

RECOVERY OF THE VALUABLE METALS FROM COMPLEX CONVERTER SLAG AT ELEVATED TEMPERATURE WITH SULFURIC ACID SOLUTION

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Abstract

The aim of this paper was exploring the effective utilization of nickel converter slag by means of the methodology of pressure oxidative leaching. The central composite design of response surface methodology was employed to optimize controlling conditions for the leaching of more valuable metals such as nickel, cobalt, and copper, while dissolution of iron was curbed. XRD, SEM-EDS were performed for characterizing the structure of leach residues for analyzing the mechanism of selective leaching. Experimental results demonstrate that the effects of temperature and sulfuric acid concentration on the metals extraction and filtration rate are significant, followed by liquid/solid (L/S) ratio. The optimized conditions for the leaching of converter slag are: temperature 208 °C, sulfuric acid concentration 0.35 mol/L, and L/S ratio 5.4 mL/g. Under these conditions, 99.60% Co, 99.20% Ni, and 96.80% Cu were extracted into solution together with only 0.21% Fe, and the filtration rate of leach slurry reached 576.86 L·m⁻²·h⁻¹. The mechanism for achieving selective leaching of nickel, cobalt, and copper against iron dissolution and good filtration performance of the leach slurry was enabled by iron that dissolved in the solution, decomposed, and hydrolyzed mainly to form hematite (α -Fe₂O₃ and γ -Fe₂O₃), and letting silicic acid form precipitated SiO₂ in the leach residue.

Key words: Nickel converter slag; Pressure oxidative leaching; Response surface methodology; Filtration property

1. Introduction

The low-nickel matte is generally transferred to an upgraded intermediate sulfide product by converting operation. Unfortunately, a large amount of valuable metals (i.e. cobalt, nickel, copper, etc.) is lost in converter slag owing to mechanical entrapment and/or chemical interactions [1-4]. Although it belongs to a group of hazardous materials due to the fact that it contains heavy metals and toxic matter like lead, nickel converter slag is typically a material enriched in cobalt, nickel, copper, and other valuable metals. For instance, the content of nickel in it is often higher than the content of laterite ores, and, therefore, it can also be considered as a secondary source for recycling nickel and cobalt [5]. Despite the fact that the production of the slag is very extensive, the utilization of the slag for suitable recovery of valuable metals pose great difficulty because valuable metals like cobalt, nickel, and copper are commonly dispersed in fayalite, one of the mineralogical phases existing in the slag. Consequently, most of the slag is dumped outside of smelters, causing land pollution and environmental problems.

With respect of the mineral phase, the slag consists mainly of fayalite and silicate. It is well known that hydrometallurgical process is the methodology superior to be chosen for extracting and recycling valuable metals in the metallurgical slag, owing to lower energy consumption and environmental friendliness. Although most of cobalt and nickel existing in the slag could be extracted by atmospheric acid leaching, significantly high required acid concentration would cause the dissolution of a substantial amount of iron and silicon, which would contribute to the puzzle of solid-liquid separation of the leach slurry [6]. Even though the dissolution of iron might be slightly decreased by pre-treating with reduction roasting/smelting before atmospheric acid leaching, the pre-treatment process causes not only a predominantly high cost and emissions of carbon dioxide but fugitive sulfur dioxide as well, contributing to environmental pollution [7-10]. Adding auxiliary oxidant like potassium dichromate, hydrogen peroxide, sodium chlorate, and etc. in the atmospheric leaching process can reduce the content of iron dissolving in the leach liquor because Fe²⁺ dissolved in solution by acid is oxidized to Fe³⁺,

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which is then subjected to hydrolysis, and deposited [11,12]. Unfortunately, the problem of separation between valuable metal and iron still exists and the additive introduction of such kinds of oxidants results in extra cost. High pressure oxidative acid leaching seems to be a suitable technology for treating the converter slag because iron is re-precipitated in-situ as hematite and silicon is transformed to filterable silica (precipitated SiO_2) instead of silica gel, improving the filtration characteristics of the slurry and reducing the burden of removal of impurities in subsequent process of leaching. However, present research mainly focuses on recovering copper from copper converter slag, and limited attention has been paid on the recovery of valuable metals from nickel converter slag. Moreover, instead of interaction influence between factors, these studies focus more on influence of single factor on the base metals' extraction, thus the experimental conditions obtained are very rigorous [1,13]. Again, only few studies found in literature, with respect of increasing extractions of nickel, cobalt, and copper and simultaneously reserving iron in the leach residue by controlling leaching conditions have been reported. Actually, the difference in the existing form of base metal values between in nickel converter slag and in copper converter slag might lead to different behavior of pressure oxidative acid leaching kinetics, and different experimental conditions of dissolving valuable metals and impurities of iron and silicon [14].

The objective of this study was to analyze and optimize the mechanism of leaching valuable metals and curbing dissolution of iron into diluted acid solution, from which the metals could be easily extracted by ion exchange methodology and/or solvent extraction process [15-18], before cleaning the hazardous metal lead and reusing the ferrous resource in nickel converter slag. However, enhancing leaching valuable metals and curbing extracting iron are two contradictory and mutually restrictive aspects, especially demanding for a good filtration property of leach slurry and proper mineralogical phase of ferrous in leach residue for easy further application. An innovation combining the extraction of base metals with inhibiting the dissolution of iron was conducted to investigate the feasibility of further application of the process in present work, which cannot only meet the request of mineralogical phase in leach residue but achieve good filtration property of the leach slurry as well. The central composite design of response surface methodology (RSM) [19-21], which renders

small deviation and high credibility, was also applied to the heterogeneously complex reaction system of pressure oxidative acid leaching of nickel converter slag to achieve the optimum conditions of selective leaching of cobalt, nickel and copper.

2. Materials and methods

2.1 Materials

Nickel converter slag used in the study was kindly provided by Jinchuan Group Co. Ltd, Gansu Province, China. The chemical composition of the slag is given in Table 1. Silicon was tested by molybdenum blue method via ultraviolet-visible spectrophotometer (UV-2550, SHIMADZU, Japan), iron was measured by chemical titration with potassium dichromate, and sulfur was measured by combustion iodometry, the others were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). All the chemicals used in the present investigation were of analytical grades and purchased from Sinopharm Chemical Regents Co. Ltd, Shanghai China.

2.2 Leaching of nickel converter slag

Prior to the leaching tests, nickel converter slag was mechanically crushed, ground, and screened by a sieve of 0.048 mm size. All leaching experiments were conducted in a vertical autoclave of 2 L volume (Model GSH2 Reactor, Weihai Chemical Machinery Instrument Company, China). Each 100 g of the converter slag with -0.048 mm particle size and constant concentration sulfuric acid were placed into the autoclave. When the reactant was heated up to the required temperature under continuous agitation (600 rpm), oxygen was continuously introduced to maintain a fixed pressure (600 kPa) for the specific duration of the experiment. After the completion of each test (80 min), 200 mL of the leaching slurry obtained was put in \varnothing 9 cm Buchner funnel using filter paper to separate leach liquor and leach residue at -0.08 MPa vacuum conditions by vacuum suction filter apparatus for determining the filter rate of the leach pulp. The leach residues obtained were dried overnight at 353 K in an electric oven and characterized by chemical analysis, XRD and SEM-EDS, and the leachate was also used for testing chemicals. Each experiment was triplicated, and all results given in the study were the averages of experiments repeated three times.

Table 1. Composition of nickel converter slag

Constituent	Ni	Co	Cu	Fe	Si	S	CaO	MgO	Al_2O_3	MnO	ZnO	PbO
Amount, wt. %	1.48	0.594	0.65	47.49	12.89	0.542	1.223	0.723	1.259	0.05	0.098	0.036



The filtration rate was determined by the formula as follows:

$$\varphi = \frac{V_1}{S \times t} \quad (1)$$

where φ is filtration rate, $L \cdot m^{-2} \cdot h^{-1}$; V_1 is volume of the leach slurry at ambient temperature, L; S is the filter area of the funnel, m^2 ; and t is the filter time, h.

The extraction efficiency of i-metal denoted as sign of η_i is calculated according to the formula as follows:

$$\eta_i = \frac{C_i V}{m \beta_i} \times 100\% \quad (2)$$

where C_i , V , m , and ω_i are the concentration of the i-metal in the filtrate (g/L), filtrate volume (L), the weight of nickel converter slag (g), and the mass fraction of metal in the sample, respectively.

2.3 Design of optimizing experiments for selective leaching

The central composite design generally adds some specific experimental points such as curb points, axial points, and center point on the basis of linear regression composite points, and combines all of them together to form the new experimental scheme. Therefore, it can greatly reduce the number of test and makes the second-order design satisfy orthogonality on the basis of the first-order design [22]. The response surface methodology involves some models such as linear, quadratic, cubic, and etc. Taking into account each linear variable, the interactions of linear variable, and second-order variable, predicted response model was explained by the following second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} X_i X_j + e \quad (3)$$

where Y is the objective function or predicted response; X_i is the independent variable; β_0 is the offset term; β_i , β_{ii} , and β_{ij} represent regression coefficient of the primary, secondary and interaction of regression coefficient, respectively; k is the number of the influencing factors; and e is the error consisting of experimental error and lack of fit error [23]. In order to facilitate the statistical calculations, the variables of tests were coded by the following equation:

$$x_i = \frac{X_i - X_{0i}}{\Delta X_i}, \quad i = 1, 2, 3 \quad (4)$$

where x_i is the dimensionless coded value of the independent variable; X_{0i} is the actual value of X_i at the zero level; and ΔX_i is the step change value of X_i .

2.4 Characterization

The phase structure and morphology features of nickel converter slag and leach residue in the present investigation were characterized by x-ray diffraction (XRD) and scanning electron microscope (SEM) with an EDAX attachment for X-ray microanalysis. XRD patterns (Bruker D8-discover) were achieved with Cu $K\alpha$ ($\lambda = 0.1542$ nm) radiation ranging from $2\theta = 10$ to 90° at rate of $2^\circ/\text{min}$ to identify the phase present. The operating voltage and current of XRD detection were kept at 40 kV and 40 mA, respectively. The morphologies and energy dispersive spectrometer (EDS) of samples were analyzed after being sputtered with a conductive layer of gold, using FEI Quanta 200 SEM with an EDAX Genesis 200 attachment for x-ray microanalysis.

3. Results and discussion

3.1 Characterization of nickel converter slag

The XRD pattern of the nickel converter slag shown in Fig. 1 testifies that the slag mainly consists of crystalline fayalite, magnetite, copper sulfide, and metal ferrates. It is also confirmed that cobalt and nickel were bounded by iron oxide in the slag. Additionally, the SEM/EDS results of the slag shown in Fig. 2 indicate that it consists mainly of matte, magnetite, silica, and fayalite. Firstly, matte was embedded in the slag as uneven droplet (Area 1), enriching large amounts of copper and small amounts of iron, showing the reason why copper was lost in the slag in metallurgical process due to mechanical entrapment of the matte. Secondly, magnetite usually appeared in large chunks (Area 2), and the small ones were surrounded by silica (Area 3). Finally fayalite presented in the slag was in the form of mesh-like structure (Area 4), which suggested that silica did not react, and was segregated during solidification. It can be concluded from the characterization of nickel converter slag that cobalt and nickel were bounded by iron oxide and that silica was dissolved in the slag, but cobalt failed to be detected by EDS because of low percentage and wide dispersion in the slag. Moreover, the other metals like calcium, magnesium, and aluminum were also dissolved in the slag, showing the complex composition of the slag.

3.2 Model establishment for selective leaching

For getting the optimal conditions to extract selectively valuable metals from the nickel converter slag, there are two goals to be achieved in this research. One is getting more valuable metals such as cobalt, nickel, and copper dissolving into solution inhibiting leaching of iron. The other one is obtaining good filtration properties of leach slurry. The major



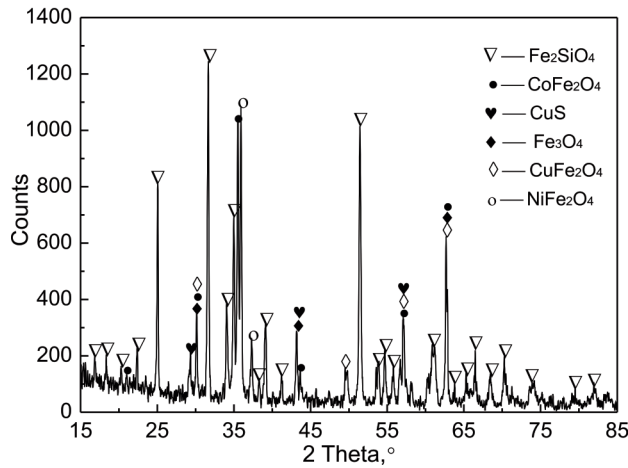


Figure 1. XRD pattern of converter slag

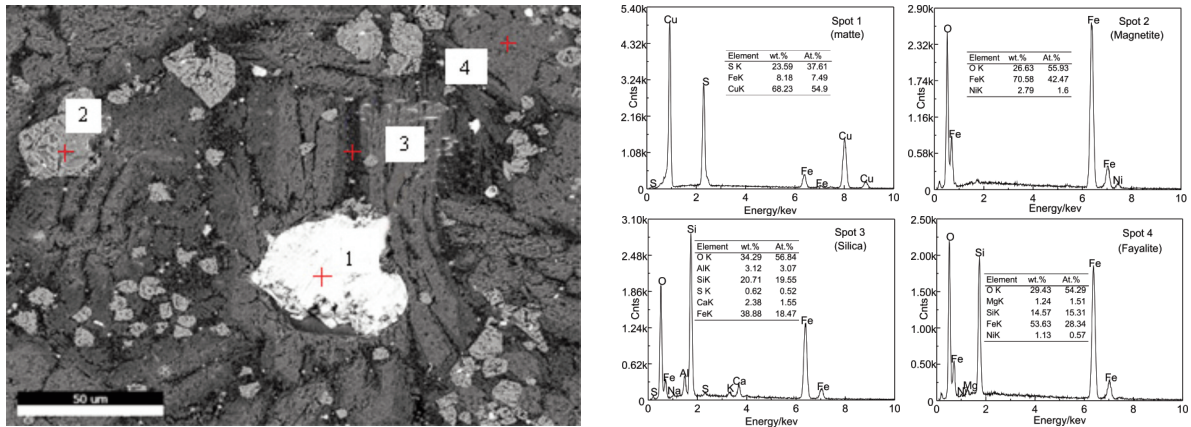


Figure 2. SEM image and EDS spectra of converter slag

factors of pressure oxidative acid leaching of the slag involve temperature, sulfuric acid concentration, liquid/solid (L/S) ratio, oxygen partial pressure, leaching time, and particle size, etc. [19, 20]. A full experimental design allows all factorial effects to be estimated independently, however, the essential factors (less than 4), which have a great effect on the result, are commonly used in practice to reduce the number of experiments and simplify analysis [24]. Accordingly, in the single factor experiments conducted in our study, it is found that the material particle size less than 0.048 mm, oxygen partial pressure more than 600 kPa, and leaching time greater than 80 min will have little impact on the leaching rate of valuable metals, thus fixed

particle size, oxygen partial pressure, and leaching time for the corresponding value were performed in the response surface methodology optimization experiments [14]. According to the previous experimental results, therefore, the three factors of temperature, sulfuric acid concentration, and L/S ratio were screened for the central composite design model. The highest leaching rate in single factor experiment was taken as the value of zero level for corresponding parameter, and step length value automatically generated by the Design - Expert 8.0 software, these factors and their levels were collected in Table 2.

The previous experiments showed that the extraction of cobalt was prior to that of nickel, and that

Table 2. Factors and levels for the central composite design

Factor	Symbol	Level				
		-1.682(- α)	-1	0	1	+1.682(+ α)
Temperature, °C	x_1	183	190	200	210	217
Sulfuric acid concentration, mol/L	x_2	0.132	0.2	0.3	0.4	0.462
Liquid/Solid ratio, mL/g	x_3	4.3	5	6	7	7.7



not only the extraction of cobalt but the dissolution of copper as well related positively with nickel leaching rate, which proved that there existed some relationship between extraction efficiencies of nickel, cobalt, and copper. To consider the integrity of leaching process and further application of the process, the filtration rate of leach slurry (denoted as the sign Y_3) was chosen as response value or objective function besides the nickel extraction (denoted as the sign Y_1), and iron extraction (denoted as the sign Y_2).

On the conditions of three factors, the experiments consisted of eight curb points ($\pm 1, \pm 1, \pm 1$), six axial points ($(\pm\alpha, 0, 0), (0, \pm\alpha, 0),$ and $(0, 0, \pm\alpha)$) and six center points. Especially, $\alpha = 2^{3/4} = 1.682$. The results of these experiments are displayed in Table 3.

According to Design-Expert 8 software, compared with various models, the quadratic model was selected to describe the leach behavior of valuable metals and filtration rate of leaching slurry. A second-order polynomial model for the three factors investigated was employed to describe the relationship between metal extraction and tested factors, and the model of two interactive factors was performed to characterize the filtration rate of leaching slurry. Consequently their regress equations of response were located as follows:

$$Y_1 = 91.41 + 3.96x_1 + 5.52x_2 + 3.13x_3 + 0.49x_1x_2 - 2.12x_1x_3 - 1.52x_2x_3 - 0.56x_1^2 - 4.59x_2^2 - 0.77x_3^2 \tag{5}$$

$$Y_2 = 1.79 - 0.65x_1 + 0.42x_2 - 0.045x_3 - 0.28x_1x_2 - 0.014x_1x_3 + 0.061x_2x_3 - 0.061x_1^2 - 0.28x_2^2 - 0.32x_3^2 \tag{6}$$

$$Y_3 = 369.71 + 90.45x_1 - 93.20x_2 - 50.10x_3 + 8.26x_1x_2 - 48.31x_1x_3 - 0.33x_2x_3 \tag{7}$$

3.3 The analysis of variance of the model

The analysis of variance (ANOVA) results for response surface quadratic model was shown in Table 4–6 for $Y_1, Y_2,$ and $Y_3,$ respectively. The p-value in ANOVA table implies whether the model or a concrete variable is significant or not. Generally, it is significant when the p-value is lower than 0.05 [25]. The p-value higher than 0.05 implies that the contribution of the factor is less than confidence level of 95%, thus indicating the factor is not significant for the response [23]. The p-value lower than 0.001 indicates the proposed model is significant. The quality of the fit of the model can be checked by the determination coefficient expressed by the sign of $R^2,$ and/or adjusted coefficient denoted by the sign of $Adj R^2.$

Table 3. Design matrix and experimental data of metals extraction and filtration rate

Run	x_1	x_2	x_3	Extraction, %				Filtration rate (Y_3), $L \cdot m^{-2} \cdot h^{-1}$
				Co	Ni (Y_1)	Cu	Fe (Y_2)	
1	1	1	1	96.87	94.72	92.11	0.68	275.45
2	0	0	0	92.67	91.21	85.21	1.57	355.7
3	1	-1	-1	84.56	81.34	79.65	0.52	667.9
4	-1.682	0	0	87.35	84.21	80.54	2.98	243.76
5	-1	1	1	91.56	89.17	87.56	2.35	149.98
6	1	-1	1	87.23	86.57	83.14	0.25	418.98
7	0	0	0	91.65	93.56	87.32	1.86	395.09
8	0	1.682	0	90.45	89.76	86.23	1.79	216.45
9	0	0	1.682	94.98	94.23	87.65	0.86	298.7
10	0	0	0	93.76	92.45	88.57	1.95	378.64
11	-1	-1	-1	70.45	69.27	73.79	1.01	382.21
12	1	1	-1	95.21	94.68	92.34	0.61	485.78
13	0	0	0	92.24	93.54	86.21	1.67	369.25
14	1.682	0	0	96.69	96.45	96.25	0.41	536.76
15	0	0	0	92.63	91.54	86.43	1.98	335.4
16	0	0	0	93.25	92.34	87.21	1.73	374.78
17	0	0	-1.682	84.31	83.21	80.35	1.05	389.25
18	0	-1.682	0	71.21	68.12	65.32	0.36	546.7
19	-1	1	-1	84.91	81.53	82.32	2.32	206.96
20	-1	-1	1	83.67	83.89	80.21	0.89	366.45



All the p-values of nickel leaching model (Table 4), iron extraction model (Table 5), and filtration rate model (Table 6) are lower than 0.0001, which indicates that the correlations between these established models is significant. Accordingly the values of adjusted coefficient of nickel leaching model, iron extraction model, and filtration rate model are 0.9379, 0.9453, and 0.9459, respectively, which demonstrate a high correlation between the experimental values and the predicted values [26]. It further suggests that the regression model provides an excellent explanation of the relationship between the independent variables and the response. On the other hand the difference between determination coefficient and adjusted coefficient of these models are 2.94%, 2.59%, and 1.71%, respectively, which shows that there is not any insignificant factor in the regress models [27].

On the basis of the statistical analysis in Table 4, three independent variables (x_1 , x_2 , and x_3), one quadratic terms (x_2^2), and one interaction term (x_1x_3) with p-values of ≤ 0.05 are determined to be significant, but other terms are non-significant. Judging from the positive and negative values of the coefficient of the interaction terms, x_1x_2 has positive effect on the extraction of nickel. On the other hand, x_1x_3 and x_2x_3 have a negative influence.

On the basis of the statistical analysis in Table 5, two independent variables (x_1 , and x_2), two quadratic terms (x_2^2 and x_3^2), and one interaction term (x_1x_2) with

Table 4. Analysis of variance (ANOVA) for the regression model of Y_1 extraction and filtration rate

Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	p-value
Model	1124.92	9	124.99	32.88	<0.0001
x_1	213.8	1	213.8	56.24	<0.0001
x_2	416.55	1	416.55	109.57	<0.0001
x_3	133.51	1	133.51	35.12	0.0001
x_1x_2	1.95	1	1.95	0.51	0.4902
x_1x_3	36.08	1	36.08	9.49	0.0116
x_2x_3	18.51	1	18.51	4.87	0.0518
x_1^2	4.49	1	4.49	1.18	0.3027
x_2^2	302.97	1	302.97	79.69	<0.0001
x_3^2	8.63	1	8.63	2.27	0.1629
Residual	38.02	10	3.8		
Lack of Fit	13.76	5	2.75	0.57	0.7257
Pure Error	24.26	5	4.85		
Cor Total	1162.94	19			
R^2	0.9673				
Adj R^2	0.9379				

p-values of ≤ 0.05 are determined to be significant, but other terms are non-significant. Judging from the positive and negative values of the coefficient of the interaction terms, hoping minor leaching efficiency of iron, x_1x_2 and x_1x_3 have positive effect on the selective extraction. On the other hand, x_2x_3 has a negative influence.

On the basis of the statistical analysis in Table 6, three independent variables (x_1 , x_2 and x_3) and one interaction term (x_1x_3) with p-values lower than 0.05 are determined to be significant, but other terms are non-significant. Judging from the positive and negative values of the coefficient of the interaction terms, x_1x_2 has positive effect on the filtration rate of leach residue. On the other hand, x_1x_3 and x_2x_3 have a negative influence.

3.4 Analysis of response surface on selective leaching

The three-dimensional response surface plots were used to visualize all of the interaction effects of the variables on the nickel extraction (Fig. 3a–c), though the interactions of temperature – sulfuric acid concentration and sulfuric acid concentration – L/S ratio are not significant. From Fig. 3a, the response surface presents a hyperboloid shape, indicating the interaction between temperature and L/S ratio is significant. The nickel extraction continually increases with the increasing of

Table 5. Analysis of variance (ANOVA) for the regression model of Y_2

Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	p-value
Model	11.17	9	1.24	37.47	<0.0001
x_1	5.71	1	5.71	172.38	<0.0001
x_2	2.37	1	2.37	71.67	<0.0001
x_3	0.027	1	0.027	0.82	0.3862
x_1x_2	0.63	1	0.63	19.1	0.0014
x_1x_3	1.51E-03	1	1.51E-03	0.046	0.8351
x_2x_3	0.03	1	0.03	0.91	0.3637
x_1^2	0.054	1	0.054	1.62	0.2325
x_2^2	1.13	1	1.13	34.13	0.0002
x_3^2	1.5	1	1.5	45.25	<0.0001
Residual	0.33	10	0.033		
Lack of Fit	0.19	5	0.039	1.4	0.3611
Pure Error	0.14	5	0.028		
Cor Total	11.51	19			
R^2	0.9712				
Adj R^2	0.9453				

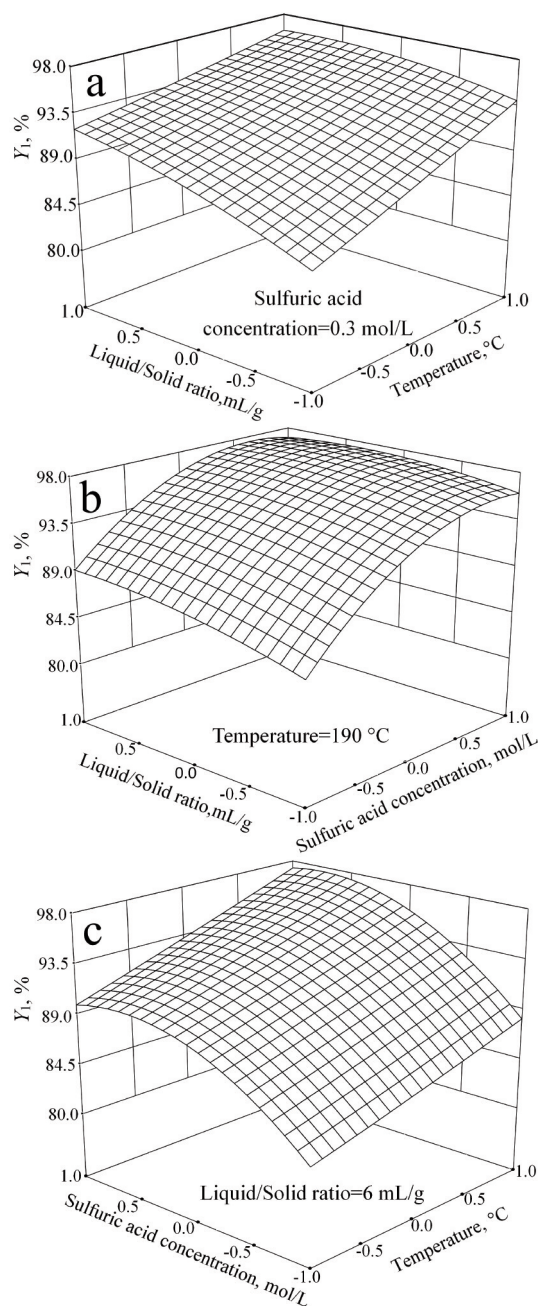


Table 6. Analysis of variance (ANOVA) for the regression model of Y_3

Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	p-value
Model	2.84E+05	6	47309.6	56.37	<0.0001
x_1	1.12E+05	1	1.12E+05	133.13	<0.0001
x_2	1.19E+05	1	1.19E+05	141.33	<0.0001
x_3	34285.65	1	34285.65	40.85	<0.0001
x_1x_2	545.66	1	545.66	0.65	0.4346
x_1x_3	18673.75	1	18673.75	22.25	0.0004
x_2x_3	0.86	1	0.86	1.03E-03	0.9749
Residual	10910.81	13	839.29		
Lack of Fit	8802.27	8	1100.28	2.61	0.1528
Pure Error	2108.54	5	421.71		
Cor Total	2.95E+05	19			
R ²	0.963				
Adj R ²	0.9459				

temperature and L/S ratio. It is because that increasing both temperature and the L/S ratio can cause the dissolution of the mineral phase of nickel [1]. However, the increase of the L/S ratio would accelerate the formation of silica gel which worsens the filterability of the slurry, and brings a large volume of the slurry leading to a big liability of filtration [28]. This is the reason why a lot of silicic acid is formed when pH value of the solution is less than 2, and that H_4SiO_4 gel is generated in the aqueous solution in which excessive water is present. Fig. 3b shows that the nickel extraction increases as sulfuric acid concentration increases, but remains the constant while sulfuric acid concentration is above 0.35 mol/L. The moderate increase of sulfuric acid concentration favors the leaching of nickel, but causes dissolution of iron. From Fig. 3c, it was found that Y_1 -value achieves a maximum when $x_1=1$, $x_2=0.655$, which means that the nickel extraction reaches 96.78% under the conditions of temperature 200 °C, sulfuric acid concentration 0.37 mol/L, and L/S ratio 6.0 mL/g.

The three-dimensional response surface plots of model Y_2 were used to visualize all of the interaction effects of the variables on the nickel extraction (Fig. 4a–c). From Fig. 4a it can be demonstrated that the interaction between temperature and sulfuric acid concentration is significant. The iron extraction continually decreases with the increasing of temperature and the decreasing of sulfuric acid concentration. This could be accounted for with two reasons. One is that increasing temperature can cause the oxidation and hydrolysis of iron, which leads to a decrease of the content of iron in solution. And the other one is that the leaching efficiency of iron becomes lower while the sulfuric acid concentration decreases. However, it is not a positive effect for decreasing iron dissolving to extraction

**Figure 3.** Response surface plots of Y_1

of nickel by controlling too low sulfuric acid concentration. It means that the change of iron extraction is not significant with the variance of L/S ratio from Fig. 4b. Accordingly Fig. 4c demonstrates that decreasing iron leaching is possible not only by increasing L/S ratio but by lowering sulfuric acid concentration. This could be accounted for with the fact that magnetite, silica, and fayalite contained in the slag could not be dissolved in low content of sulfuric acid solution.

To observe all of the interaction effects of the variables on the filtration rate of leach slurry, the three-

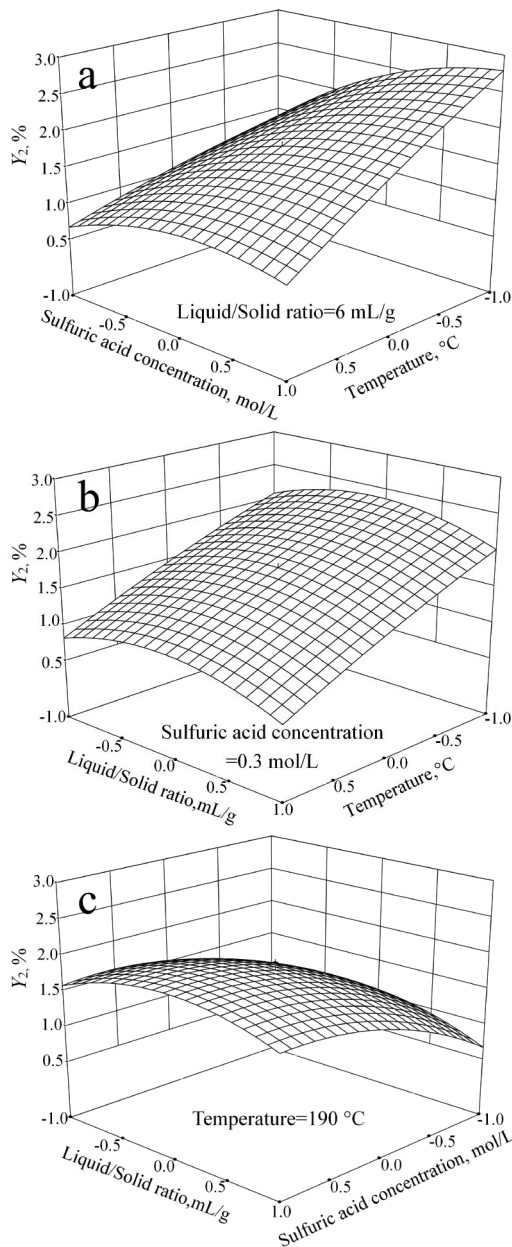


Figure 4. Response surface plots of Y_2

dimensional response surface plots of model Y_3 were depicted in Fig. 5a–c. From Fig. 5a the result can be drawn up that the filtration rate of leach slurry increases promptly with the intensifying of temperature and the decreasing of sulfuric acid solution. The interaction between temperature and L/S ratio has great influence on filtration rate of leaching slurry, which can be seen in Fig. 5b. Filtration rate increases continually with increasing temperature while L/S ratio maintains lower value, which indicates it will improve filtration rate with lower L/S ratio and higher temperature. Accordingly, Fig. 5c demonstrates that it is necessary to decrease not only L/S ratio but sulfuric acid solution for enhancing the

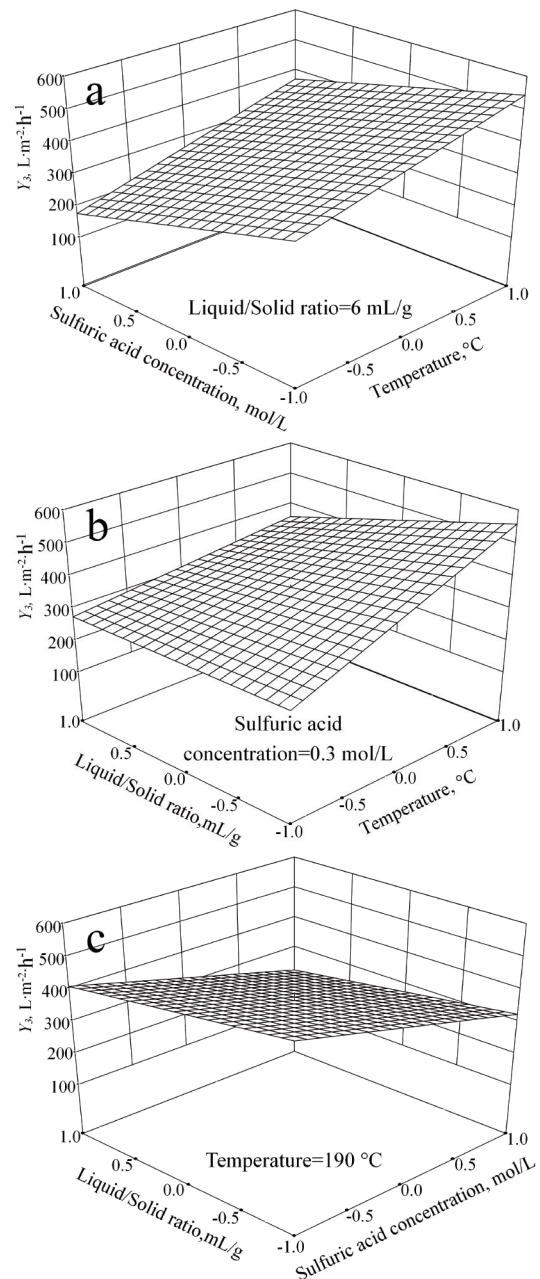


Figure 5. Response surface plots of Y_3

filtration rate of leach slurry.

Based on the analysis it can be concluded that, the optimal conditions deduced from Design-Expert software for leaching valuable metals from nickel converter slag can be safely drawn up as temperature of 208 °C, sulfuric acid concentration of 0.35 mol/L, and L/S ratio of 5.4 mL/g. Under these conditions the expected nickel extraction and iron extraction would be 99.48% and 0.21%, respectively. Accordingly, the filtration rate of leach slurry would be 571.78 $L \cdot m^{-2} \cdot h^{-1}$.

3.5 Testing of the model

The correlation between experimental data and predicted values of the regression model was shown in Fig. 6. The line in the figure means the situation that experimental value equals to predicted value. From Fig. 6 it can be found that the experimental values are located on the line or beside the line, indicating that all the predicted values of the model are in close agreement with the experimental values. The result suggests that the model equation would be sufficient to represent the response of the experimental values associated with selective extraction.

In order to confirm the adequacy of the model for predicting extractions and filtration rate, validation experiments were carried out under the optimum conditions, and the results are shown in Table 7.

It was found that extractions of more than 99.20% for cobalt and nickel, more than 96.80% copper, and 0.21% iron, with a filtration rate as much as 576.86 L·m⁻²·h⁻¹, were achieved at the above mentioned conditions. Compared to the results reported in previous studies, the optimized condition causes high selective leaching of valuable metals (i.e. cobalt, nickel, and copper) against iron, indicating strongly thorough removal of iron in leach liquor. During pressure oxidative acid leaching of copper, cobalt, and nickel from the copper converter slag, it was reported that all extractions of cobalt, nickel, and copper reached more than 95%, and the dissolution of iron was 2.2%, and yet not only the high temperature of 250 °C was used, but the high consumption of sulfuric acid was used (the consumption of acid was 60 kg per ton slag, and initial sulfuric acid concentration was above 0.7 mol/L) [1, 5, 28].

3.6 Mechanism of selective leaching

The chemical composition of the typical leach residue under the optimal leaching condition mentioned

and obtained above is presented in Table 8. It can be concluded that the residue contains very lower content of valuable metals and sulfur than that of nickel slag before leaching. Correspondingly, the leachate containing 2.45 g/L of nickel, 0.98 g/L of cobalt, 1.05 g/L of copper, and 0.16 g/L of iron was achieved, from which nickel, cobalt, and copper are easily recovered and separated by traditional process such as ion exchange methodology and solvent extraction process [29-31]. The XRD pattern of the residue (Fig. 7) demonstrates that it consists mainly of hematite (α -Fe₂O₃ and γ -Fe₂O₃) which could be further used in steel and iron industry. As the reason that it exists with the amorphous form in the residue, the phases of silicon are not detected by the XRD, even though the content of Si is 12.702% as listed in Table 8. Moreover, low percentages of some metals, such as calcium, aluminum, and magnesium presented as either crystalline or amorphous silicates and sulfates in the residue did not allow to be detected in the sample. Correspondingly, the digraph of SEM-EDS of leach residue is shown in Fig. 8. Additionally, the color of the leach residue being in brownish-red is different from that of the raw materials before leaching with gray, which could be found in Fig. 9.

According to the characterization of raw materials and leaching residues by XRD, SEM/EDS, and chemical element analyzing, the mechanism of base metals selective leaching under the optimal leaching condition can be summed up as follows: the compounds combining with nickel, cobalt and copper are dissolved to form corresponding sulfate respectively, and ferrous silicates transform to ferrous sulfate and filterable silica, then ferrous sulfate is oxidized to form ferric sulfate which hydrolyze to form ferric oxide. The main reactions that take place during the leaching process are expressed as follows:

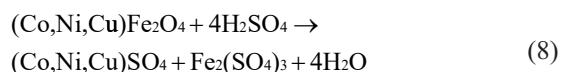


Table 7. Results of verification tests

Test	Extraction, %				Filtration rate (Y_3), L·m ⁻² ·h ⁻¹
	Co	Ni (Y_1)	Cu	Fe (Y_2)	
1	99.66	99.14	96.61	0.29	550.56
2	99.38	99.01	96.78	0.14	605.72
3	99.81	99.65	97.01	0.21	582.31
4	99.56	99.03	96.8	0.21	568.86
Mean	99.6	99.2	96.8	0.21	576.86

Table 8. Chemical composition of the typical leaching residue

Constituent	Ni	Co	Cu	Fe	Si	S	Ca	Mg	Al	Mn	Zn	Pb
Amount, wt. %	0.037	0.015	0.031	47.301	12.702	0.168	0.474	0.016	0.667	<0.01	<0.01	0.034



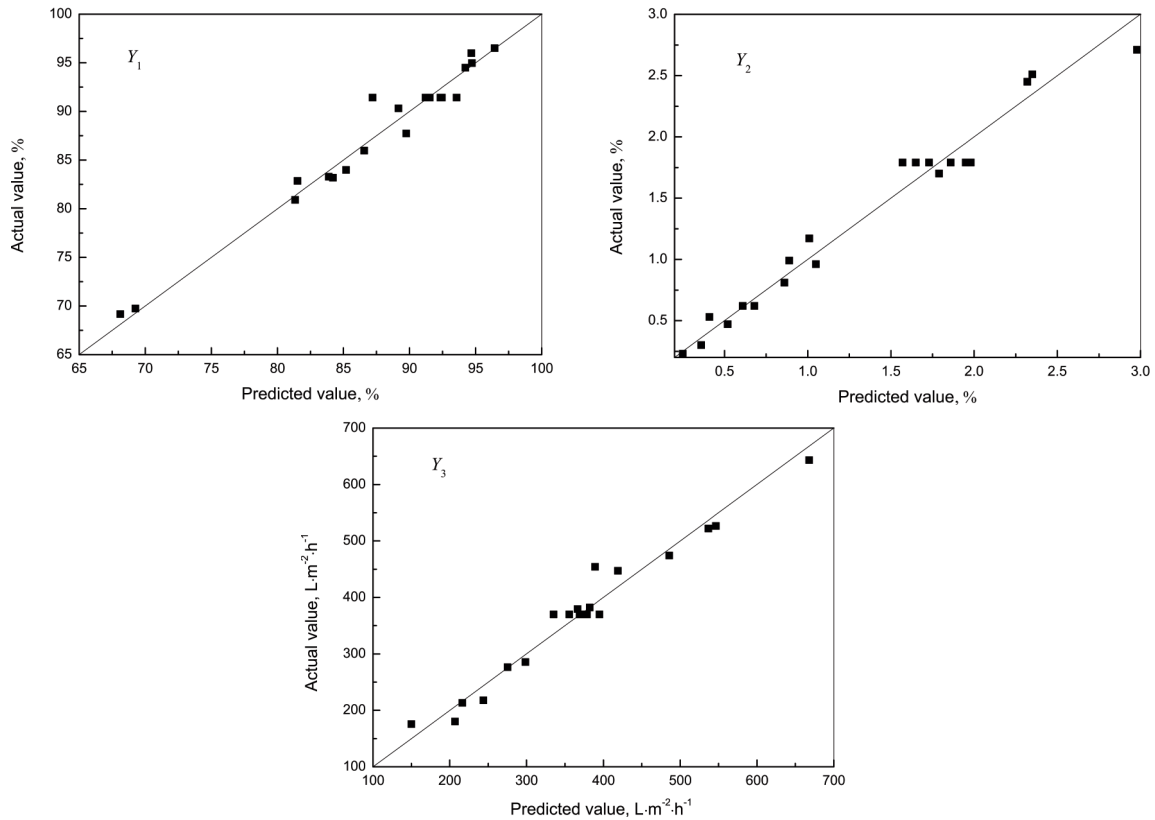


Figure 6. Correlation between experimental and predicted values based on the central composite design

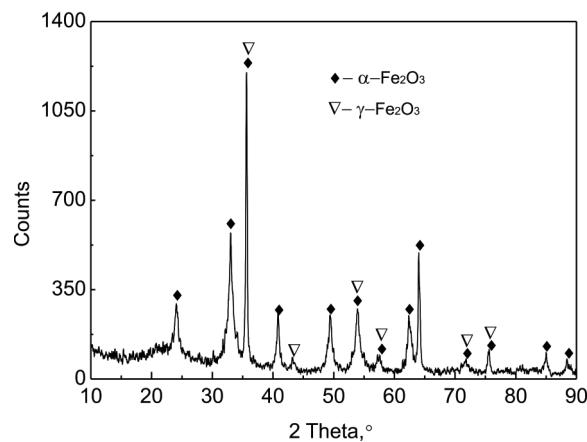
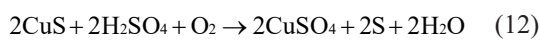
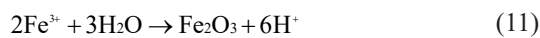
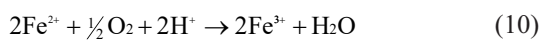
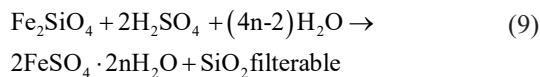


Figure 7. XRD pattern of leach residue



Two side reasons influence the filtration property of

the leach slurry. On the one hand, the dissolution of iron not only leads to more consumption of sulfuric acid but also produces colloid of $\text{Fe}(\text{OH})_3$. On the other hand, the production of silica gel during the process of leach results in difficulty in filtration of the leach slurry. And the main methodology performed in the present work for selective leaching nickel, cobalt and copper against iron dissolution and for achieving good filtration performance of the leach slurry is not only letting iron be dissolved in the solution at the beginning of leaching

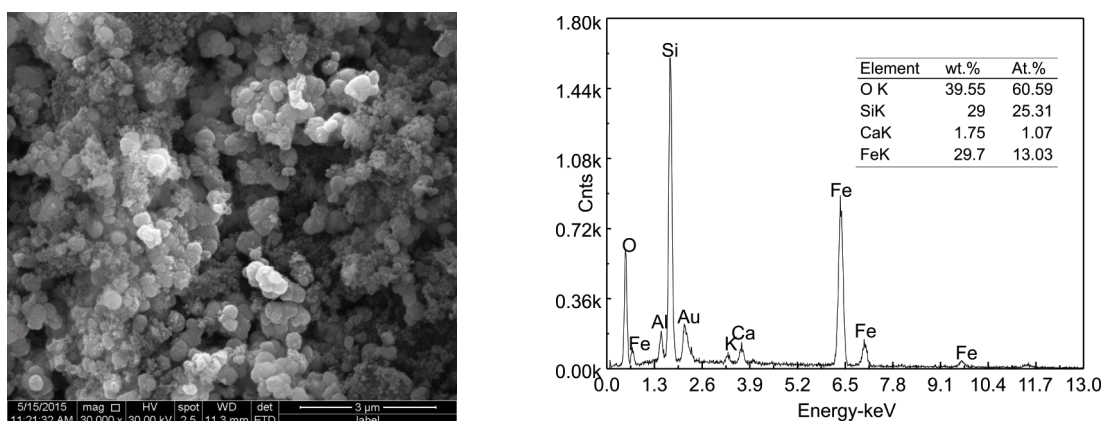


Figure 8. SEM image and EDS spectra of leach residue

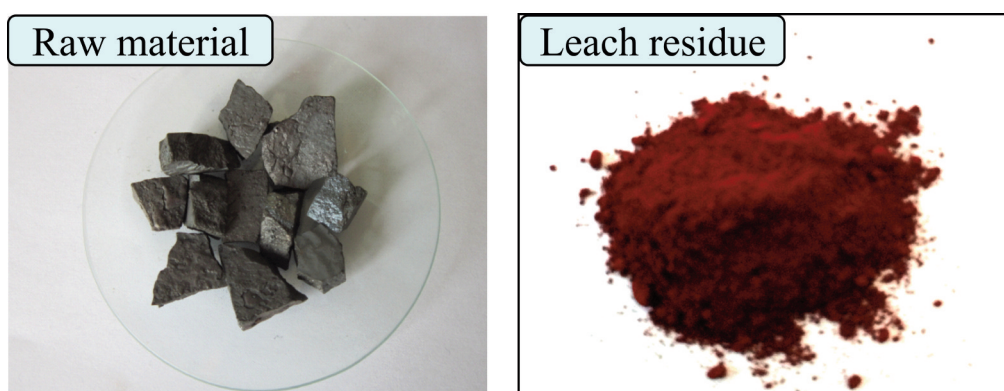


Figure 9. The colors of raw material and leach residue

process decomposed and hydrolyzed to form hematite (α - Fe_2O_3 and γ - Fe_2O_3) at the final stage of the process, but also making few silica gel forming by letting silicic acid formed precipitated SiO_2 . It can be concluded that the objective of utilizing most of the nickel converter slag could be achieved, by leaching valuable metals and curbing dissolution of iron into diluted acid solution, from which the metals could be easily extracted by ion exchange methodology and/or solvent extraction process, especially a good filtration property of leach slurry and an easy application of leach residue with proper mineralogical phase of ferrous is realized.

4. Conclusions

(1) The optimized parameters for leaching more valuable metals and curbing extracting iron with a good filtration property of leach slurry from the converter slag are temperature of 208 °C, sulfuric acid concentration of 0.35 mol/L, and L/S ratio of 5.4 mL/g.

(2) Under the above conditions, the extraction efficiency of nickel, cobalt, copper, and iron is 99.20%, 99.60%, 96.80%, and 0.21%, respectively. Moreover, the leach slurry has good filtration property with filtration rate as much as 576.86 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.

(3) Under the optimal leaching condition mentioned and obtained in present work, the leach residue contains very lower content of valuable metals and sulfur than that of nickel slag before leaching, demonstrating easily further application in steel and iron industry for the reason that it consists mainly of hematite.

(4) The experimental results obtained are coincident with that predicted by the model simulated by central composite design of response surface methodology in the study, confirming the adequacy of the model.

(5) Not only iron dissolved in the solution at the beginning of leaching process decomposed and hydrolyzed to form hematite (α - Fe_2O_3 and γ - Fe_2O_3) at the final stage of the process, but also precipitated SiO_2 instead of silica gel formed in the leach residues are the accounts for realizing selective leaching nickel, cobalt and copper against iron dissolution and good filtration performance of the leach slurry.

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DOBIJANJE VREDNIH METALA IZ KOMPLEKSNE KONVERTORSKE ŠLJAKE NA POVIŠENIM TEMPERATURAMA U PRISUSTVU RASTVORA SUMPORNE KISELINE

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Apstrakt

U ovom radu je ispitivano iskorišćenje konvertorske šljake sa sadržajem nikla primenom metodologije oksidacionog luženja pod pritiskom. Centralni kompozitni dizajn metodologije odgovora površine je korišćen za optimizaciju kontrolnih uslova luženja vrednijih metala kao što su nikel, kobalt i bakar; dok je rastvaranje gvožđa suzbijeno. XRD i SEM-EDS analize su izvršene za karakterizaciju strukture ostatka luženja da bi se odredio mehanizam selektivnog luženja. Eksperimentalni rezultati su pokazali da su uticaj temperature i koncentracije sumporne kiseline na ekstrakciju metala i brzinu filtracije značajani, kao i uticaj odnosa tečno/čvrsto. Optimalni uslovi za luženje konvertorske šljake su sledeći: temperatura 208 °C, koncentracija sumporne kiseline 0.35 mol/L i odnos tečno/čvrsto 5.4 mL/g. Pod ovim uslovima u rastvoru se dobije 99.60% Co, 99.20% Ni i 96.80% Cu, dok je dobijeni procenat Fe 0.21%, a brzina filtracije suspenzije dobijene luženjem iznosi 576.86 L·m⁻²·h⁻¹. Mehanizam za postizanje selektivnog luženja nikla, kobalta i bakra i suzbijanja rastvaranja gvožđa, kao i postizanje dobre brzine filtracije suspenzije dobijene luženjem, dobijen je zbog gvožđa koje se rastvorilo u rastvoru, a zatim se hidrolizovalo do formiranja hematita (α -Fe₂O₃ i γ -Fe₂O₃), a takođe je omogućilo da silicijumska kiselina stvori talog SiO₂ u ostatku luženja.

Ključne reči: Konvertorska šljaka sa sadržajem nikla; Oksidaciono luženje pod pritiskom; Metodologija odgovora površine; Svojsva filtracije

