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Response surface design for nickel recovery from laterite by sulfation-roasting-leaching process

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Abstract: The present study deals with the nickel extraction and iron dissolution from nickeliferous laterite by a process of sulfation-roasting-leaching. To optimize the roasting process, response surface methodology (RSM) was utilized which employed two-level and two-factor full factorial central composite design (CCD). The factors of roasting temperature and time were studied. Experiments were carried out for fitting two non-linear regression models of nickel extraction and iron dissolution. Predicted values obtained were close to experimental values, indicating the suitability of the models. Three-dimensional surface plots and contour plot were helpful to predicting the results by performing only limited set of experiments. An area of nickel extraction from 75% to 78% and iron dissolution from 5% to 10% is obtained by an overlaid contour plot. The samples roasted at different temperatures and for different durations were characterized by XRD, which show a good agreement to iron dissolution analysis.

Key words: response surface methodology; sulfation-roasting-leaching; nickel extraction; iron dissolution

1 Introduction

On account of the rapid increase in the world consumption of nickel and the shortage of sulfide ores, the laterite has become significant source of nickel. It is reported that 72% of the world land-based nickel resources originated from laterites although only accounted for 42% of the world nickel production [1−2]. Large deposits of laterites have been found in Philippines, New Caledonia, Cuba, Indonesia and Central South America.

Various hydrometallurgical processes have been tried to extract nickel and cobalt from these lateritic ores, which involved ammonia-ammonium carbonate leaching [3−4], atmospheric leaching with sulfuric acid[5−7] and high pressure acid leaching[8−10]. High pressure acid leaching is the main process for industrial production of nickel and cobalt with lateritic ore, but it is applicable only for limonite (high iron laterite) in order to minimize acid consumption. Another disadvantage of this process is that it requires expensive autoclaves and also needs high maintenance costs. Recently, interest has been created to recover metal values using sulfation-roasting process due to its ease of operation[11−15]. In this process, nickel is preferentially sulfated with the addition of sulfuric acid less than the stoichiometric amount due to the higher stabilities of its sulfate than iron sulfate. The nickel extraction could be enhanced in the presence of additives. The roasting condition, including roasting temperature and time, are quite important and sensitive for the nickel extraction.

In the present work, attempts have been made to extract nickel from laterite by sulfation-roasting-leaching process. The experimental work aims to optimize the roasting conditions. In addition to this, the effect of roasting temperature and time were evaluated by using response surface methodology (RSM), which is a statistical and graphical technique. A variety of factorial designs are available to accomplish this task. Here, two-level and two-factor full factorial central composite design (CCD) model was used. The predicted result by the response surface CCD model was then compared with the experimental results.

2 Materials and methods

2.1 Raw material

The lateritic ore was collected from Tubay region, Mindanao, Philippines. The raw material used in this study was typical limonitic laterite ore with high iron

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content and was ground to <250 μm after drying. A representative sample was subjected to acid digestion and analyzed by atomic absorption spectrophotometer (AAS, maker: Rayleigh, China) and the ore contains 1.11% nickel. Iron was analyzed by standard volumetric method and the ore contains 47.74% iron.

2.2 Experimental

The sulfation-roasting experiments were carried out at a laboratory scale (10 g). The lateritic ore was moistened with 20% water and 40% concentrated sulfuric acid (mass fraction) in a silica crucible. The preliminary tests showed that 20% water is required for good mixing and that the addition of 40% acid (mass fraction) is suitable for the considerations of more nickel extraction and less iron dissolution. The mixture was dried at 110 ℃ for 5 h, followed by roasting in a muffle electric furnace. The roasted sample was then cooled to room temperature and leached with water at 80 ℃ for 30 min at a solid/liquid ratio of 1:20 g/mL. The sludge was filtered and residue was washed thoroughly several times with distilled water. A material balance was performed for each experiment based on the total nickel and iron present in the feed, leached solution and residue. Based on the material balance, the leaching rate was calculated.

The experiments were designed and sulfation-roasting-leaching process was carried out using RSM. RSM is an empirical statistical technique employed for multiple regression analysis by using quantitative data. It solves multivariable data which were obtained from properly designed experiments to solve multivariable equation simultaneously. As an easy way to estimate response surface, factorial designs is the most useful schemes for the optimization of variables with a limited number of experiments. CCD is the most successful and best factorial design which is accomplished by adding two experimental points along each coordinate axis at opposite sides of the origin and at a distance equal to the semi-diagonal of the hyper cube of the factorial design and new extreme values (low and high) for each factor added in this design. In this study, the factors varied were temperature and time in two levels.

For optimization of roasting temperature and time, a 2^2 factorial CCD with 4 axial points, 4 cube points and 5 central points resulting in a total of 13 experimental points were used in a single block. The temperature was varied from 629 ℃ to 771 ℃, and the time was varied from 9 min to 51 min. This design helped to understand the interaction of variables and this interaction can be inspected with the help of contour plots and 3D surface plots. The variable factors and their coded values are given in Table 1.

3 Results and discussions

3.1 Data analysis

Table 1 shows the combined effects of temperature and time on experimental leaching efficiencies of nickel and iron. Generally, it is observed that nickel extraction increases with the increase of temperature and time, but decreases as temperature and time reaches a higher level due to the decomposition of nickel sulfate to oxide. Iron dissolution is the maximum at the lower temperature and time level, and then decrease sharply with the increase of temperature and time due to the decomposition of iron

Table 1 Data processed by MINITAB® software

StdOrder	RunOrder	PtType	Block	Temperature/℃	Time/min	Mass fraction of Ni/%		Mass fraction of Fe/%	
						Experimental	Predicted	Experimental	Predicted
1	9	1	1	650	15	70.5	68.7	15.0	15.5
2	11	1	1	750	15	77.1	73.8	7.4	7.9
3	4	1	1	650	45	76.2	79.5	13.0	11.9
4	8	1	1	750	45	55.8	57.6	0.2	−0.89
5	1	−1	1	629	30	72.3	71.2	14.9	15.8
6	3	−1	1	771	30	58.4	59.4	0.5	1.4
7	5	−1	1	700	9	72.6	76.4	14.3	13.0
8	6	−1	1	700	51	76.0	72.6	3.4	4.2
9	13	0	1	700	30	74.5	74.5	8.6	8.6
10	7	0	1	700	30	74.2	74.5	8.5	8.6
11	10	0	1	700	30	75.0	74.5	8.7	8.6
12	2	0	1	700	30	74.4	74.5	8.9	8.6
13	12	0	1	700	30	75.2	74.5	8.2	8.6

sulfate to oxide.

The data generated from sulfation-roasting-leaching experiments were statistically analyzed to identify the significant main effects and interaction effects. Multi-regression analysis was performed as the data to obtain quadratic response surface models for nickel extraction (Table 2) and iron extraction (Table 3). The response surface regression results give the coefficient for all the terms in the two models and each effect is estimated independently. It was found that the reduced quadratic models as given in Eq.(1) and Eq.(2) could best fit the experimental data in uncoded units:

$$\%\text{Ni extraction}=-958.888+2.774A+6.216B-0.002A*A-0.009A*B \quad (1)$$

$$\%\text{Fe extraction}=49.6659-0.0499A+1.0125B-0.0017A*B \quad (2)$$

where A is temperature and B is time.

Table 2 Estimated regression coefficients for nickel extraction

Term	Coefficient	S.E.Coefficient	P
Constant	−958.888	200.224	0.001
A	2.774	0.565	0.001
B	6.216	1.248	0.001
$A*A$	−0.002	0.000	0.002
$A*B$	−0.009	0.002	0.001

R^2=89.5%; and R^2_{adj}=84.3%.

Table 3 Estimated regression coefficients for iron extraction

Term	Coefficient	S.E.Coefficient	P
Constant	49.665 9	13.455 2	0.005
A	−0.049 9	0.019 2	0.029
B	1.012 5	0.422 8	0.040
$A*B$	−0.001 7	0.000 6	0.018

R^2=97.5%; and R^2_{adj}=96.7%.

As shown in Table 2, small P values for A(0.001), B(0.001), $A*A$ (0.002) and $A*B$ (0.001) suggesting their effects on nickel extraction are important in the model. The determination coefficient (R^2) for nickel extraction is evaluated as 89.5%, the value of adjusted R^2 (R^2_{adj}) was 84.3%. The R^2 value shows that there is a good agreement for nickel extraction between the experimental and predicted values.

For iron dissolution, small P values of this estimated regression coefficient for A(0.029), B(0.040) and $A*B$ (0.018) suggesting their effects on iron dissolution are important in the model, as shown in Table 3. Both temperature and time have a negative effect on iron dissolution. This means that iron dissolution decreased when temperature and/or time increased. The temperature multiplying time is the most important factor and also has a negative effect on iron dissolution. In addition, the R^2 value for iron extraction is 97.5%, which shows perfect agreement. Since there is not much difference between the experimental and predicted values, the two models are acceptable.

3.2 Contour plot

Fig.1 shows a Contour plot where nickel extraction was represented by varying simultaneously roasting temperature from 629 ℃ to 771 ℃ and the time from 9 min to 51 min. From this response surface plot, it is also clear that to obtain a higher nickel extraction, the roasting should be conducted at a higher temperature and shorter time, or a middle temperature and time, or a lower temperature and longer time. For example, the predicted values for nickel extraction are 77.8%, 75.5% and 77.6% at the roasting condition of 660 ℃, 40 min, 700 ℃, 20 min and 730 ℃, 10 min, respectively.

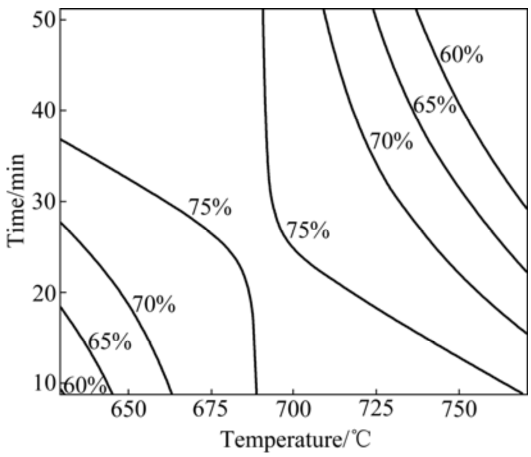

Fig.1 Contour plot of nickel extraction showing interaction between roasting temperature and time at variable levels

Fig.2 shows the effect of temperature and time on the iron dissolution. The effects of these two variables on iron dissolution are significant. Different from nickel, the factors, including the independent variable temperature and time, temperature and time combined, all have negative effects on iron dissolution. The decrease of iron dissolution with the increase in temperature and time is due to the decomposition of iron sulfate to oxide mentioned above. It is obvious that the higher the temperature and/or the time increases, the less the iron dissolution is achieved. However, in order to achieve high level nickel extraction, the optimum temperature and time should be fixed on the consideration of their effects on nickel extraction.

The response contour plots of nickel extraction and iron dissolution between temperature and time is given in Fig.3. The lines of contour plots predict the values of nickel extraction and iron dissolution for different temperatures at different interaction time. The optimum condition is obtained as the shaded area which varies the values from 75% to 78% for nickel extraction and from 5% to 10% for iron dissolution. The contour plot also indicates that while the case of more than 75% nickel extraction and less than 5% iron dissolution is needed, the best way is to increase the roasting time to about 1 h and keep the temperature at about 700 ℃.

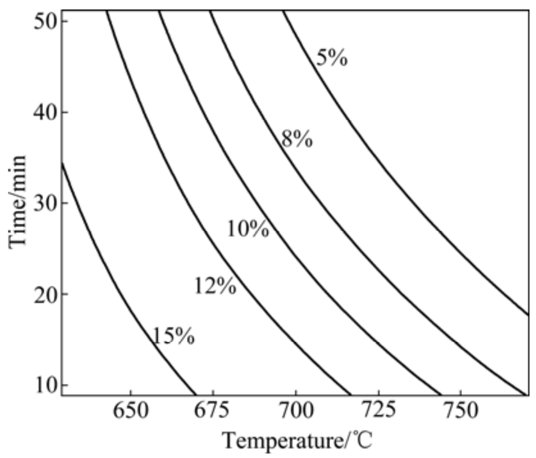

Fig.2 Contour plot of iron dissolution showing interaction between roasting temperature and time at variable levels

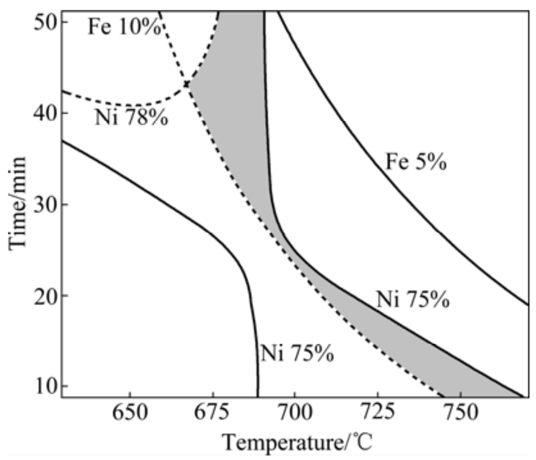

Fig.3 Overlaid contour plot of combined effect of roasting temperature and time on nickel extraction and iron dissolution

3.4 Characterization of roasted samples

Fig.4 shows the XRD patterns of roasted samples at different temperature and time. The sample roasted at 650 ℃ for 15 min is $Fe_2(SO_4)_3$ as major mineral and Fe_2O_3 as minor one (Fig.4(a)), which shows the same result with the one roasted at 629 ℃ for 30 min. As the temperature and time increased, the peaks of $Fe_2(SO_4)_3$ become weaker due to the decomposition of $Fe_2(SO_4)_3$ to Fe_2O_3 and finally disappear. On the contrary, the peaks of Fe_2O_3 become stronger and finally become dominant as the temperature and time increased. Due to the high content of iron in laterite ore, the behaviors of nickel in this process are impossible to characterize by XRD analysis. However, the basic chemical reactions occurred:

$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3+3SO_3 \quad (3)$$

$$NiSO_4 \longrightarrow NiO+3SO_3 \quad (4)$$

The XRD results show a good agreement with iron dissolution which was discussed in above sections.

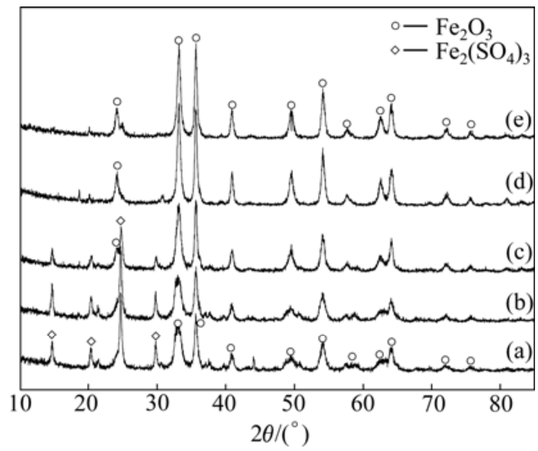

Fig.4 XRD patterns of samples roasted at different temperature for different duration of time: (a) 650 ℃, 15 min; (b) 629 ℃, 30 min; (c) 700 ℃, 30 min; (d) 750 ℃, 45 min; (e) 771 ℃, 30 min

4 Conclusions

1) The present studies were carried out to optimize the nickel extraction and iron dissolution from roasted nickel laterite. The experiments were designed using central composite design technique, to carry out a systematic and optimized approach to experimentation.

2) The factors studied were roasting temperature and time, and the interactions between different factors also exist. Two non-linear regression models were obtained based on the statistical analysis and factors were optimized within the desirable operating range to achieve a higher nickel extraction and lower iron dissolution.

3) An area of nickel extraction from 75% to 78% and iron dissolution from 5% to 10% is obtained by an overlaid contour plot. The roasted samples at different temperature and time were characterized by XRD results which show a good agreement with iron dissolution analysis.

References

[1] SUDOL S. The thunder from down under: Everything you wanted to know about laterites but were afraid to ask [J]. Canadian Mining Journal, 2005, 126(5): 8−12.

[2] ANTHONY M T, FLETT D S. Nickel processing technology: A review [J]. Minerals Industry International, 1997, 1: 26−42.

[3] PANDA S C, SUKLA L B, JENA P K. Extraction of nickel through

reduction roasting and ammoniacal leaching of lateritic nickel ores [J]. Transactions of Indian Institute of Metals, 1980, 33: 161−165.

[4] VALIX M, CHEUNG W H. Effect of sulfur on the mineral phases of laterite ores at high temperature reduction [J]. Minerals Engineering, 2002, 15: 523−530.

[5] ARROYO J C, NEUDORF D A. Atmospheric leach process for the recovery of nickel and cobalt from limonite and saprolite ores: USA, Patent 6261527 [P]. 2001−07−17.

[6] ARROYO J C, NEUDORF D A. Atmospheric leach process for the recovery of nickel and cobalt from limonite and saprolite ores: USA, Patent 6680035 [P]. 2004−01−20.

[7] MCDONALD R G, WHITTINGTON B I. Atmospheric acid leaching of nickel laterites review (Part I): Sulfuric acid technologies [J]. Hydrometallurgy, 2008, 91: 35−55.

[8] GEORGIOU D, PAPANGELAKIS V G. Sulfuric acid pressure leaching of a limonitic laterite: Chemistry and kinetics [J]. Hydrometallurgy, 1998, 49: 23−46.

[9] RUBISOV D H, PAPANGELAKIS V G. Sulfuric acid pressure leaching of laterites—A comprehensive model of a continuous autoclave [J]. Hydrometallurgy, 2000, 58: 89−101.

[10] JOHNSON J A, MCDONALD R G, MUIR D M, TRANNE J P. Pressure acid leaching of arid-region nickel laterite ore (Part Ⅳ): Effect of acid loading and additives with nontronite ores [J]. Hydrometallurgy, 2005, 78: 264−270.

[11] BAINBRIDGE D W. Sulfation of a nickeliferous laterite [J]. Metallurgical Transactions, 1973, 4: 1655−1658.

[12] HANSEN B J, STENSRUD J C, ZAMBRANO A R, CHILCOTE D D. Nickel and magnesia recovery from laterites by low temperature self-sulfation: USA, Patent 4125588 [P]. 1978−11−14.

[13] NICOLAS. Promotion agents in the sulphation of oxidized nickel and cobalt bearing ores: USA, Patent 3367740 [P]. 1968−02−06.

[14] KAR B B, SWAMY Y V. Some aspects of nickel extraction from chromitiferous overburden by sulphatization roasting [J]. Minerals Engineering, 2000, 13: 1635−1640.

[15] SWAMY Y V, KAR B B, MOHANTY J K. Physicochemical characterization and sulphatization roasting of low-grade nickeliferous laterites [J]. Hydrometallurgy, 2003, 69: 89−98.

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