

Statistical and kinetic study for leaching of covellite in a chloride media

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Abstract

Covellite is a relatively rare copper sulfide with slow dissolution kinetics. The present investigation used the surface optimization methodology to evaluate the effect of three independent variables (time, chloride concentration and sulfuric acid concentration) on the rate of extracting Cu from covellite. The effects of chloride concentration and temperature over time were also studied. An ANOVA indicated that the linear variables of time and chloride concentration have the greatest influence, this being highly representative ($R^2 = 0.9945$). The highest copper extraction rate (71.23%) at room temperature, was obtained with a high chloride concentration (100 g/L), a low concentration of sulfuric acid (0.5 M), and a leaching period of 600 h. The dissolution is described by the model of the unreacted core, the rate of leaching of the covellite is controlled by the chemical surface reaction at temperatures between 50 and 90°C, with concentrations of 0.5 M of H₂SO₄, 100 g/L of chloride, and a leaching period of up to 6 hours, where an activation energy of 72.36 kJ/mol was obtained.

Keywords: Leaching, covellite, chloride media, kinetic study

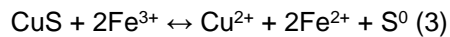
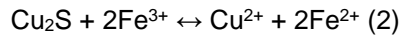
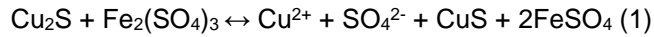
1. Introduction

While Covellite is not abundant, it is found in many copper deposits as a supergenic mineral, usually as a coating in the sulfide enrichment zone. It is associated with other minerals, mainly chalcocite, chalcopyrite, bornite and enargite, from which it is derived by alteration (Klein & Hurlbut, 1996). Covellite is of interest because of the quantity found in oxide ores, and because it is an intermediate product in converting chalcopyrite (Lundström et al., 2016) and in transforming digenite to covellite in oxygenated media (Ruiz et al., 1998; Senanayake, 2007)

Sulfurized copper ores are generally treated by flotation-smelting-refining (Schlesinger et al., 2011; Shuva et al., 2016; Turan et al., 2017). Although they have reported economic (Kelm et al., 2014) and metallurgical viability, there are environmental problems associated with the emission of sulfur dioxide and arsenic (Afif et al., 2008; Dijksira et al., 2017; Dimitrijević et al., 2009; Sánchez de la Campa et al., 2008; Serbula et al., 2017). Arsenic emissions, which have been increasing steadily in recent decades with increasing extraction of copper sulfide (Balladares et al., 2018), present a danger to human health related to higher incidence of cardiovascular and respiratory diseases and cancer (World Health Organization, 2018). This has resulted in stricter environmentally-motivated controls. Hydrometallurgical methods are generally preferred to recover copper from complex low-grade minerals because of the low cost, short construction time, operational simplicity, and good

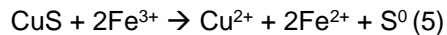
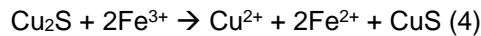
performance (Baba et al., 2017), as well as environmental benefits (González et al., 2005; Lü et al., 2018; Rabadjieva et al., 2009), in terms of yielding solid waste that is not considered hazardous.

Sulfuric acid and an oxidizing agent are required to break down sulfurized copper ores and release Cu^{2+} in solution. All copper sulfides require the presence of Fe^{3+} and O_2 as oxidizing agents for leaching to occur. Copper sulfide is oxidized by the presence of Fe^{3+} . The resulting Fe^{2+} is reoxidized to Fe^{3+} by O_2 . The redox pair $\text{Fe}^{2+}/\text{Fe}^{3+}$ act as a catalyst in these reactions. The following reactions occur with the main secondary copper mineral, chalcocite, when the temperature is high (Equation 1) and the sulfur is in the form of sulphate and not elemental sulfur, as in natural conditions (Equations 2 and 3) (Schlesinger et al., 2011):

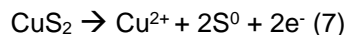
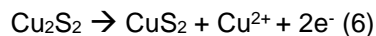


Several investigations into leaching covellite have proposed hydrometallurgical approaches with different dissolution media, including ammonia (Baba et al., 2017; Reilly & Scott, 1976), nitrates (Fisher, 1994; Vračar, et al., 2003), chlorides (Cheng & Lawson, 1991; Miki et al., 2011; Nicol & Basson, 2017; Senanayake, 2007) and bioleaching with bacteria like thiobacillus ferrooxidans, acidithiobacillus ferrooxidans and acidithiobacillus thiooxidans, which can grow under anaerobic conditions where ferric ions are used as electron receptors (Donati et al., 1997; F. Monteiro et al., 1999; Falco et al., 2003; Lee et al., 2011).

The oxidative dissolution of the chalcocite occurs in two stages in sulphated or chlorinated media (Cheng & Lawson, 1991; Miki et al., 2011; Niu et al., 2015; Ruiz et al., 2007; Senanayake, 2009).



According to Niu et al. (2015), leaching from chalcocite to covellite is rapid (Equation 4) because of the low activation energy needed (4-25 kJ/mol), the reaction being controlled by the diffusion of the oxidant on the mineral surface, while the process expressed in Equation 5 is slower. Ruan et al. (2013) and Miki et al. (2011) argued this Equation 5 is slow because this reaction is chemically and/or electrochemically controlled and therefore requires activation energy of around 71.5-72 kJ/mol to transform covellite into dissolved copper. Nicol & Basson (2017) recently suggested that covellite oxidation occurs as an intermediate stage in which it is transformed into polysulfide CuS_2 :



Covellite can be oxidized over a wide range of chloride concentrations or potential to the CuS_2 polysulfide, but oxidation of CuS_2 can only occur under conditions of high chloride concentrations or high potentials (Nicol & Basson, 2017).

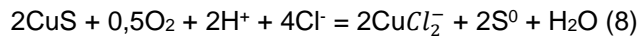
Copper chloride-based processes are especially suitable for leaching non-ferrous minerals like chalcocite, digenite and covellite, since in these cases the leaching solutions contain low levels of dissolved iron (Ruiz et al., 1998).

In this study, two pure covellite leaching tests will be carried out in a chlorided medium in addition to oxygen. The first one will be under temperature and pressure ambient to determine the influence of the parameters to be statistically analyzed; such as sulfuric acid dosage, sodium chloride dosage

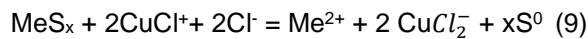
and the effect of time in copper extraction until a representative quadratic model of copper extraction is obtained based on these parameters. The second part consists of tests with the temperature to analyze its effect on the kinetics of copper dissolution, calculate the activation energy and the controlling stage of the mineral under the described conditions and according to the model of the unreacted core.

Thermodynamics

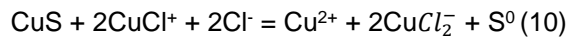
A covellite leaching is performed with the injection of O₂ at ambient pressure into a solution of H₂SO₄-NaCl. In this leaching investigation of copper sulfide, no ferric ions are added but copper-chloride complexes are added, hence, the leaching agents change. It is proposed to obtain a soluble product of CuCl₂⁻ so the general reaction is:



The general reaction for the dissolution of a sulfide with metal in a chlorinated environment is described by Lundstrom et al. (2016) in equation:



And in the case of the leaching of covellite in chlorinated environment, the following reaction is obtained:



According to the information given in table 1, the difference between equation 8 and 10 is the addition of O₂ and H⁺, with equation 8 above 10 being very favorable due to the diffusion of oxygen in covellite leaching.

Cu²⁺, CuCl⁺ and CuCl₂⁻ are the stable species of Cu²⁺/Cu⁺ in a solution at 25 ° C, and with a chloride concentration range of between 0.02 - 2 M. According to Senanayake (2007), CuCl⁺ is the predominant species of Cu²⁺ at a low chloride concentration (<0.5 M) (Cheng & Lawson, 1991), while CuCl₂⁻ is the predominant Cu⁺ species at 25 ° C. In contrast, CuCl₂ is the most stable Cu²⁺ species at high temperature (102 °C) and high concentrations of chloride.

Within the reactions that occur in the leaching of covellite with the use of NaCl, Cu²⁺ and the addition of O₂, leaching agents, such as Cu²⁺, CuCl⁺, CuCl₂ and CuCl₃⁻, are continuously generated during leaching (Herreros & Viñals, 2007; Senanayake, 2007) where finally a soluble product of CuCl₂⁻ (chloro complex), and a residue of elemental sulfur (S⁰) will be obtained.

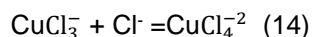
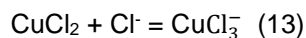
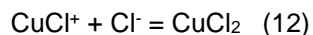
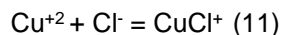
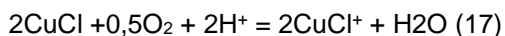
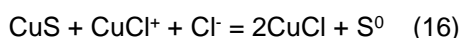
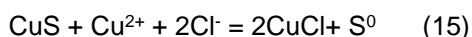


Table 1 shows all the interesting reactions within the leaching of covellite in a chlorinated medium, analyzing the free energy of Gibbs at temperatures of 25 ° C and 90 ° C. Equilibrium constants are based on Outokumpu HSC 5,1 Software.

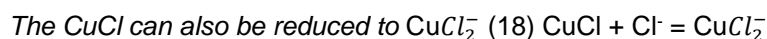
Table 1. Equilibrium constants for reactions at temperatures of 25°C and 90°C.

No Rx	Equilibrium constant (K)		Gibbs free energy (kJ)
	25°C	90°C	25°C
3	$4,433 \times 10^4$	6.962×10^5	-26,521
8	$6,253 \times 10^{14}$	6.942×10^{11}	-84,448
10	$5,033 \times 10^{-7}$	2.276×10^{-5}	35,946
11	2,982	5.343	-2,708
12	$2,843 \times 10^{-5}$	1.185×10^{-3}	25,947
13	$6,053 \times 10^1$	1.318	-10,17
14	5×10^{-3}	1.207×10^{-3}	13,133
15	$4,249 \times 10^{-3}$	3.206×10^{-1}	13,536
16	$1,425 \times 10^{-3}$	6.002×10^{-2}	16,244
17	$2,924 \times 10^{23}$	9.513×10^{16}	-133,93
18	$3,245 \times 10^{-2}$	$4,501 \times 10^{-2}$	8,497

In the reactions of the covellite solution, there is the possibility of obtaining a solid product of CuCl, although this can be reoxidized in CuCl⁺ which is used as a leaching agent.



It is emphasized that with the addition of oxygen and H⁺, this reaction is spontaneous.



However, this reaction is not spontaneous even at a temperature of 90 ° C.

2. Experimental

2.1 Materials

The covellite sample used in this research was obtained from Michilla mine Using a porcelain mortar, the sample (apparently pure) was reduced to a size range of -150 to +106 μm, and then chemically analyzed by atomic emission spectrometry via induction-coupled plasma (ICP-AES) at the applied geochemistry laboratory of the Geological Sciences Department of the Universidad Católica del Norte. Table 2 shows the chemical composition of the samples.

Table 2. Chemical analysis of the covellite ore

Element	Cu	S	Ca	O	H
Mass (%)	56.14	31.08	3.66	8.76	0.36

The studied sample was also analyzed mineralogically. Fig. 1 shows the chemical species identified by QEMSCAN. Covellite was the most abundant mineral present (84.29%), followed by a much lower percentage of gypsum (15.71%).

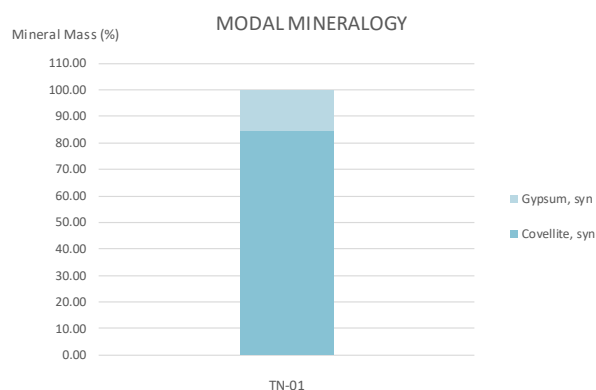


Fig. 1. Detailed modal mineralogy

2.2 Reagent and leaching test

The sulfuric acid used in the leaching tests was grade P.A, Merck brand, with a purity of 95-97%, a density of 1.84 kg/L, and a molecular weight of 98.08 g/mol.

The leaching tests were carried out in a 50-mL glass reactor with a 0.01 S/L ratio of leaching solution. A total of 200 mg of covellite ore was maintained in agitation and suspension in a 5-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at a speed of 600 rpm with an oxygen addition of 6 mL/min connecting a hose to the reactor. The tests were conducted at a room temperature of 25°C, with variations in sulfuric acid and chloride concentrations and leaching time. In the temperature-controlled experimental trials, a coolant was added to the top, thereby avoiding evaporation losses. The coolant was added in combination with water, at ambient temperature (25°C), and interacts with the outgoing hot gas, causing it to condense back into liquid form. Also, the tests were performed in duplicate, measurements (or analyses) were carried on 5 mL 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). The solution ORP was measured in a combination ORP electrode cell composed of a platinum working electrode and a saturated Ag/AgCl reference electrode.

2.3 Experimental Design

The effects of independent variables on Cu extraction rates from leaching covellite were studied using the response surface optimization method (Aguirre et al., 2016; Bezerra et al., 2008; Dean et al., 2017; Toro et al., 2018). The central composite face design (CCF) and a quadratic model were applied to the experimental design for leaching CuS.

Twenty-seven experimental tests were carried out to study the effects of time, and chloride and H₂SO₄ concentrations as independent variables. Minitab 18 software was used in the modeling and experimental design to study the linear and quadratic effects of the independent variables. The experimental data were fitted by multiple linear regression analysis to a quadratic model, considering only those factors that helped to explain the variability of the model. The empirical model contained coefficients of linear, quadratic, and two-factor interaction effects.

The general form of the experimental model is represented by (Equation 19):

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 \quad (19)$$

Where, x_1 is time, x_2 is Chloride, x_3 is H₂SO₄ concentration, and b is the variable coefficients

Table 3 shows the ranges of the parameters used in the experimental model. The following equation (Equation 20) transformed real values (Z_i) into coded values (X_i) according to the experimental design:

$$X_i = \frac{Z_i - \frac{Z_{high} + Z_{low}}{2}}{\frac{Z_{high} - Z_{low}}{2}} \quad (20)$$

Where Z_{high} and Z_{low} are respectively the highest and lowest levels of a variable (Montgomery, 2012).

Table 3. Experimental configuration and Cu extraction data

Exp. No.	Time (h)	Cl (g/L)	H ₂ SO ₄ (M)	Cu extraction rate (%)
1	48	20	0.5	2.50
2	48	50	0.5	3.50
3	48	100	0.5	6.00
4	48	20	1	3.00
5	48	50	1	3.63
6	48	100	1	9.13
7	48	20	2	3.25
8	48	50	2	5.50
9	48	100	2	11.38
10	72	20	0.5	5.13
11	72	50	0.5	8.75
12	72	100	0.5	11.25
13	72	20	1	5.88
14	72	50	1	9.25
15	72	100	1	13.88
16	72	20	2	6.38
17	72	50	2	11.63
18	72	100	2	18.75
19	144	20	0.5	24.63
20	144	50	0.5	24.88
21	144	100	0.5	28.75
22	144	20	1	26.25
23	144	50	1	29.75
24	144	100	1	35.00
25	144	20	2	28.75
26	144	50	2	31.25
27	144	100	2	38.75

The statistical R^2 , R^2_{adj} , p-values and Mallows's C_p indicate whether the model obtained is adequate to describe Cu extraction under a given domain. The R^2 coefficient is a measure of the goodness of fit, that is, it measures the proportion of total variability of the dependent variable with respect to its mean, which is explained by the regression model. The p-values represent statistical significance, which indicates whether there is a statistically significant association between the response variable and the term. The predicted R^2 was used to determine how well the model predicts the response for new observations. Finally, Mallows's C_p is a precise measure in the model, estimating the true parameter regression (Montgomery et al., 2012).

3. Results

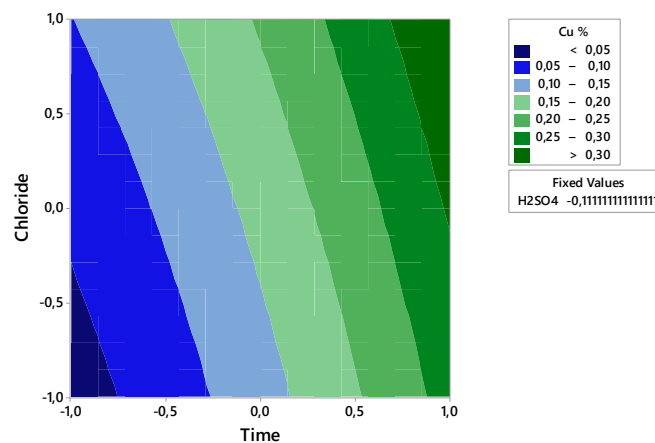
3.1. Methodology

An ANOVA analysis (Table 4) showed no significant effect of the interaction {time, Cl} ($p > 0.05$) on the copper extraction rate. The effects of the curvature of chloride are not significant in explaining the variability of the model. However, the effects of the curvature of time and H_2SO_4 must also be considered ($p < 0.1$).

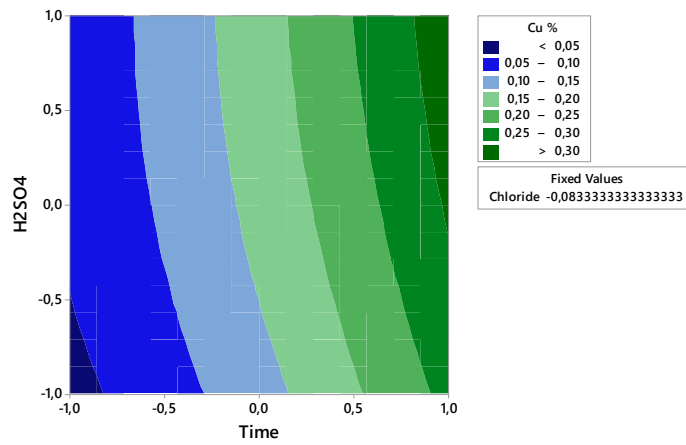
Table 4. ANOVA Cu extraction

Source	F-Value	p-Value
Regression	371.42	0.000
Time	2624.36	0.000
Cl	257.04	0.000
H_2SO_4	105.5	0.000
Time*Time	9.7	0.006
Cl*Cl	0.56	0.466
H_2SO_4 * H_2SO_4	3.39	0.083
Time*Cl	0.81	0.379
Time* H_2SO_4	11.22	0.004
Cl* H_2SO_4	22.6	0.000

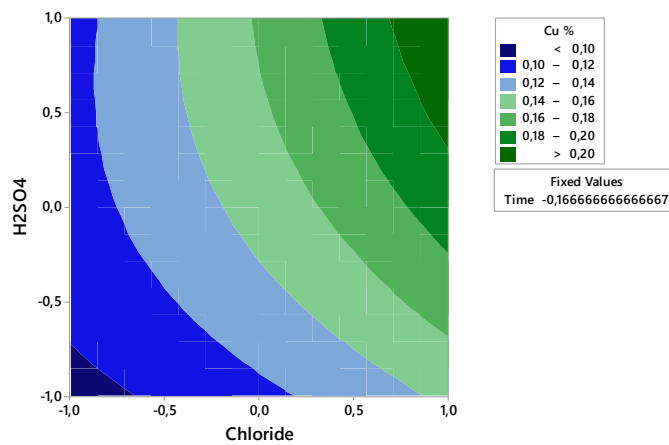
The contour plot in Fig. 2 shows that the Cu extraction rate increases with more time, and higher concentrations of chloride and H_2SO_4 .



(a)



(b)



(c)

Fig. 2. Experimental contour plot of Cu extraction in response to the independent variables of time and chloride (a), time and H₂SO₄ concentration (b), and chloride concentration and H₂SO₄ concentration (c).

Fig. 3 and 4 show that the interactions of time, chloride and H₂SO₄ concentration, and of time-H₂SO₄ and Cl-H₂SO₄ affected the Cu extraction rate.

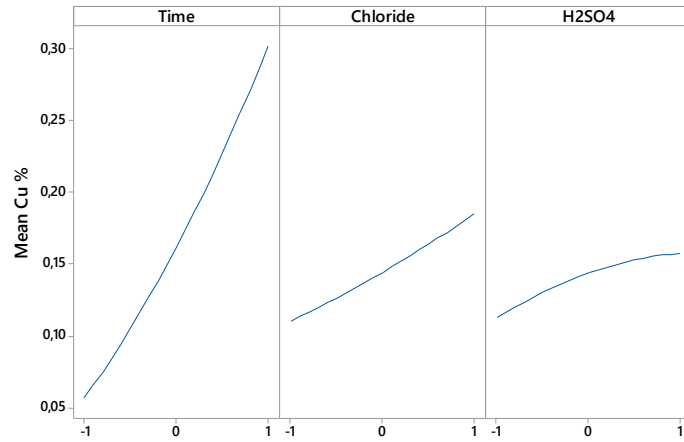
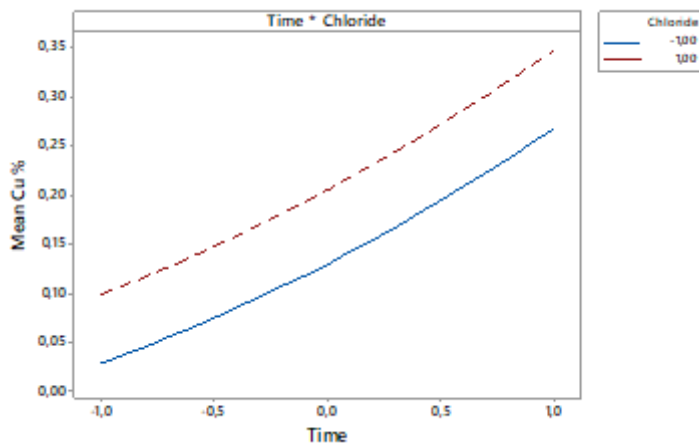
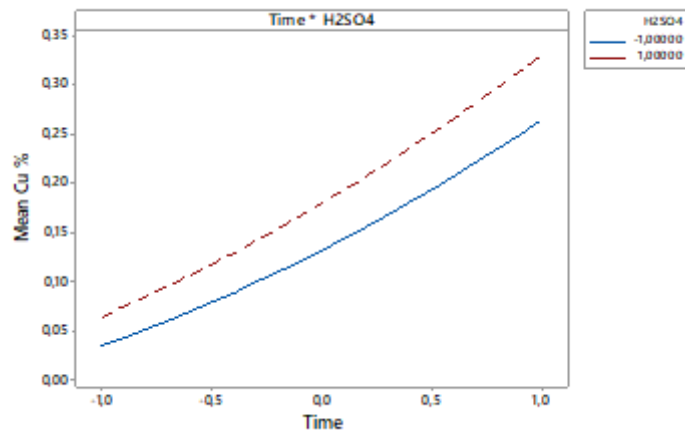


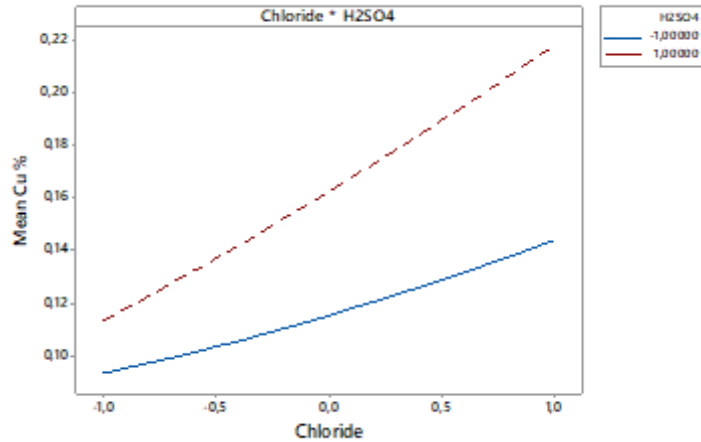
Fig. 3. Linear effect plot for Cu extraction



(a)



(b)



(c)

Fig. 4. Plot for the effect on Cu extraction of the Interactions of time-chloride (a), time-H₂SO₄ concentration (b), and chloride-H₂SO₄ (c).

Equation (21) presents the Cu extraction rate over the range of experimental conditions after eliminating non-significant coefficients.

$$\begin{aligned} \% \text{ Extraction} = & 0,16969 + 0,12332 x_1 + 0,03904 x_2 + 0,02502 x_3 + 0,01782 x_1^2 - 0,00870 x_3^2 \\ & + 0,00921 x_1 x_3 + 0,01347 x_2 x_3 \end{aligned} \quad (21)$$

where x_1, x_2 y x_3 are codified variables that respectively represent time and chloride and H₂SO₄ concentrations.

An ANOVA test indicated that the quadratic model adequately represents Cu extraction from CuS under the established ranges of the parameters. The model did not require adjustment and was validated by the R^2 (0.9945) and R^2_{adj} values (0.9925). The ANOVA showed that the indicated factors influence Cu extraction from CuS, as indicated by regression $F_{reg} (371.42) > F_{T,95\% \text{ confidence level } F_{7,19}} (2.543)$.

The p-value of the model is $0.000 < 0.05$, as represented by Equation (21), which indicates that the model is statistically significant.

The Mallows's $C_p = 7.37$ (constant + 7 predictors) indicates that the model is accurate and does not present bias in estimating the true regression coefficients. It also allows for prediction with an acceptable margin of error of $R^2_{pred} = 0.9888$.

Finally, the adjustment of the ANOVA analysis indicated that the factors considered explained the variations in the response. The difference between R^2 and R^2_{pred} of the model was minimal, thus reducing the possibility that the model was overly adjusted, that is, a lower probability that the model only fits the sample data. The ANOVA analysis indicated that time, chloride and H₂SO₄ concentrations, and the interactions of time-H₂SO₄ and chloride-H₂SO₄ are the most important factors in explaining the behavior of the system for the sampled data set.

3.2 Effect of chloride concentration

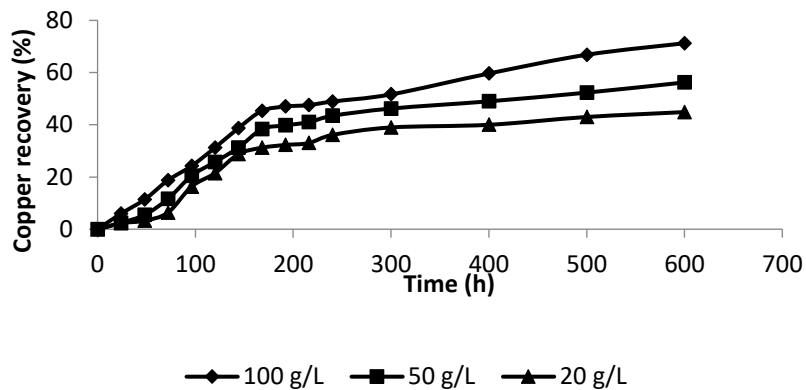


Fig. 5. Extraction of Cu (%) vs time (h), depending on the addition of chloride

Fig. 5 shows that the highest rate of copper extraction (71.23%) was obtained with high concentrations of chloride ions (100 g/L), thus demonstrating the effect of a higher chloride ion concentration on copper extraction (Miki et al., 2011; Senanayake, 2007). However, according to Cheng and Lawson (1991), there is a ceiling of 0.25 M, above which higher concentrations of chloride have insignificant effects on covellite dissolution, while in the range of 20 to 50 (g/L), chloride has no positive effects based on the leaching time, obtaining maximum copper extractions of 44.87 and 56.23%, respectively. This concurs with the results of other investigations (Miki et al., 2011), which indicate that CuS oxidation to CuS₂ is possible with any chloride concentration, but the oxidation of CuS₂ is only possible with very high potential or high chloride concentrations (Nicol & Basson, 2017).

3.3 Effect of temperature

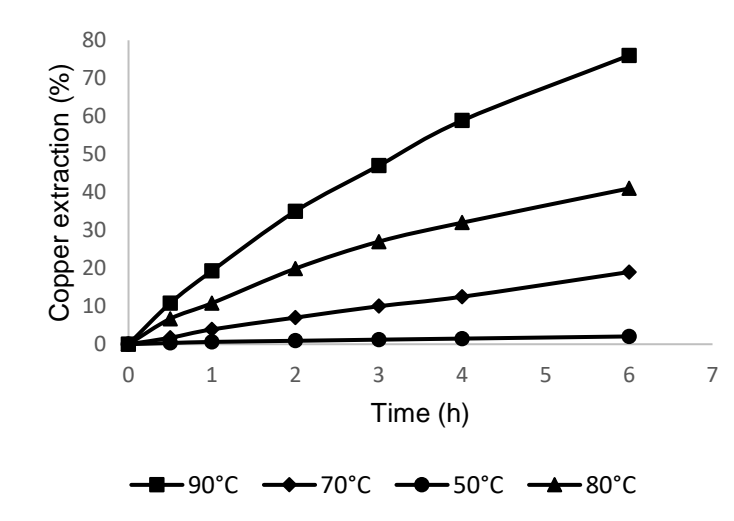


Fig. 6. Cu extraction (%) vs time (h), based on the T ° C

Fig. 6 shows the effect of temperature on a covellite solution in a medium with a high concentration of chloride and a low concentration of sulfuric acid. The copper extraction rate varied by up to 74% with temperatures of 90 °C and 50 °C, with a leaching period of 6 hours. The analysis of the effect of

temperature on the copper extraction rate confirmed the significant effect of this parameter on leaching, and in this case, the increase in leaching kinetics with 0.5 M of H₂SO₄, 100 g/L of chloride and a leaching time of up to 9 hours. According to Ruan et al. (2013) and Miki et al. (2011), covellite dissolution is controlled by chemical surface reaction. The unreacted core model is used to describe the kinetics of covellite leaching with the application of Equation 22:

$$Kt=1-(1-\alpha)^{1/3} \quad (22)$$

where:

α is the fraction of dissolved copper, t is leaching time, and k is the reaction rate constant

Using the slopes of the extraction curves as a function of temperature, the linear zones were shortened by approximately 2 hours), yielding the Arrhenius plot in Fig. 7, and resulting in an activation energy of 72.36 kJ/mol, which was similar to the levels in other investigations under similar conditions, such as in Cheng and Lawson (1991), who obtained an activation energy of 77 kJ/mol with the addition of 0.5 M of H₂SO₄ and 0.5 M of NaCl, and in Miki et al. (2011), who obtained an activation energy of 72 kJ/mol, with low temperature (25-45 °C), an extended leaching period, and the addition of iron and copper catalysts.

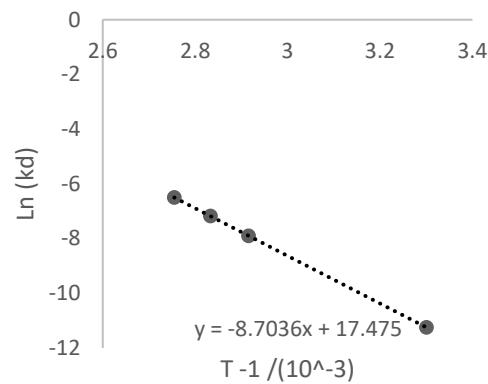


Fig. 7: Arrhenius plot for covellite dissolution using linear slopes of the curves in Fig. 6.

Residues analysis:

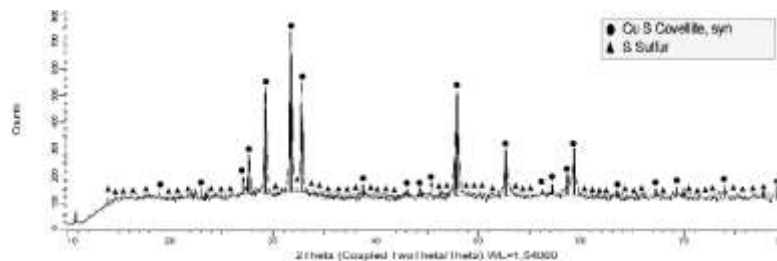


Fig. 8: X-ray diffractogram for the covellite mineral after being leached at 90 ° C in a time of two hours.

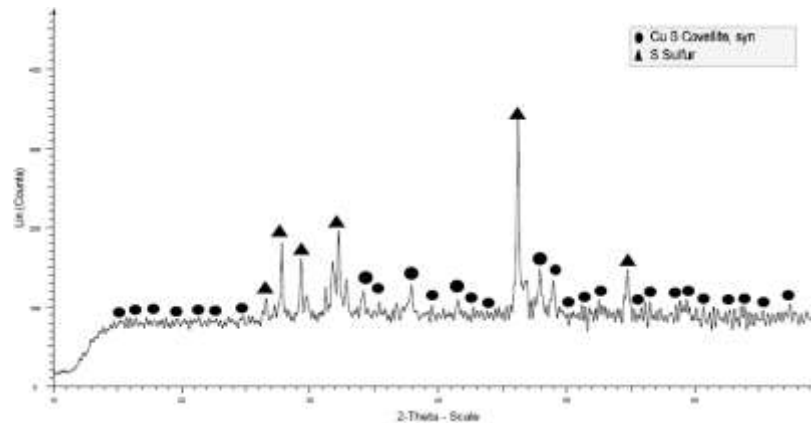


Fig. 9: X-ray diffractogram for the covellite mineral after being leached at 90 ° C in a time of six hours

An analysis is made about the XRD of the residues comparing them with the initial state which contains an approximate 15.71% of gypsum. In fig. 8, the diffractogram is presented where the transformation of the covellite is observed after a leaching of two hours at a temperature of 90 ° C under conditions of 1 M H₂SO₄ and 100 g/L NaCl a 35% of copper is extracted in solution, with 85.34% covellite and 14.66% elemental sulfur remain in the residue. In fig. 9, the XRD shows the covellite transformation after six hours of leaching at a temperature of 90 ° C under conditions of 1 M H₂SO₄ and 100 g/L NaCl, achieving the extraction of 76% of copper, remaining in the residual of 47% “synthetic covellite”, which is presumed to be CuS and CuS₂, as mentioned by Nicol & Basson (2017). Although the XRD only shows a synthetic covellite, accompanied by 53% of elemental sulfur, what stands out is that the gypsum remains that were present in the initial mineral were not observed in figures 8 and 9. The CuS₂ mineral is slower than the covellite and therefore requires more demanding conditions and/or longer times to complete the extraction of Cu.

4. Conclusions

The present investigation shows the laboratory results of dissolving Cu from covellite in chlorinated media. The highest Cu extraction rate was obtained with high concentrations of chloride in the system. The findings of this study were:

1. The linear variables of time and chloride concentration have the greatest influence in the model.
2. Under normal conditions of pressure and temperature, H₂SO₄ concentration-time and chloride concentration-time have synergistic effects on copper extraction from covellite.
3. The Anova analysis indicates that the presented quadratic model adequately represents copper extraction, which is validated by the R² value (0.9945).
4. The highest copper extraction rate working at room temperature of 71.23% was obtained with a low concentration of sulfuric acid (0.5 M), a high concentration of chloride (100 g/L) and an extended leaching time (600 h).
5. Regarding the temperature control (50-90°C) in leaching conditions of 0.5 M of H₂SO₄, 100 g/L chloride and leaching time of 6 hours, an activation energy of 72.36 kJ/mol is observed, indicating that the rate of dissolution of the mineral is indeed limited by the chemical reaction.
6. In the XRD carried out in the leaching residues at 2 and 6 hours at a temperature of 90 ° C, the formation of elemental sulfur is observed, which is expected as a stable and non-polluting residue.

Acknowledgments: The authors are grateful for the contribution of the Scientific Equipment Unit-MAINI of the Universidad Católica del Norte for aiding in generating data by automated electronic microscopy QEMSCAN® and for facilitating the chemical analysis of the solutions. We are also grateful to Marina Vargas Aleuy and Carolina Ossandón Cortés of the Universidad Católica del Norte for supporting the experimental tests

References

- Afif, C., Chélala, C., Borbon, A., Abboud, M., Adjizian-Gérard, J., Farah, W., ... Rizk, T. (2008). So₂in Beirut: Air quality implication and effects of local emissions and long-range transport. *Air Quality, Atmosphere and Health*, 1(3), 167–178. <https://doi.org/10.1007/s11869-008-0022-y>
- Aguirre, C. L., Toro, N., Carvajal, N., Watling, H., & Aguirre, C. (2016). Leaching of chalcopyrite (CuFeS₂) with an imidazolium-based ionic liquid in the presence of chloride. *Minerals Engineering*, 99, 60–66. <https://doi.org/10.1016/j.mineng.2016.09.016>
- Baba, A. A., Balogun, A. F., Olaoluwa, D. T., Bale, R. B., Adekola, F. A., & Alabi, A. G. F. (2017). Leaching kinetics of a Nigerian complex covellite ore by the ammonia-ammonium sulfate solution. *Korean Journal of Chemical Engineering*, 34(4), 1133–1140. <https://doi.org/10.1007/s11814-017-0005-5>
- Balladares, E., Jerez, O., Parada, F., Baltierra, L., Hernández, C., Araneda, E., & Parra, V. (2018). Neutralization and co-precipitation of heavy metals by lime addition to effluent from acid plant in a copper smelter. *Minerals Engineering*, 122(March), 122–129. <https://doi.org/10.1016/j.mineng.2018.03.028>
- Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escalera, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, 76(5), 965–977. <https://doi.org/10.1016/j.talanta.2008.05.019>
- Cheng, C. Y., & Lawson, F. (1991). The kinetics of leaching covellite in acidic oxygenated sulphate-chloride solutions. *Hydrometallurgy*, 27(3), 249–268. [https://doi.org/10.1016/0304-386X\(91\)90053-O](https://doi.org/10.1016/0304-386X(91)90053-O)
- Dean, A., Voss, D., & Draguljic, D. (2017). Response Surface Methodology. In *Design and Analysis of Experiments* (pp. 565–614). <https://doi.org/10.1007/978-3-319-52250-0>
- Dijksira, R., Senyard, B., Shah, U., & Lee, H. (2017). Economical abatement of high-strength SO₂off-gas from a smelter. *Journal of the Southern African Institute of Mining and Metallurgy*, 117(11), 1003–1007. <https://doi.org/10.17159/2411-9717/2017/v117n11a2>
- Dimitrijević, M., Kostov, A., Tasić, V., & Milosević, N. (2009). Influence of pyrometallurgical copper production on the environment. *Journal of Hazardous Materials*, 164(2–3), 892–899. <https://doi.org/10.1016/j.jhazmat.2008.08.099>
- Donati, E., Pogliani, C., & Boiardi, J. L. (1997). Anaerobic leaching of covellite by *Thiobacillus ferrooxidans*. *Applied Microbiology and Biotechnology*, 47(6), 636–639. <https://doi.org/10.1007/s002530050987>
- F. Monteiro, V., Garcia, O., & Tuovinen, O. (1999). *Oxidative dissolution of covellite by Thiobacillus ferrooxidans*. *Process Metallurgy* (Vol. 9). [https://doi.org/10.1016/S1572-4409\(99\)80028-5](https://doi.org/10.1016/S1572-4409(99)80028-5)
- Falco, L., Pogliani, C., Curutchet, G., & Donati, E. (2003). A comparison of bioleaching of covellite using pure cultures of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* or a mixed culture of *Leptospirillum ferrooxidans* and *Acidithiobacillus thiooxidans*. *Hydrometallurgy*, 71(1–2), 31–36. [https://doi.org/10.1016/S0304-386X\(03\)00170-1](https://doi.org/10.1016/S0304-386X(03)00170-1)
- Fisher, W. W. (1994). Comparison of chalcocite dissolution in the sulfate, perchlorate, nitrate,

- chloride, ammonia, and cyanide systems. *Minerals Engineering*, 7(1), 99–103.
[https://doi.org/10.1016/0892-6875\(94\)90150-3](https://doi.org/10.1016/0892-6875(94)90150-3)
- González, C., Parra, R., Klenovcanova, A., Imris, I., & Sánchez, M. (2005). Reduction of Chilean copper slags: A case of waste management project. *Scandinavian Journal of Metallurgy*, 34(2), 143–149. <https://doi.org/10.1111/j.1600-0692.2005.00740.x>
- Herreros, O., & Viñals, J. (2007). Leaching of sulfide copper ore in a NaCl-H₂SO₄-O₂ media with acid pre-treatment. *Hydrometallurgy*, 89(3–4), 260–268.
<https://doi.org/10.1016/j.hydromet.2007.07.011>
- Kelm, U., Avendaño, M., Balladares, E., Helle, S., Karlsson, T., & Pincheira, M. (2014). The use of water-extractable Cu, Mo, Zn, As, Pb concentrations and automated mineral analysis of flue dust particles as tools for impact studies in topsoils exposed to past emissions of a Cu-smelter. *Chemie Der Erde*, 74(3), 365–373. <https://doi.org/10.1016/j.chemer.2013.12.001>
- Klein, C., & Hurlbut, C. S. (1996). *Manual de mineralogía*. Reverté. Retrieved from https://books.google.cl/books/about/Manual_de_mineralogía.html?id=4z8EMkxqfe4C&redir_esc=y
- Lee, J., Acar, S., Doerr, D. L., & Brierley, J. A. (2011). Comparative bioleaching and mineralogy of composited sulfide ores containing enargite, covellite and chalcocite by mesophilic and thermophilic microorganisms. *Hydrometallurgy*, 105(3–4), 213–221.
<https://doi.org/10.1016/j.hydromet.2010.10.001>
- Lü, C., Wang, Y., Qian, P., Liu, Y., Fu, G., Ding, J., ... Chen, Y. (2018). Separation of chalcopyrite and pyrite from a copper tailing by ammonium humate. *Chinese Journal of Chemical Engineering*, 26(9), 1814–1821. <https://doi.org/10.1016/j.cjche.2018.02.014>
- Lundström, M., Liipo, J., Taskinen, P., & Aromaa, J. (2016). Copper precipitation during leaching of various copper sulfide concentrates with cupric chloride in acidic solutions. *Hydrometallurgy*, 166, 136–142. <https://doi.org/10.1016/j.hydromet.2016.10.017>
- Miki, H., Nicol, M., & Velásquez-Yévenes, L. (2011). The kinetics of dissolution of synthetic covellite, chalcocite and digenite in dilute chloride solutions at ambient temperatures. *Hydrometallurgy*, 105(3–4), 321–327. <https://doi.org/10.1016/j.hydromet.2010.11.004>
- Montgomery, D. C. (2012). Cap. 3, 6, 7 and 10. In *Design and Analysis of Experiments*. Wiley; 8 edition (April 10, 2012).
- Nicol, M., & Basson, P. (2017). The anodic behaviour of covellite in chloride solutions. *Hydrometallurgy*, 172(June), 60–68. <https://doi.org/10.1016/j.hydromet.2017.06.018>
- Niu, X., Ruan, R., Tan, Q., Jia, Y., & Sun, H. (2015). Study on the second stage of chalcocite leaching in column with redox potential control and its implications. *Hydrometallurgy*, 155, 141–152. <https://doi.org/10.1016/j.hydromet.2015.04.022>
- Rabadjieva, D., Tepavitcharova, S., Todorov, T., Dassenakis, M., Paraskevopoulou, V., & Petrov, M. (2009). Chemical speciation in mining affected waters: The case study of Asarel-Medet mine. *Environmental Monitoring and Assessment*, 159(1–4), 353–366.
<https://doi.org/10.1007/s10661-008-0634-6>
- Reilly, I. G., & Scott, D. S. (1976). The Leaching of Cupric Sulfide in Ammonia. *Industrial and Engineering Chemistry Process Design and Development*, 15(1), 60–67.
<https://doi.org/10.1021/i260057a012>
- Ruan, R., Zou, G., Zhong, S., Wu, Z., Chan, B., & Wang, D. (2013). Why Zijinshan copper bioheapleaching plant works efficiently at low microbial activity-Study on leaching kinetics of copper sulfides and its implications. *Minerals Engineering*, 48, 36–43.
<https://doi.org/10.1016/j.mineng.2013.01.002>

- Ruiz, M. C., Abarzúa, E., & Padilla, R. (2007). Oxygen pressure leaching of white metal. *Hydrometallurgy*, 86(3–4), 131–139. <https://doi.org/10.1016/j.hydromet.2006.10.009>
- Ruiz, M. C., Honores, S., & Padilla, R. (1998). Leaching kinetics of digenite concentrate in oxygenated chloride media at ambient pressure. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 29(5), 961–969. <https://doi.org/10.1007/s11663-998-0064-4>
- Sánchez de la Campa, A. M., de la Rosa, J. D., Sánchez-Rodas, D., Oliveira, V., Alastuey, A., Querol, X., & Gómez Ariza, J. L. (2008). Arsenic speciation study of PM_{2.5} in an urban area near a copper smelter. *Atmospheric Environment*, 42(26), 6487–6495. <https://doi.org/10.1016/j.atmosenv.2008.04.016>
- Schlesinger, M. E., King, M. J., Sole, K. C., & Davenport, W. G. (2011). *Extractive Metallurgy of Copper* (fifth edit). Elsevier.
- Senanayake, G. (2007). Chloride assisted leaching of chalcocite by oxygenated sulphuric acid via Cu(II)-OH-Cl. *Minerals Engineering*, 20(11), 1075–1088. <https://doi.org/10.1016/j.mineng.2007.04.002>
- Senanayake, G. (2009). A review of chloride assisted copper sulfide leaching by oxygenated sulfuric acid and mechanistic considerations. *Hydrometallurgy*, 98(1–2), 21–32. <https://doi.org/10.1016/j.hydromet.2009.02.010>
- Serbula, S. M., Milosavljevic, J. S., Radojevic, A. A., Kalinovic, J. V., & Kalinovic, T. S. (2017). Science of the Total Environment Extreme air pollution with contaminants originating from the mining – metallurgical processes. *Science of the Total Environment*, 586, 1066–1075. <https://doi.org/10.1016/j.scitotenv.2017.02.091>
- Shuva, M. A. H., Rhamdhani, M. A., Brooks, G. A., Masood, S., & Reuter, M. A. (2016). Thermodynamics data of valuable elements relevant to e-waste processing through primary and secondary copper production: A review. *Journal of Cleaner Production*, 131, 795–809. <https://doi.org/10.1016/j.jclepro.2016.04.061>
- Toro, N., Herrera, N., Castillo, J., Torres, C., & Sepúlveda, R. (2018). Initial Investigation into the Leaching of Manganese from Nodules at Room Temperature with the Use of Sulfuric Acid and the Addition of Foundry Slag—Part I. *Minerals*, 8(12), 565. <https://doi.org/10.3390/min8120565>
- Turan, M. D., Sari, Z. A., & Miller, J. D. (2017). Leaching of blended copper slag in microwave oven. *Transactions of Nonferrous Metals Society of China (English Edition)*, 27(6), 1404–1410. [https://doi.org/10.1016/S1003-6326\(17\)60161-4](https://doi.org/10.1016/S1003-6326(17)60161-4)
- Vračar, R. Ž., Vučković, N., & Kamberović, Ž. (2003). Leaching of copper(I) sulphide by sulphuric acid solution with addition of sodium nitrate. *Hydrometallurgy*, 70(1–3), 143–151. [https://doi.org/10.1016/S0304-386X\(03\)00075-6](https://doi.org/10.1016/S0304-386X(03)00075-6)
- World Health Organization. (2018). *World Health Statistics*. Retrieved from <http://e-journal.uajy.ac.id/14649/1/JURNAL.pdf>