

Effect of curing time on the dissolution of a secondary copper sulphide ore using alternative water resources

V Quezada^{1,2}, L Velásquez³, A Roca¹, O Benavente², E Melo² and B Keith⁴

¹ Departamento de Ciencia de los Materiales y Química Física, Universidad de Barcelona, Barcelona, España.

² Departamento de Ingeniería Metalúrgica y Minas, Universidad Católica del Norte, Antofagasta, Chile.

³ Departamento de Ingeniería en Minas, Universidad de Santiago, Santiago, Chile.

⁴ Departamento de Ingeniería de Sistemas y Computación, Universidad Católica del Norte, Antofagasta, Chile.

vquezare7@alumnes.ub.edu

Abstract. In the north of Chile, due to water shortages, the depletion of oxide ores and the abundance of chalcopyrite ore, mining industry is searching for sustainable hydrometallurgy processes that can use alternative water resources. The leaching process must enhance the dissolution of copper sulphide ore that are refractory to conventional leaching. This paper reports a study on the effect of addition of chloride ion using seawater and discard brine in the agglomeration stage of a secondary copper sulphide ore. The effect of curing time on the same ore also is reported. The leaching tests have been carried out in column irrigated with raffinate under ambient conditions. A size distribution with a P80 of 17 mm is used. A maximum of 72% of copper extraction is obtained using discard brine and 68% using seawater. The use of discard brine and seawater are favorable in all the tests performed. Through an Analysis of Variance (ANOVA), it is determined that the curing time has the highest contribution (92.37%) on the percentage of copper extraction.

1. Introduction

Chile is the largest copper producer in the world [1], exporting 5,552 tons of copper in 2016 [2]. Antofagasta is the main copper producer region in Chile and Chuquicamata and Escondida Mine are located in this region. Because of that Antofagasta Region have supported the economic development of the region to the point where the per capita GDP is the highest in the country [3]. However, the Antofagasta Region is located in the Atacama Desert, the most arid in the world. Antofagasta has the lowest availability of fresh water in Chile [4]. To sustain copper production over time and supply the region's water shortages, copper producing companies have incorporated seawater into their processes (e.g. Michilla, Esperanza, Algorta Norte and Las Luces) [5]. The advantage of seawater is that it has



20 g/L of chloride ion that, according to research data, can enhance the dissolution of copper sulphide ores [6].

1.1. Leaching of copper sulphide ores

Besides to facing the water shortage, some companies go through the depletion of oxidized copper minerals (leachable minerals) facing sulphide deposits that are refractory to conventional leaching [7]. Copper sulphide ores are classified in two zones, secondary and primary. Covellite and chalcocite predominate in the secondary sulphide zone, the latter being the most common [8]. With respect to the primary sulphide zone, the most abundant is the chalcopyrite [9]. Traditionally, the sulfurized zones are processed through concentration by flotation and subsequent treatments at high temperatures. However, this alternative is not economically viable when the copper grade of the deposit fails to cover comminution costs. This becomes a problem when companies already have hydrometallurgical plants and the production of the company is limited to mineralogy. Given this problem is that companies see the continuity of operations in the leaching of copper sulphide ores.

1.2. Pretreatment and chloride leaching

Several leaching media have been studied for the dissolution of copper sulphide ores, of these, the chloride media turns out to be the most efficient due to the reactivity of the chloride ion with sulphide ores [6]. The reactivity of the chloride ion has been declared as beneficial with respect to the dissolution of copper from sulphide ores, since, under certain conditions of pH and solution potential, it is capable of dissolving and reversing the passivating layer that inhibits dissolution [10-11]. Recent research has qualified curing time as a favorable variable in the extraction of copper from sulphide ores [12]. The curing time is a treatment prior to the leaching stage in which the reactivity of the sample with the solution is benefited. According to Dhawan [13], curing time generates a homogeneous distribution of the acid in the mineral bed, increases the kinetics of copper dissolution as well as benefiting the inhibition of aluminum-silicate minerals. However, scarce research has been performed on curing period, which generates limited theoretical background [14]. Thus, this work evaluates the effect of curing time in the extraction of copper from secondary sulphide ores using seawater and discard brine from a desalination company. Leaching experiments were performed in columns, at room temperature and the variables have been analyzed through ANOVA.

2. Experimental

2.1. Ore sample

A secondary sulphide copper ore is used to develop leaching tests. The chemical analysis of the ore indicates a copper grade of 1.19% and an iron presence of 5%. According to the mineralogical analysis presented in table 1, it can easily be seen that the copper present in the system is mainly contributed by secondary sulphide ore such as chalcocite and covellite, both contributions exceed 80% of the total copper in the system. The size distribution, corresponding to the ore, can be seen in figure 1. It is obtained a P80 of 17 mm.

Table 1. Mineralogical composition of the ore sample as determined by QEMSCAN.

	Amount (wt %)	Cu (wt %)	Cu contribution (wt %)
Chalcocite	1.10	0.88	74.14
Chalcopyrite	0.27	0.09	7.76
Covellite	0.11	0.07	6.03
Bornite	0.06	0.04	3.45
Atacamite	0.07	0.04	3.45
Others Cu minerals	-	0.06	5.17
Total		1.19	100

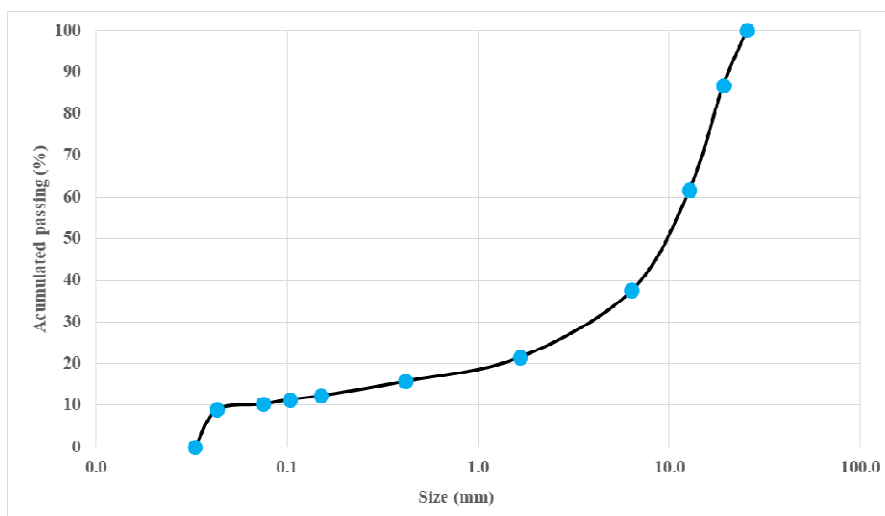


Figure 1. Particle size distribution of the ore.

2.2. Reagents

All tests were performed using sulfuric acid (H_2SO_4) p.a. of 97%. Seawater and discard brine were used as water resources in this study. Seawater was collected from the shore in the southern area of Antofagasta, in a location close to the Universidad Católica del Norte. Discard brine was provided by a desalination company located in Antofagasta. The concentration of chloride in seawater and discard brine is 20 and 32 g / L, respectively.

2.3. Pretreatment to leaching process

Agglomeration tests were conducted in a batch laboratory-scale polypropylene drum through a system of rotating rollers operated at 60 rpm speed. For all agglomeration tests, 4 kg of crushed well-mixed ore with a particles size fraction of 17 mm of P80 were used. Previous results (not shown) indicate that 30 kg of sulfuric acid per ton of mineral and 9.1% moisture are the optimal values to be added in the agglomeration. Curing time studied were 15, 30, 50 and 80 days. All samples were sealed without being exposed to the environment (avoid evaporation).

2.4. Leaching process

Leaching of all agglomerate samples was carried out in acrylic columns, 10.7 cm in diameter and 41 cm in height (figure 2). The leaching solution has 6 g/L of sulfuric acid and the irrigation rate used was 5 L/h/m² (0.76 mL/min). All columns leaching test were irrigated with a standard solution (6 g/L of acid). Liquid feed flow rate to the columns was 0.76 mL/min using a peristaltic pump for all the leaching samples, the pH and the redox potential were measured. All pH measurements were performed using a Metrohm 826 pH meter and probe, which was calibrated at pH 2.0 and 7.0, each time before used. The redox potentials were measured using a Metrohm 826 voltmeter with an Ag/AgCl reference electrode and it was converted and reported with respect to the standard hydrogen electrode (SHE). The precision of the measurements was tested using Oxidation-Reduction Potential (ORP) standard solution having a potential of 470 mV at 25°C. During each test, liquid samples were withdrawn periodically and analyzed for Cu and Fe using ASS.

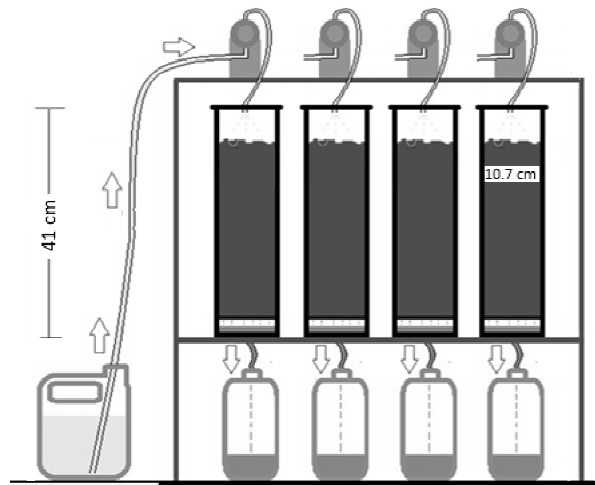


Figure 2. Schematic of column leaching system.

2.5. ANOVA analysis

An ANOVA analysis of two factors without replications was used to compare the effects of curing and the water resource used, with a level of significance of 0.01 on the data [15]. The factors correspond in particular to: curing time (in days) with four levels (3, 10, 30 and 50) and the level of chloride concentration associated with the water resource (in g/L) with two levels (20 and 32, associated with seawater and discard brine, respectively). The response variable corresponds to the final percentage of copper extraction.

Due the number of factors and levels is relatively low, a complete factorial experimental design is used, obtaining a total of 8 samples (8 tests in columns). A summary of the experimental design used is shown in table 2, the curing time has been labeled as A, and the chloride concentration as B.

Table 2. Experimental design used.

A	B	Curing time (days)	Chloride (g/L)
1	1	3	20
2		10	20
3		30	20
4		50	20
1	2	3	32
2		10	32
3		30	32
4		50	32

The data were analyzed using an additive linear model without interaction, under the assumption that this type of model is able to explain the variance of the data in an adequate manner. The effects produced by the interaction of the parameters have not been taken into account in this analysis, since preliminary tests show that they can be disregarded. The predictive results of the model support this assumption, although it could be confirmed by carrying out additional experiments. The additive linear model is shown in equation 1 given by

$$Y_i = \mu + X_i + e_i \quad (1)$$

where: μ is the general average of the performance value, X_i is the fixed effect of the combination of parameter levels used in the i -th experiment and e_i is the random error of the i -th experiment.

On the other hand, the calculation of the F value is performed to evaluate the process parameters and determine if they have significant effects on the performance value. The F value of each parameter of the process is the ratio between the average of the squared deviations with respect to the mean of the squared error. In general, the higher the F value, the more significant the effect on the yield value due to the change in the parameter. This analysis of variance is followed by Tukey tests at a significance level of $p = 0.01$ for the comparison of means.

To perform the analysis of results, the application of ANOVA and the performance of the Tukey tests, the R language [16] and the DoE.base experiments design library [17] were used.

3. Results and discussion

3.1. Column leaching

In figure 3 it is possible to appreciate that the test with the longest curing time (50 days) is the one that reports the highest extraction, reaching 71.5% after 22 days of irrigation. Opposite case is the test with 3 days of curing, which reaches 58%. As can be seen, there is a directly proportional relationship between curing and final copper extraction. In addition to the above, it is possible to visualize also the slope of the line is greater for those tests that have more curing time. Thus, for the 50-day test, 50% extraction is achieved for the first 48 hours. Regarding the results of the tests using seawater, they can be seen in figure 4. The test with 50 days of curing reaches an extraction close to 68% while the test with 3 days of curing reaches 54.5% of copper dissolution. The same trend is observed regarding the tests with discard brine.

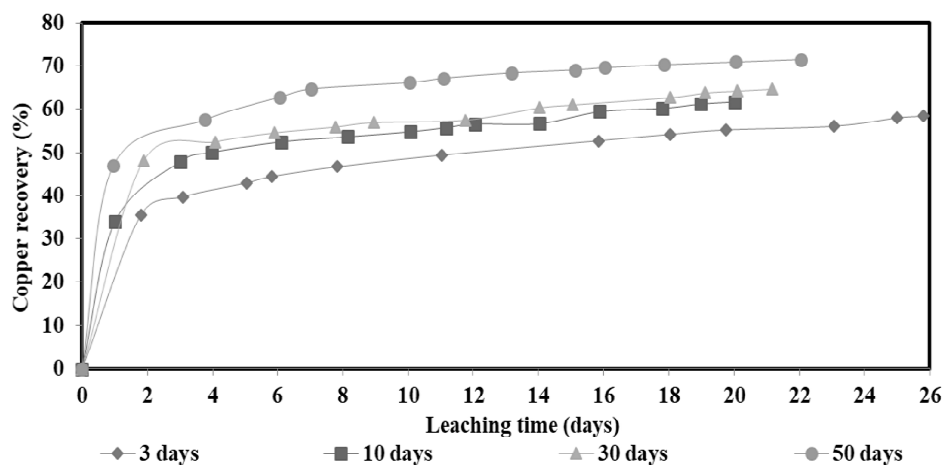


Figure 3. Effect of the curing time on the rate of column leaching of copper sulphide ore in a solution of 6 g/L H_2SO_4 at ambient temperature using discard brine with: 3 curing days (\blacklozenge), 10 curing days (\blacksquare), 30 curing days (\blacktriangle) and 50 curing days (\bullet).

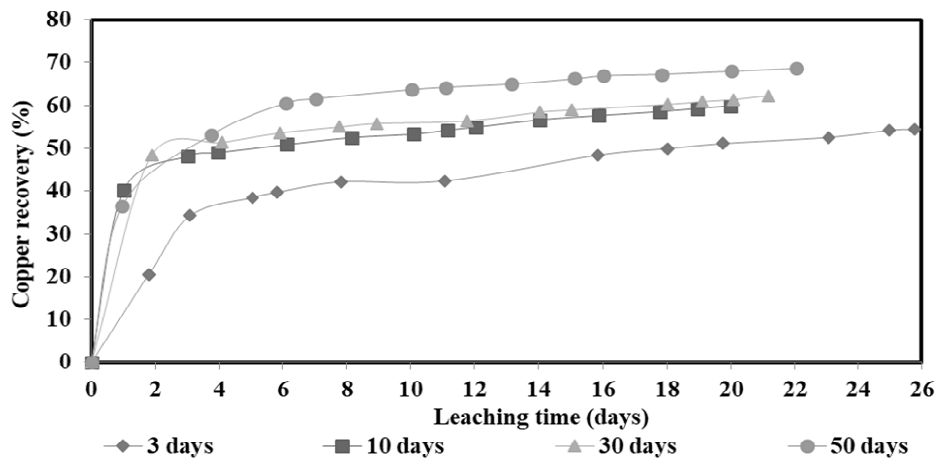


Figure 4. Effect of the curing time on the rate of column leaching of copper sulphide ore in a solution of 6 g/L H_2SO_4 at ambient temperature using seawater with: 3 curing days (♦), 10 curing days (■), 30 curing days (▲) and 50 curing days (●).

In figures 5 and 6 it is possible to appreciate the behavior of the solution potential for the tests with discard brine and seawater, respectively. From both graphs a constant behavior of the potential through time is observed, resulting in a range between 600 and 660 mV for all the tests carried out. This range of variation has been described as beneficial in the dissolution of copper from minerals such as chalcocite [10], but it would tend to be difficult for a potential close to 500 mV.

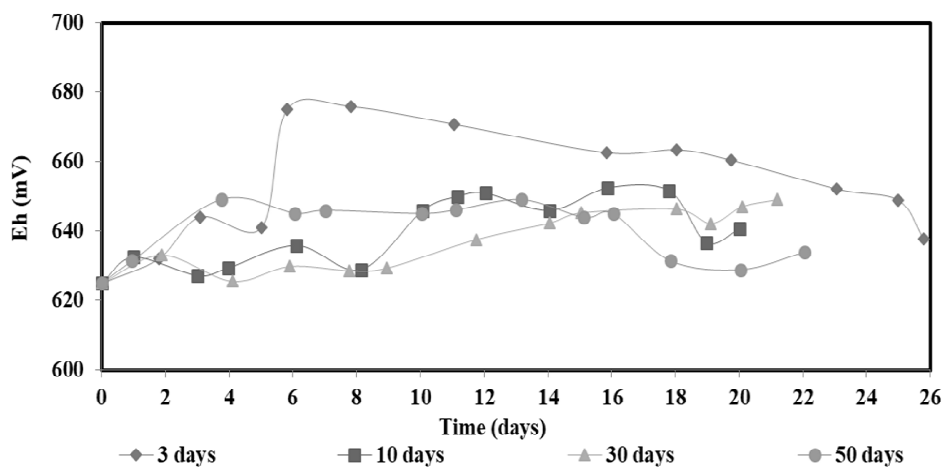


Figure 5. Variation of potential in the leaching solution of copper sulphide ore in a solution of 6 g/L H_2SO_4 at ambient temperature using discard brine with: 3 curing days (♦), 10 curing days (■), 30 curing days (▲) and 50 curing days (●).

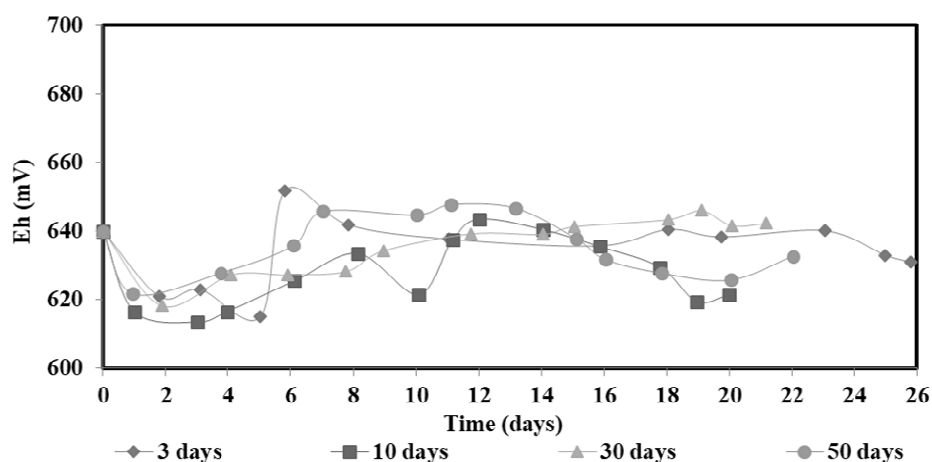


Figure 6. Variation of potential in the leaching solution of copper sulphide ore in a solution of 6 g/L H_2SO_4 at ambient temperature using seawater with: 3 curing days (\blacklozenge), 10 curing days (\blacksquare), 30 curing days (\blacktriangle) and 50 curing days (\bullet).

3.2. ANOVA analysis

The results of the ANOVA performed are shown in table 3. According to the results, parameter *A* has the highest contribution on the percentage of extraction of Cu obtained (92.37%), being able to explain practically all the variance of the data, on the other hand, parameter *B* has a much smaller contribution (7.05%). Furthermore, 99.42% of the variance of the data can be explained between these the two factors, based on these results it can be assumed that the additive linear model is adequate to describe the data. Finally, these contributions are statistically significant according to the obtained *p*-values (all significant at a 99% confidence level). The degree of influence or effect that the parameters have can be visualized in figures 7 and 8.

Table 3. Results of the ANOVA analysis of the parameters for the percentage of Cu extraction (*df* = degrees of freedom, *SSE* = sum of square errors, *MSE* = mean square errors).

Parameters	<i>df</i>	<i>SSE</i>	<i>MSE</i>	<i>F</i> Value	Contribution (%)	<i>p</i> -Value
A Curing time (days)	3	195.264	65.088	160.658	92.37%	0.0008244
B Cl ⁻ (g/L)	1	14.906	14.906	36.792	7.05%	0.0089928
Error	3	1.215	0.405			
Total	7	211.385			99.42%	

From the adjusted additive linear model, it is possible to obtain predictions about the percentages of copper extraction that should be obtained in each configuration. In table 4 these results are detailed and the level of error they present with respect to the empirical results.

In figure 7 it can be seen that the optimum is obtained with level 4, corresponding to 50 days of curing. In general, a positive trend is observed as the days of curing increase, a result that agrees with the theoretical intuition regarding the benefit of curing time in copper extraction.

Table 4. Experimental results and predictions of the model.

<i>A</i>	<i>B</i>	Empirical value (% Cu)	Prediction (% Cu)	Error
1	1	54.49	55.08	-0.59
2		59.93	59.46	0.48
3		62.29	62.11	0.19
4		68.63	68.71	-0.08
1	2	58.39	57.81	0.59
2		61.71	62.19	-0.48
3		64.65	64.84	-0.19
4		71.51	71.44	0.08

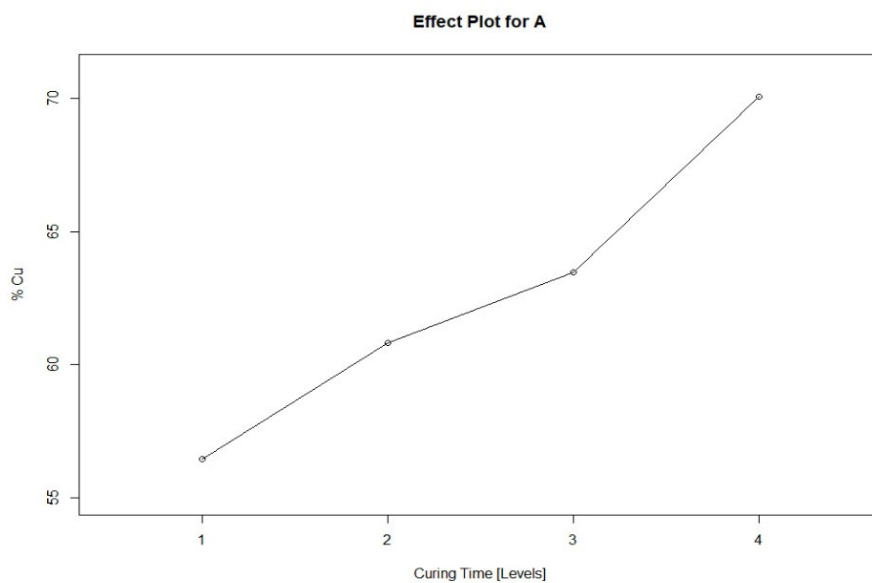
**Figure 7.** Effect of parameter A (curing time level) on the percentage of Cu extraction.

Figure 8 shows that, at least for these data, a slightly higher yield is obtained when using discard brine (level 2), corresponding to 32 g / L of chloride. It can be seen that the effect is much smaller than that produced by the curing time (note that both graphs are on the same scale on the ordinate axis).

Finally, Tukey's post-hoc test [18] based on the value of Honestly Significant Difference (HSD) is reported that there is a significant difference (at a 0.01 level of significance) between different configurations. In particular, the configuration (4.1) and configurations (1.1), (1.2) and (1.3) show statistically significant differences with adjusted p-values of 0.0007, 0.0022 and 0.0058 respectively, where the difference is in favor of the configuration (4.1). In addition, a statistically significant difference is reported even between the configuration (2.1) and (1.1) with an adjusted p-value of 0.0090, reporting an increase in the percentage of copper extraction. These results correspond to the previous graphic analysis and reinforce the main conclusion of this analysis: the curing time has a statistically significant influence on the percentage of copper extraction.

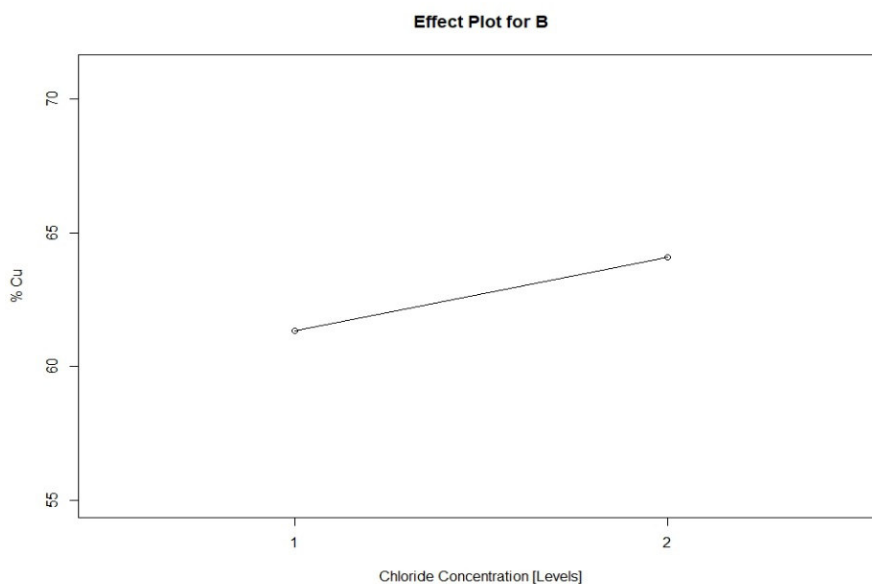


Figure 8. Effect of parameter B (chloride concentration level) on the percentage of Cu extraction.

4. Conclusions

- It has been demonstrated that ore agglomerated with acid and chloride ions and cured for long periods of time enhances the dissolution rate of a secondary copper sulphide ore. 72 and 68% of extraction is achieved when the ore is agglomerated and curing for 50 days using discard brine and seawater as the type of water, respectively. In the same medias, 58 and 52% of extraction is obtained with 3 days of curing.
- Despite the difference of the chloride content in each chloride solution type used in the column leach tests at different curing times, similar dissolution was obtained. Thus, it could be concluded that either type of chloride solution in the raffinate for agglomeration and irrigation can be used. Furthermore, the copper sulphide ore dissolution is enhanced at potential between 600 and 660 mV (SHE).
- According to the Analysis of Variance, curing time is the variable that has the greatest contribution in copper extraction (92.37%) versus chloride concentration (7.05%), under the conditions studied.

References

- [1] Ghorbani Y, Kuan SH 2016 A review of sustainable development in the Chilean mining sector: past, present and future *Int J Min Reclam Environ* **30** pp 1–29
- [2] Chilean Copper Commission (COCHILCO) 2017 Proyección de la producción de cobre en Chile 2017 – 2028. Available at: <http://www.cochilco.cl/>
- [3] Tapia J S, Valdés J, Orrego R, Tchernitchin A, Dorador C, Bolados A and Harrod C 2018 Geologic and anthropogenic sources of contamination in settled dust of a historic mining port city in northern Chile: health risk implications *PeerJ* **6** pp e4699
- [4] Quezada V and Velásquez L 2016 Dissolution kinetics of copper ores and concentrate with sea water and discard brine *Hydrometallurgy Conference 2016. Sustainable Hydrometallurgical Extraction of Metals* Cape Town South Africa pp 101 – 9
- [5] Torres C M, Taboada M E, Graber T A, Herreros O O, Ghorbani Y and Watling H R 2015 The effect of seawater based media on copper dissolution from low-grade copper ore *Minerals Engineering* **71** pp 139-45

- [6] Velásquez -Yévenes L 2009 The kinetics of the dissolution of chalcopyrite in chloride media (Doctoral dissertation, Murdoch University)
- [7] Ibáñez T and Velásquez L 2013 Lixiviación de la calcopirita en medios clorurados. *Revista de Metalurgia* **49**(2) pp 131-44
- [8] Niu X, Ruan R, Tan Q, Jia Y and Sun H 2015 Study on the second stage of chalcocite leaching in column with redox potential control and its implications *Hydrometallurgy* **155** pp 141-52
- [9] Dutrizac J E 1978 The kinetics of dissolution of chalcopyrite in ferric ion media. *Metallurgical Transactions B* **9**(3) pp 431-9
- [10] Miki H, Nicol M J and 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) pp 321-7
- [11] Nicol M, Miki H and Zhang S 2017 The anodic behaviour of chalcopyrite in chloride solutions: Voltammetry *Hydrometallurgy* **167** pp 72-80
- [12] Velásquez-Yévenes L and Quezada-Reyes V 2018 Influence of seawater and discard brine on the dissolution of copper ore and copper concentrate *Hydrometallurgy* **180** pp 88-95
- [13] Dhawan N, Safarzadeh M S, Miller J D, Moats M S and Rajamani R K 2013 Crushed ore agglomeration and its control for heap leach operations. *Minerals Engineering* **41** pp 53-70
- [14] Lu J, Dreisinger D and West-Sells P 2017 Acid curing and agglomeration for heap leaching. *Hydrometallurgy* **167** pp 30-5
- [15] Iversen G R, Wildt A R, Norpoth H and Norpoth H P 1987 *Analysis of variance* (No. 1) Sage
- [16] R Core Team 2017 R A language and environment for statistical computing (Vienna: R Foundation for Statistical Computing)
- [17] Groemping, U 2018 DoE.base: Full Factorials, Orthogonal Arrays and Base Utilities for DoE Packages. R package version 0.32. <https://CRAN.R-project.org/package=DoE.base>
- [18] Tukey J W 1949 Comparing individual means in the analysis of variance. *Biometrics* pp 99-114