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Optimization of Cu and Mn Dissolution from Black Coppers by Means of an Agglomerate and Curing Pretreatment

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Abstract: Black coppers are mineraloids with a high content of Cu and Mn. These have an amorphous crystalline structure that makes them refractory to conventional leaching processes. For this reason, these mineral resources are not incorporated in industrial leaching heap processes and are taken to dumps. In the present study, an agglomerate pretreatment process incorporating NaCl is evaluated, and a curing stage, followed by acid-reducing leaching for Cu and Mn dissolution from a high-grade black copper mineral. For this, an experimental design was developed both to evaluate the impact of the dependent variables on the response, to generate analytical models that represent the copper and manganese recoveries under the set of sampled conditions. The models indicate that the curing time and the NaCl concentration have a primary effect on the recovery of both elements. In contrast, the optimization model suggests that the optimal operating levels are reached at relatively high levels of time (>130 h) and of NaCl concentration (>22 kg/t).

Keywords: exotic minerals; black copper; chloride reduction; pretreatment; modeling

1. Introduction

Historically, the two processes most used to extract Cu from mineral ores are the leaching and flotation processes [1–3], with the flotation process being much more used in the world (80–85% of total Cu production) [4]. However, flotation processes have a more significant negative impact on the environment due to the vast generation of tailings [5]. For every ton of Cu that is generated through flotation processes, 151 tons of tailings are produced [6]. Vast tailings dams are formed that cause acid drains due to the oxidation of pyrite, which leads to the contamination of the subsoil and nearby environment [7].

Currently, there is a depletion of high-grade copper minerals on the earth's surface. In 1900 copper ore grades averaged 4%, while today they are approximately 0.5% Cu [8]. Added to this is the depletion

of the oxidized minerals from the upper zone in the deposits, which forces to face exotic deposit areas with content of black oxides, green oxides and the presence of limonites associated with copper [9]. An example is northern Chile, where there are many porphyry copper-bearing deposits, which have developed supergene enrichment zones. In turn, underlying bodies with exotic mineralization because of lateral migration of solutions [10]. These exotic deposits have large areas, which is why they are a critical copper reserve that in the future must be exploited, where high-grade Cu oxides are present as copper pitch and copper wad [11]. The mentioned minerals are dark-colored Si-Fe-Cu-Mn-rich silicates that are difficult to recognize due to their complex mineralogical composition. Furthermore, they are defined as mineraloids by their amorphous crystallization [12].

Leaching processes are efficient for the treatment of low-grade copper ores at the industrial level using heap leach processes [13]. However, black copper minerals are refractory to conventional leaching processes due to their amorphous crystal structure [14]. For this reason, these mineral resources are not incorporated in current heap leaching processes [12].

Studies for the treatment of black copper are relatively recent. It has been shown that black copper minerals can be treated by the same acid-reducing mechanisms applied in previous investigations for the dissolution of manganese nodules [15–20]. Pérez et al. [12] carried out leaching tests using H_2SO_4 and ferrous ions for two black copper mineral samples, one with high purity and the other with a high content of tailings. The authors mention that the best results of their study (over 90% of Mn recovery) are obtained by working in a ferrous ions/black copper ratio of 2 and a concentration of H_2SO_4 of 1 mol/L. For the dissolution of black copper with H_2SO_4 and Fe^{2+} , the authors proposed the following reactions:

Subsequently, Torres et al. [21] developed a study to dissolve copper and manganese from pure black copper ore. In this study, pretreatment tests for agglomerate and curing by adding sulfuric acid and sodium chloride were carried out, followed by a leaching process with a reducing agent (Fe^{2+}) and standard condition (without reducing agent). The authors concluded that by working with a reducing agent, the highest manganese dioxide solutions are obtained. Furthermore, when working at standard condition, low Mn extractions are reached, and NaCl pretreatment did not influence the extractions. In contrast, a reducing acid medium, the pretreatment process contributed to getting higher Cu and Mn dissolutions.

For Cu and Mn dissolution from black coppers with Fe^{2+} and NaCl in an acidic medium, the following reactions are proposed [21]:

Chlorides are commonly used as an oxidizing agent for the extraction of Cu from oxidized and sulfided copper ores [22,23]. However, being in direct contact for prolonged periods, it can act as a reducing agent for MnO_2 [21]. Wang and Zou [24] reported standard redox potentials for the reduction of MnO_2 and chloride ions of $\text{Mn}_3\text{O}_4/\text{Mn}^{2+} = 1.76 \text{ V}$ and $\text{Cl}_2/\text{Cl}^- = 1.39 \text{ V}$, respectively.

Large-scale copper mining presents a series of challenges to overcome in the short term, such as the depletion of high-grade ores and the significant environmental liabilities generated by their processes.

Then, hydrometallurgical operations incorporate other mineral resources that had been considered to be waste in the past, but they arise as an exciting alternative. It is crucial to diversify the production, through the extraction of other abundant elements as Mn, and export them as a Cu by-product, for which black coppers are an abundant and high-grade Cu and Mn alternative.

In the present work, it is studied the manganese and copper recovery from black coppers using Fe^{2+} and NaCl, operating in an acidic medium and 25 °C. An experimental design is developed evaluating the responses to different configurations of the variables curing time and NaCl concentration (Fe^{2+} , H_2SO_4 , and temperature are considered constant). Samples were generated for seven levels of each independent variable, and multiple regression models were adjusted for explaining each response variable based on the variability of the regressors. Finally, the analytical models were optimized, considering the sampling domain of the independent variables as restrictions. This allows identification of the operating conditions (time and concentration of NaCl) that maximize the recovery of both responses.

2. Materials and Methods

2.1. Black Copper Sample

It is worked with the same mineral sample used in the study carried out by Torres et al. [21]. The ore was ground in a porcelain mortar to sizing between -173 and $+147\ \mu\text{m}$. The chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), where the mineral has 22.01% of Cu and 40.24% of Mn. A QEMSCAN (Quantitative Evaluation of Minerals by SCANning, (FEI Company, Brisbane, Australia) analysis was applied, which is a modified electronic scanning microscope, both in hardware and software. This performs the identification and automated quantification of ranges of elementary definitions that can be associated with inorganic solid phases (minerals, alloys, etc.). The samples were mounted on briquettes and polished to determine the mineralogical composition. The identification, mapping of 2-D distribution, and quantification of inorganic phases were made by combining the emissions of retro-dispersed electrons (BSE), with a Zeiss EVO series, a Bruker AXS XFlash 4010 detector (Bruker, Billerica, MA, USA), and the iDiscover 5.3.2.501 software (FEI Company, Brisbane, Australia). The QEMSCAN analyses are based on the automated obtaining of EDS spectra (dispersed energy from X-rays), in hundreds of thousands or millions of collected analysis points, each in a time of milliseconds. Each EDS spectrum was classified in a hierarchical and descending compositional list, known as the “SIP List.” The BSE image was used to discriminate between resin and graphite in the sample, to specify entries in the SIP List, and to establish thresholds for acceptance or rejection of particles. As a result, pixelated, 2-D and false-color images of a specimen or a representative subsample of particles are obtained. Each pixel retains its elementary and BSE brightness information, which allows subsequent offline data processing. Through software, customized filters are generated that quantify the ore and gangue species, mineral release, associations between inorganic phases, classifying particles according to criteria of shape, size, texture, etc. (See Table 1).

Table 1. Mineralogical composition of the black copper sample.

Mineral (% Mass)	Black Copper
Native Cu/Cuprite/Tenorite	0.12
Cu-Mn Wad	78.90
Chrysocolla	16.72
Other Cu Minerals	2.69
Goethite	0.01
Quartz	1.41
Feldspars	0.02
Kaolinite Group	0.01
Muscovite/Sericite	0.01
Chlorite/Biotite	0.01
Others	0.09
Total	100

2.2. Ferrous Ions

The ferrous ions used for this investigation ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$) were WINKLER brand, with a molecular weight of 278.01 g/mol. These were incorporated during the leaching process in stirred reactors, after the pretreatment process.

2.3. Pretreatment and Subsequent Leaching in Reactors

For the pretreatment, it is worked with 10 g of ore, adding 20 kg of $\text{H}_2\text{SO}_4/\text{t}$ (according to the level to be studied) (0.1 cm^3 of H_2SO_4) and different concentrations of NaCl (see Table 2). The sample and reagents were homogenized and subsequently placed on a Petri dish, which was covered with plastic to avoid evaporation. The temperature during the resting time (curing time) was controlled at 25°C with the use of an air conditioner. Subsequently, leaching tests in a time of 20 min, were carried out in a 100 cm^3 glass reactor with a 0.01 S/L ratio. A total of 10 g of black copper ore at different concentrations were mixed and dispersed with a five-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm. The temperature was controlled at 25°C using an oil-heated circulator (Julabo) (Julabo, St. Louis, MO, USA). All the tests were duplicated, and the measurements (or analyses) were carried out on 5 cm^3 undiluted samples using atomic absorption spectrometry with a coefficient of variation $\leq 5\%$ and a relative error between 5% to 10%. Measurements of pH and oxidation-reduction potential (ORP) of leach solutions were made using a pH-ORP meter (HANNA HI-4222) (HANNA instruments, Woonsocket, RI, USA). The ORP solution was measured in a combination ORP electrode cell of a platinum working electrode and a saturated Ag/AgCl reference electrode.

Table 2. Experimental levels of explanatory variables.

Curing Time (h)	NaCl (kg/t)
24	0
48	5
72	10
96	15
120	20
144	25
168	30

2.4. Design of Experiments

Two explanatory variables were selected for the experimental design, evaluating seven levels per factor, where: curing time and NaCl concentration represent the explanatory variables that explain the dependent variables manganese and copper recovery from black coppers in an acid medium [25]. The analysis through an experimental design allows the identification of the effect of both the factors and their levels in one or more explained variables, contributing to understanding the relevance of the factors considered. This generates an experimental model that allows optimization of the response refining the determining coefficients using a model of relevant factors [26]. The experimental design involved seven levels for each of the factors considered, resulting in 49 assays. The modeling, experimental design, and fitting of the multiple regression models were carried out using Minitab 18 software [27].

Then, the explained variable is expressed as a function of the linear, interaction and curvature effect of the explanatory variables, and the model to fit is presented in Equation (7). Where the parameter β_0 is the overall constant, x_s are the explanatory variables, β_s are the coefficients of the linear and the interactions between factors, n is the number of levels per factor, and Cu and Mn recovery are the explained variables copper and manganese recovery respectively.

$$\text{Cu, Mn Recovery (\%)} = \beta_0 + \sum_{i=1}^n \beta_i \times x_i + \sum_{i=1}^n \sum_{j=i}^n \beta_{ij} \times x_i \times x_j + \beta_{ijk} \times x_{ijk} \quad (7)$$

Table 2 presents the levels for each factor, while Appendix A presents the results obtained for each factor-level configuration.

3. Results and Discussions

3.1. Graphic Analysis and Analytical Models

From the principal component analysis (see Figure 1), the main effect is caused by curing time and NaCl concentration, since the variation between the levels of explanatory variables affects the copper (see Figure 2) and manganese (see Figure 3) recovery [28]. The multiple regression adjustment models for copper and manganese recovery are given by Equations (8) and (9).

$$\text{Cu Recovery (\%)} = 44.72 + 0.3340x_1 + 1.417x_2 - 0.001249x_1^2 - 0.03014x_2^2 \quad (8)$$

$$\text{Mn Recovery (\%)} = 37.20 + 0.3058x_1 + 1.215x_2 - 0.000971x_1^2 - 0.02714x_2^2 \quad (9)$$

where x_1 and x_2 represents curing time and NaCl concentration, respectively. Then, the linear and curvature effects of both factors help to explain the variability of analytical models fitted (Equations (8) and (9)).

Figure 1. Main effects plot of Cu recovery (a) and Mn recovery (b) versus curing time (h) and NaCl concentration (kg/t).

Figure 2. Contour plot of Cu recovery (%) versus NaCl concentration and curing time (h).

Figure 3. Contour plot of Mn recovery (%) versus NaCl concentration and curing time (h).

The ANOVA results indicate that both analytical models (Equations (8) and (9)) adequately represent the copper and manganese extraction in acidic media for the sampled domain. The regression models do not require additional adjustments and are validated by p-value and R^2 statistics. The p-value of both models ($p < 0.05$) and R^2 statistics, 81.80% (Equation (8)) and 85.2% (Equation (9)) indicate that these are statistically significant, while the predictive R^2 statistics are 77.4% and 81.3%, indicating that both models can adequately describe the explained variables in front of new observations [29]. Additionally, F tests $F_{\text{regression}}(49.45, 63.43) > F_{\text{Table}}(3, 0.0279)$, reinforce the explanatory capacity of both models.

The residual normality test indicates that these are distributed between -4×10^{-3} and -3×10^{-3} , with standards deviations of 1.010 and 1.014, and p values of the Kolmogorov–Smirnov test are higher than the significance level. This support the hypothesis that the data follow a normal distribution. On the other hand, the response surface of the analytical models adjusted for copper (see Figure 4a) and manganese recovery (see Figure 4b) from black copper indicates that the optimal levels of operation are high ranges of curing time and NaCl concentration. It has been shown in previous studies for Cu sulfurized minerals that long curing times and high chloride concentrations in the system favor the extraction of this element [23,30–32]. In the study carried out by Cerda et al. [23] the authors performed a pretreatment process with H_2SO_4 (20 kg/t) and NaCl at different concentrations (20, 50 and 90 kg/t). It was concluded that the curing time is the most important factor to increase copper extractions, while that chloride concentration in the system being less relevant.

Figure 4. Response surface for Cu (a) and Mn (b) recovery as function of the independent variables curing time and NaCl concentration.

Furthermore, Pérez et al. [12] dissolved MnO_2 from black coppers using sulfuric acid and ferrous ions, the authors indicate that the best results are obtained by operating in high concentrations of reducing agent in the system, significantly decreasing leaching times. On the other hand, Torres et al. [21]

indicate that by successfully dissolving MnO_2 from black copper, it is possible to facilitate the extraction of Cu from this type of minerals; therefore, the dissolution rate of Cu is proportional to the dissolution rate of Mn and the concentration of reducing agent. The results obtained in the analytical models for the extraction of copper and manganese are consistent with the results obtained in previous studies, where it is indicated that long curing times and a high concentration of reducing agent significantly favor Cu and Mn extraction.

Optimizing the response for the analytical models that model manganese and copper recovery, the optimal recovery for both manganese and copper analytical models is approximately 75% and 84%, respectively, as shown in Figures 5 and 6. The level of the factors in the optimal conditions are presented in Table 3.

Figure 5. Settings and sensitivity for optimal solution for Mn recovery (%).

Figure 6. Settings and sensitivity for optimal solution for Cu recovery (%).

Table 3. Optimal configurations of response variables.

Model/Variable	Curing Time (h)	NaCl (kg/t)	Optimal (%)
Mn recovery	157.8	22.4	74.9
Cu recovery	133.0	23.6	83.7

3.2. Effects of Redox Potential and pH on the System

It is found that there are significant differences in the redox potential of the system for the different levels of the curing time variable ($p < 0.05$). Meanwhile, there is no evidence to conclude that the mean values of potential differ with varying concentrations of NaCl, at a significance level of 0.05, which is validated by the comparisons of the intervals of the mean values shown in Figure 7, and the statistics presented in Table 4.

Additionally, there are significant differences in the pH for different levels of curing time ($p < 0.05$) and NaCl concentrations ($p < 0.05$). However, for the intermediate levels of the domain of NaCl concentration (Figure 8b), the intervals overlap, indicating that there are no differences in this subdomain.

Table 4. ANOVA of the effects of cure time and NaCl concentration on system potential and pH.

Response	Variable	F-Value	p-Value
Eh (V)	Curing time	225.96	0.000
	NaCl concentration	0.1	0.996
pH	Curing time	8.07	0.000
	NaCl concentration	2.79	0.022

Figure 7. Comparison plots of means for the potential of the system in function of different levels of curing time (a) and NaCl concentration (b).

Figure 8. Comparison plots of means for pH of the system in function of different levels of curing time (a) and NaCl concentration (b).

The response surface for the redox potential (Figure 9a) and pH (Figure 9b) indicate that the curing time is the most important variable to reduce the potential of the system. This agrees with what was stated by Wang [24] who mention that chloride shows good results as a MnO_2 reducing agent in long contact times. Additionally, it is observed that the concentration of NaCl also contribute to decreasing the redox potential, as the cure time increases. This is consistent with what was stated in previous studies for MnO_2 acid-reducing processes, where it is indicated that with a higher concentration of reducing agent, both kinetics and Mn extraction increased [19,33].

Figure 9. Surface plot for Eh (a) and pH (b) in function of different levels of curing time and NaCl concentration.

4. Conclusions

The present research studied the dynamics of a black copper acid-reducing leaching process, determining the impact of curing time and NaCl concentration on copper and manganese recovery. A statistical model was generated for each response variable, and the main findings:

(1) The ANOVA test indicates that both independent variables (curing time and NaCl concentration) influence the responses, and the principal component analyzes, and goodness of fit indicators validate it. On the other hand, the optimal operating parameters for both manganese and copper recovery are found when operating at relatively high levels of time (>130 h) and NaCl concentration (>22 kg/t).

(2) Prolonged curing times favor the reduction of MnO_2 present in black coppers, and in turn, increase Cu solutions in a subsequent leaching process.

(3) High curing times and high NaCl concentrations favor the decrease of the potential of the system, allowing a more efficient dissolution of MnO_2 .

(4) When working at long curing times, there is no need for a significant increase in the NaCl concentration in the system.

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Conflicts of Interest: The authors declare they have no conflict of interest.

Appendix A

Table A1. Sampling Results of the Experiment Design.

No.	Curing Time (h)	NaCl (kg/t)	Mn Recovery (%)	Cu Recovery (%)	Eh (V)	pH
1	24	0	45	49	1.5	−0.4
2	24	5	51	58	1.5	−0.3
3	24	10	52	60	1.4	−0.4
4	24	15	52	61	1.4	−0.4
5	24	20	52	61	1.4	−0.4
6	24	25	53	66	1.3	−0.5
7	24	30	54	69	1.4	−0.5
8	48	0	51	59	1	−0.4
9	48	5	62	74	1	−0.3
10	48	10	64	74	0.5	−0.1
11	48	15	64	75	0.5	−0.2
12	48	20	65	77	0.5	0.1
13	48	25	65	77	0.1	0.1
14	48	30	67	79	0.2	0.1
15	72	0	52	53	−0.3	−0.3
16	72	5	63	76	−0.4	−0.1
17	72	10	63	77	−0.3	−0.1
18	72	15	64	78	−0.3	−0.2
19	72	20	65	79	−0.6	−0.2
20	72	25	65	79	−0.5	−0.1
21	72	30	67	80	−0.6	0.2
22	96	0	55	61	−1.1	−0.4

Table A1. Cont.

No.	Curing Time (h)	NaCl (kg/t)	Mn Recovery (%)	Cu Recovery (%)	Eh (V)	pH
23	96	5	68	75	−1	−0.2
24	96	10	70	77	−0.8	0.1
25	96	15	70	78	−1	0.2
26	96	20	70	80	−0.9	0.1
27	96	25	71	81	−0.9	0.2
28	96	30	73	81	−1	0.2
29	120	0	54	63	−0.8	−0.4
30	120	5	67	75	−0.9	0.1
31	120	10	70	77	−1	0.1
32	120	15	69	78	−1.2	0.1
33	120	20	70	80	−1.1	0.3
34	120	25	70	81	−1.2	0.5
35	120	30	73	81	−1.2	0.6
36	144	0	55	64	−1.3	−0.3
37	144	5	69	77	−1.1	0.3
38	144	10	71	77	−1.5	0.2
39	144	15	71	79	−1.4	0.4
40	144	20	72	79	−1.4	0.2
41	144	25	72	80	−1.4	0.3
42	144	30	74	82	−1.5	0.5
43	168	0	56	66	−1.2	−0.1
44	168	5	72	79	−1.2	0.2
45	168	10	74	79	−1.1	0.2
46	168	15	75	80	−1.3	0.2
47	168	20	75	82	−1.6	0.2
48	168	25	76	83	−1.5	0.5
49	168	30	76	83	−1.6	0.4

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