox process, the selective leaching of chalcopyrite over pyrite occurs (Dixon et al., 2008). It has been found that pyrite samples from different sources affect the rate of chalcopyrite leaching differently. Some pyrite samples accelerate the rate significantly while others have little and/or no influence. The effectiveness of pyrite has a strong correlation with the level of silver occurring in the pyrite. The acceleration of chalcopyrite leaching in the presence of silver-enhanced pyrite was attributed to the galvanic interaction between pyrite and chalcopyrite and is sufficient to ensure rapid chalcopyrite leaching kinetics in the Galvanox process (Ahmadi et al., 2012; Nazari et al., 2012b).

Optimization can be defined as a process of improving an existing condition, apparatus, or system such as a metallurgical process. Therfore, investigation on modelling and optimization to discover the best qualification of these processes is very important. In order to overcome this problem, optimization studies have been carried out using response surface methodology (RSM). RSM consists of a group of mathematical and statistical techniques, used in the development of an adequate functional relationship between a response of interest, y, and a number of associated control (or input) variables denoted (x_1, x_2,... , x_k) (Andre et al., 2010). RSM reduces the number of experimental trials needed to evaluate multiple parameters and their interactions. Thus, it is less difficult and time consuming than other approaches (Hichem et al., 2008). Box et al. (2005) suggested to use a first-degree polynomial model to approximate the response variable. They acknowledged that this model is only an approximation, and is not accurate, but such a model is easy to estimate and to be applied, even when little is known about the process (Box et al., 2005; Montgomery, 2005). The D-optimality criterion enables a more efficient construction of a quadratic model (Myers and Montgomery, 2002). From a statistical point of view, a D-optimal design arrives to response surface models for which the maximum variance of the predicted responses is minimized. This means that the indication of the experiment will minimize the error in the estimated coefficients of the response model (Montgomery, 2005).

The objective of this research work was to optimize the leaching conditions of chalcopyrite concentrate with assisting galvanic and catalytic effect of pyrite and silver, using software based design, RSM, and evaluate the main effects of some physicochemical and operational parameters, as well as their interactions.

Materials and methods

Chalcopyrite sample and characterization

A representative copper sulfide concentrate sample was supplied from the Sarcheshmeh copper flotation circuit at Kerman, Iran. X-ray diffraction (XRD) demonstrated that chalcopyrite ($CuFeS_2$) is the major mineral of the sample. The XRD pattern of the representative sample is shown in Figure 1.

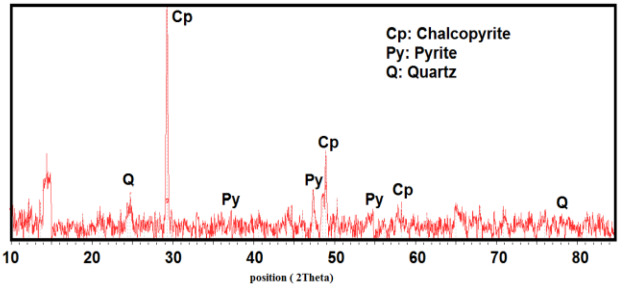

Fig. 1. XRD pattern of copper concentrate sample

Preparation of silver-coated pyrite

Pure crystals of pyrite were obtained from the Meydook Copper Mine (Kerman, Iran). In order to prepare silver-coated pyrite, 50 g of pyrite crystals were ground down to -75 µm which was then immersed into a 500 cm^3 solution, containing the solution 50 g per 1 kg pyrite of silver (nitrate solution). The pulp was then mixed, using a magnetic stirrer at 500 rpm and 25 °C (Nazari et al., 2012a) for 4 hours. After treating the pyrite with silver ions, the solid residue was filtered and rinsed several times with water, in order to wash any unreacted silver from the pyrite surfaces. Silver content in the solution was then determined by atomic absorption spectroscopy.

Leaching experiments

The leaching experiments were carried out in a stirred tank reactor containing 500 cm^3 suspensions at pulp density 5%, stirring rate of 850 rpm and initial pH of 1.2. The desired temperature was obtained with an electrical heater. After setting the pH, with concentrated H_2SO_4, the solution was prepared with appropriate amounts of ferrous and ferric sulfide solutions when the total iron concentrate was set at 0.1 M. Sulfuric acid was used to set the initial pH, then ferrous and ferric salts were added to scale down, and H_2O_2 were added for reaching to the desired redox potential. Then, concentrate and silver-coated pyrite are added to the reactor. The fife cm^3 pulp samples were taken periodically for analysis from the reactor and centrifuged for 3 minutes at 5000 rpm, to remove the solids. After centrifugation, the sample was returned to the reactor and the volume of the condensed liquid was daily filled by adding distilled water. Then, samples were analyzed for copper content by atomic absorption spectroscopy. Distilled water was used in all the experiments.

In these experiments, pyrite acted as a catalyst. To prevent the pyrite dissolution, the potential was maintained in 420-460 mV range, in which only chalcopyrite dissolves and the other minerals could not be dissolved in the leach solution. It indicates that copper extraction happened with controlling the potential in 420-460 mV range. However, iron concentration in ferric forms, in solution could produce jarosite, which prevents the chalcopyrite dissolution. Pyrite as a catalyst increases the solution cationic surface, and accordingly reduces its ferric ions. It should be noted that three major factors increase the presence of jarosite in solution, temperature, ferric ions and pH, all of them were controlled within the experiments.

Experimental design

RSM is useful approach for the modeling and analysis of problems, in which a response of interest is influenced by several variables and the objective is to optimize the response (Montgomery, 2005). D-optimal designs are the forms of design provided by a computer algorithm. The mathematical model found after fitting the function to the data can sometimes not satisfactorily describe the experimental domain. More reliable way to evaluate the quality of the model fitting is the application of analysis of variance (ANOVA). The central idea of ANOVA is to compare the variation, due to the treatment (change in the combination of variable levels) with the variation due to random errors inherent to the measurements of the generated responses (Vieira et al., 1989). From this comparison, it is possible to evaluate the significance of the regression used to foresee responses, considering the sources of experimental variance. Response surfaces were drown for the experimental results procured from the effect of four variables on the particle size, redox potential, temperature and silver-coated pyrite to chalcopyrite ratio, in order to determine the single and cumulative effects of these variables, and also their reciprocal interactions. In this research, the experimental data were analyzed, using Design-Expert software (Demo version 7.0.0) from Stat-Ease Inc. The four parameters at three levels were considered to be independent variables in the examination. To simplify the calculations, factors were given coded, namely particle size in μm (*A*), temperature in °C (*B*), silver-coated pyrite to chalcopyrite ratio in g/g (*C*), and redox potential in mV (*D*). Levels and coded factors of several parameters are shown in Table 1.

Table 1. Levels and coded factors of parameters for D-optimal design

Parameters	Levels		
	–1	0	+1
Particle size (μm)	–38	–53+38	–75+53
Temperature (°C)	70	80	90
Silver-coated pyrite to chalcopyrite ratio (g/g)	2	4	6
Redox potential (mV)	420	440	460

Results and discussion

The results of the 25 experiments were used in D-optimal approach to estimate the response variable which is copper recovery. The experimental conditions and copper recovery in each case are presented in Table 2.

Table 2. D-optimal design matrix and the results of experiments

Std. No.	Coded parameters and values				
	A	*B*	*C*	*D*	Response (Cu Recovery %)
1	0	85	5	450	69
2	+1	+1	+1	-1	62
3	-1	-1	0	+1	68
4	+1	+1	0	+1	62
5	-1	-1	+1	-1	71
6	-1	-1	-1	-1	62
7	+1	-1	-1	+1	60
8	+1	-1	+1	0	58
9	+1	+1	-1	-1	57
10	-1	+1	-1	+1	68
11	+1	0	+1	+1	62
12	0	0	+1	0	66
13	-1	+1	0	-1	66

Table 2. Continued

Std. No.	Coded parameters and values				
	A	*B*	*C*	*D*	Response (Cu Recovery %)
14	-1	+1	+1	+1	67
15	+1	-1	0	-1	60
16	0	-1	0	0	63
17	0	0	+1	0	69
18	0	0	0	-1	66
19	-1	0	0	0	66
20	+1	0	0	0	61
21	+1	-1	-1	+1	60
22	+1	+1	-1	-1	61
23	-1	-1	-1	-1	63
24	-1	-1	+1	-1	71
25	+1	+1	+1	-1	62

A: particle size (μm); *B*: temperature (°C); *C*: silver-coated pyrite to chalcopyrite ratio (g/g); redox potential (mV)

Statistical analysis

The statistical significance of the model was evaluated by the values of *F*, *P*, correlation coefficient and the analysis of variance (ANOVA), as presented in Table 3. The effects for all model terms were calculated and statistics such as *F-(Fisher)* values, lack of fit, and R^2-values were used for comparing the models. The statistical analysis showed that quadratic model fitted the experimental data the best. This statistical tool is required to test the significance and adequacy of the model. F-value and a very low p-value, inferred the significance of the model. The model *F-value* of 17.62 implies that the model is significant.

Table 3. Summary of analysis of variance results for model of copper extraction

Parameter	Value
R^2	0.96
R^2_{adj}	0.90
F value	17.62
Probe.>F	<0.0001
Sum of square	350.69
Df	14
Mean of square	25.05
Std.dev.	1.19

Fitting the model

The variation of experimental data is adequately revealed when the F-value is higher than unity, and accordingly the effects of different paramerts would be more real (Myers and Montgomery, 2002). The correlation coefficient (R^2) values examined the fitted model. The correlation coefficient values provide a measure of how much variability in the observed response values can be explained by the experimental factors, and their interactions. When correlation coefficient approaches unity, accordingly the fitted model would be better. The smaller values of correlation coefficient is an indication of the less relevance of the dependent variables in the model. In this case, the value of R^2 was equal to 0.96 which is a good indication. The value of adjusted coefficient ($R^2_{adj} = 0.90$) is also high, showing a high significance of the model. The value of predicted correlation coefficient is also high to support a high significance of the model and coefficient R^2, this implies that there is a 96% chance that the independent variables explain the changes in leaching efficiency, and there is only about 6% (0.96–0.90) chance that the changes in efficiency cannot be explained by the model. The regression equation after the analysis of variances represented the level of copper recovery as a function of the particle size, temperature, silver-coated pyrite to chalcopyrite ratio and redox potential. By implementing multiple regression analysis on the experimental data, the experimental results of the D-optimal design were fitted with a quadratic polynomial equation. Final equation in terms of coded factors was developed based on experimental design as:

$$Y = +\,66.52 - 3.22\,A + 0.32\,B + 1.21\,C + 0.55\,D + 0.49\,AB - 0.62AC - 0.34\,AD \\ + 0.66\,BC + 0.43\,BD - 1.60\,CD - 2.51\,A^2 - 2.34\,B^2 + 0.12\,C^2 + 2.11\,D^2$$

where Y is copper recovery (response) in percentage, and A, B, C and D are the coded values of the design variables. Furthermore, p-value of those variables included in each model are presented in Table 4. It can be postulated that A and C variables and the quadratic term of A^2, B^2 and D^2 are obviously significant; while the interactions between silver-coated pyrite to chalcopyrite ratio and redox potential (CD) is significant, and between other parameters are not significant. Also, according to the greater F-value of the particle size, it is the most important variable on the response.

Table 4. F-value and p-value for each variable in the polynomial model

Factors	Statistics		Factors	Statistics		Factors	Statistics	
	F-value	p-value		F-value	p-value		F-value	p-value
A	111.35	<0.0001	AC	3.23	0.102	A^2	11.72	0.006
B	0.90	0.365	AD	0.97	0.348	B^2	9.28	0.012
C	13.14	0.004	BC	3.60	0.086	C^2	0.047	0.832
D	3.13	0.107	BD	1.56	0.239	D^2	7.48	0.021
AB	2.12	0.176	CD	21.67	0.001			

Studies on effect of parameters and their interactions on copper recovery

Effects of silver-coated pyrite-to-chalcopyrite ratio and redox potential

The interaction, three-dimensional and contour plots in Figure 2 show the effects of silver-coated pyrite to chalcopyrite ratio and redox potential (CD) on copper recovery. Figure 2 indicates that at the high potential, the increase of silver-coated pyrite-to-chalcopyrite ratio did not affect the recovery of chalcopyrite, but at the low potential, recovery of chalcopyrite increases with increasing of silver-coated pyrite to chalcopyrite ratio. At less potential, it has been found that increase of chalcopyrite leaching is due to the galvanic interaction between pyrite and chalcopyrite particles. In addition, this high recovery of chalcopyrite at lower potential can be attributed to a decrease in both pyrite and silver oxidation, and therefore, in the loss of reacted silver to solution. Nazari et al. (2011) reported that at higher potentials more pyrite and silver are oxidized and more silver is lost.

Effects of particle size and temperature

The response surface and contour plots presented in Figure 3 show the effects of interaction between particle size and temperature (AB) on copper recovery from chalcopyrite sample, at the redox potential of 440 mV, and silver-coated pyrite to chalcopyrite ratio of 4. It indicates that temperature has a significant effect at the larger particle size, while this parameter has no significant effect on copper recovery at the lower particle size. Significant effects of temperature on copper leaching rate have also been observed by other researchers (Cordoba et al., 2008; Padilla et al., 2008). It can be concluded that temperature has more significant effect on copper recovery for minerals with a larger particle size.

Effects of silver-coated pyrite-to-chalcopyrite ratio and temperature

The interaction effect of the mass of silver-coated pyrite-to-chalcopyrite and temperature (CB) was shown in Figure 4. It can be indicated that increase of silver-coated pyrite-to-chalcopyrite ratio in the temperature range from 70 to 90 ºC will decrease the solubility, especially at lower temperatures (70 to 80 ºC). At lower mass ratio, the increase in temperature does not have a large impact on recovery of chalcopyrite. This shows that simultaneous increase in the mass ratio of silver-coated pyrite-to-chalcopyrite ratio and temperature, have a positive impact on dissolution of chalcopyrite.

Effects of particle size and silver-coated pyrite-to-chalcopyrite ratio

Figure 5 shows the effect of particle size and silver-coated pyrite-to-chalcopyrite ratio (AC) interaction, on the recovery of chalcopyrite. It was indicated that increase of silver-coated pyrite-to-chalcopyrite ratio for the small particle size, will increase the solubility. For the large particle size, the increase of the silver-coated pyrite-to-chalcopyrite ratio does not have any impact. It is remarkable that at the high silver-coated pyrite-to-chalcopyrite ratio, the particle size decrease would increase the copper recovery.

Optimization

As mentioned before, the objective of this study was to determine the conditions that maximize the recovery of copper. Therefore, when the fitted model was checked for adequacy of fitting in the region defined by the coordinates of the design, and was found to be adequate, the model was accordingly used to locate the coordinates of the stationary point (Mirazimi et al., 2011). In the numerical optimization, the desired goal for each factor and response was chosen. The possible goals are: maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only). A minimum and a maximum level must be provided for each parameter included. A weight can be assigned to each goal to adjust the shape of its particular desirability function. The importance of each goal can be changed in relation to other goals.

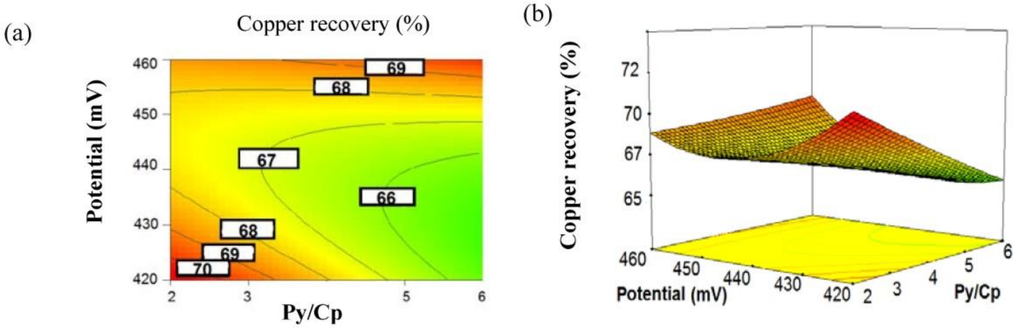

Fig. 2. Contour plots (a) and 3D (b) plot of effects of silver-coated pyrite-to-chalcopyrite ratio and redox potential, d_{80}: 56μm and 80 ºC

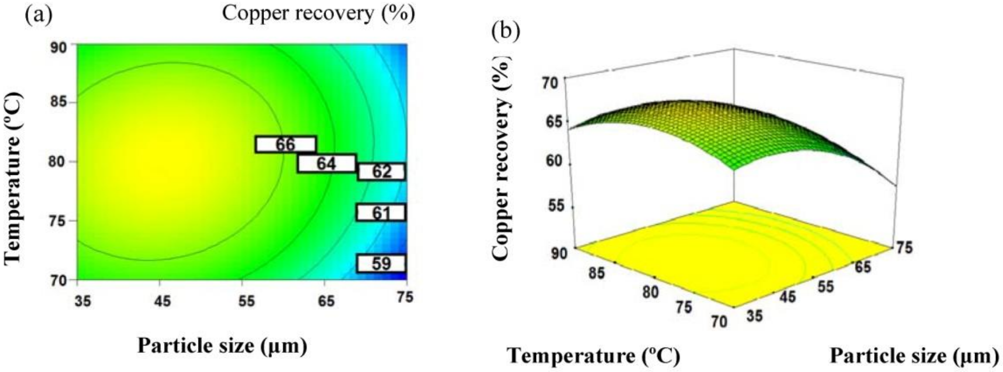

Fig. 3. Response surface contour plots (a) and 3D (b) diagram for effects of particle size and temperature on copper recovery from chalcopyrite sample, at the silver-coated pyrite-to-chalcopyrite ratio of 4:1 and redox potential of 440 mV

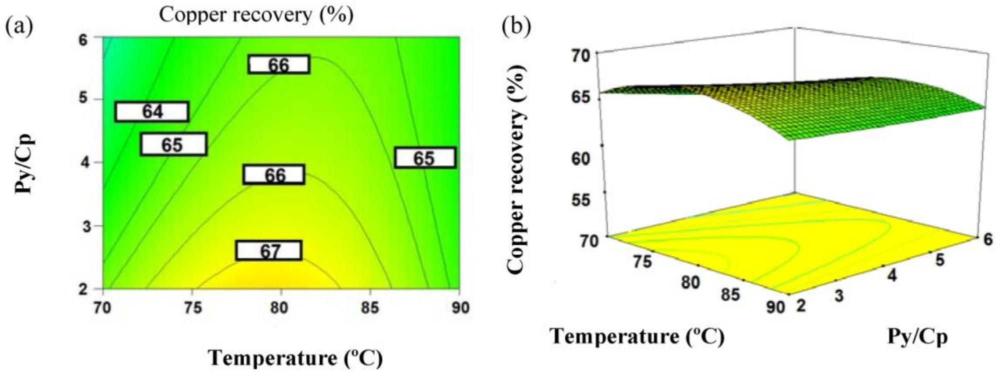

Fig. 4. Response surface plots of contour plots (a) and 3D (b) for effects of temperature and silver-coated pyrite-to-chalcopyrite ratio, particle size of 56.50 μm and redox potential of 440 mV

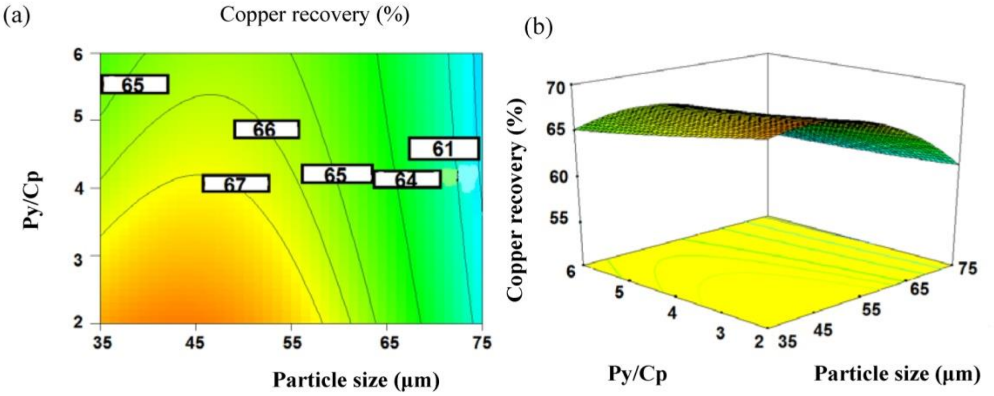

Fig. 5. Response surface plots of contour plots (a) and 3D (b) for effects of particle size and silver-coated pyrite-to-chalcopyrite, redox potential of 440 mV and 80 °C

Table 5. Optimal values of variables for maximal copper recovery

Maximum recovery (%)	Independent values				Goal
	A	*B*	*C*	*D*	
71	38.72	78.15	5.93	420	All the parameters in range
68	67.57	79.01	6	420	Maximize the particle size
71	45.77	82.23	2	460	Minimize the Ag-coated FeS_2 to chalcopyrite ratio

The goals are combined into an overall desirability function. It was found that the numerical optimization approach was a good tool to maximize the function desirability, for example to obtain the maximum copper recovery via maximum particle size or via minimum silver-coated pyrite to chalcopyrite ratio. Critical values for maximum copper recovery predicted from the data analyzed with the statistical technique are shown in Table 5. The predicted values were then tested. Under optimal conditions, the copper recovery was 71%, when all the parameters were set in the range.

Conclusions

The response surface methodology based on a D-optimal design was used to determine the effect of particle size, temperature, silver-coated pyrite-to-chalcopyrite ratio and redox potential on the copper recovery from chalcopyrite concentrate. Second-order regression models were developed using Design Expert software to predict the responses in all experimental regions. The analysis showed that:

-response surface methodology was effective for the optimization of the leaching process and a quadratic model suggested by the methodology was in good agreement with the experimental data at correlation coefficient of 0.96

-particle size and the ratio of silver-coated pyrite-to-chalcopyrite ratio had a positive effect on the response. The copper recovery significantly increases with decreasing of particle size and by increasing the silver-coated pyrite-to-chalcopyrite ratio, copper recovery also increased

-the quadratic terms of A^2, B^2 and D^2 were obviously significant

-the interaction between redox potential and the silver-coated pyrite-to-chalcopyrite ratio (*CD*) was more important than other interactions (*AC*, *AB* and *BC*)

-it was indicated that at the high potential, increase in the silver-coated pyrite-to-chalcopyrite ratio did not affect copper recovery. Albeit at the low potential, with increasing silver-coated pyrite-to-chalcopyrite ratio, the copper recovery also increases

-it was concluded that temperature had a significant effect at larger particle sizes while this parameter had no significant effect on copper recovery at lower particle sizes. It can also be concluded that temperature has a more significant effect on copper recovery for minerals with a larger particle size

-it could be observed that the increase of the mass ratio of silver-coated pyrite-to-chalcopyrite and temperature have a positive impact on the dissolution of chalcopyrite and accordingly increases the copper recovery

-the increase of the silver-coated pyrite-to-chalcopyrite ratio at small particle sizes will increase the solubility. At the large particle size, increase in the silver-coated pyrite-to-chalcopyrite ratio has no impact on the solution. At the high silver-coated pyrite-to-chalcopyrite ratio, the particle size decrease would clearly increase copper recovery

-under optimal conditions the copper recovery was 71%. The optimum level of the four variables, was determined to be: for maximum copper recovery concentration, 38.72 μm; particle size, 78.15 °C; temperature, 420 mV; redox potential and silver-coated pyrite to chalcopyrite ratio in g/g; 5.93 in 8 hours.

Acknowledgments

This research was supported by the National Iranian Copper Industries Company (NICICO), especially management and personals of Sarcheshmeh Research and Development center. Thus, the authors would like to thank all persons for their contribution.

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