Development of an analytical model for copper heap leaching from secondary sulfides in chloride media in an industrial environment

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Abstract

In multivariate analysis, a predictive model is a mathematical/statistical model that relates a set of independent variables to dependent or response variable(s). This work presents a descriptive model that explains copper recovery from secondary sulfide minerals (chalcocite) taking into account the effects of time, heap height, superficial velocity of leaching flow, chloride concentration, particle size, porosity, and effective diffusivity of the solute within particle pores. Copper recovery is then modelled by a system of first-order differential equations. The results indicated that the heap height and superficial velocity of leaching flow are the most critical independent variables while the others are less influential under operational conditions applied. In the present study representative adjustment parameters are obtained, so that the model could be used to explore copper recovery in chloride media as a part of the extended value chain of the copper sulfides processing.

Keywords: copper extraction, phenomenological modeling, chloride leaching, modelling, hydrometallurgy.

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1. INTRODUCTION

Copper mining is an industry in constant growth [1]. Currently, 19.7 million tons of copper are produced world-wide [2], 75 % of which are processed by pyrometallurgical processes, while the rest is processed by hydrometallurgical routes [3–5]. Pyrometallurgical processes generate large environmental liabilities, such as tailings dams [6–8] produced by flotation processes, which can affect acid rains and increase local pollution [9,10]. Hydrometallurgical processes, together with copper bioleaching processes [11–13], have proven to be more environmentally friendly.

Leaching processes in recent years have been used to treat oxidized copper ores, being a useful technological alternative to treat low-medium grade ores [14–17]. However, oxides available for treatment are becoming scarce mainly due to overexploitation [18]. In Chile, for example, copper oxides that are processed by this route currently represent 30.8 % of the country's production and are projected to decline to 12 % of the production by 2027 [2]. Despite the problem, this option is currently being used not only for oxides, but also for secondary sulfides, especially low-grade minerals [19,20], or copper sulfide minerals [21–26], like chalcocite or covellite, ores that are processed in acidic environments with the addition of chlorides [27], found naturally in seawater. This resource has begun to be exploited in recent decades in Chilean mining [28], mainly due to the situation of water scarcity in the country. It is worth highlighting the rise in copper leaching in chloride media, finding applications, as stated in the literature, from processing of secondary copper sulfide minerals [22,23,29,30], to copper smelting slag leaching [31,32]. On the other hand, though

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leaching of primary copper sulfides, such as chalcopyrite [33,34], is also possible, it is economically infeasible at industrial scale.

In line with the above, considerable pressure is currently exerted on water resources required for population, urban and economic growth [35]. Due to water scarcity and the lack of surface and subsurface water recharge, it has become a priority focus for decision makers in the world [36]. Chile, for its part, has 1,251 rivers, which are in 101 main basins of the country whose recharge comes mainly from rains. However, it is a country highly vulnerable to climate change [37]. Reports indicate that there is an increase in temperature [38–40], increase in wind intensity [38,41], appearance of flow-type landslides [42] and a decrease in rainfall [38,39,41]. Considering that a large part of the Chilean economy is based on the economic contribution of the mining sector [43] and flotation metallurgical processes being the ones that consume the most water in the country, promoting hydrometallurgy can help in this regard [44]. In turn, the mining nucleus of Chile is located in the Atacama Desert, characterized as the driest desert in the world. This extreme aridity is due to the fact that in the western regions there is a combination of the barrier effect of the high Andes Mountain Range, permanence of the Southeast Pacific anticyclone and the existence of the Humboldt Current-coastal upwelling system that prevents this region from receiving the moist Atlantic air masses. Its scant rainfall is due to climatic anomalies, the main one being the ocean-climatic anomaly ENSO (El Niño-Southem Oscillation) [45,46]. On the other hand, in the eastern highland regions, recharge is due to summer rainfall, fed by moisture of Amazonian origin, which became, in certain years, very abundant [45]. The groundwater recharge comes from precipitation, melting ice or lacustrine origin from the Andes Mountains and surrounding areas [47].

Mean annual rainfall in the Atacama Desert is less than 20 mm and has been a desert for 12000 ± 1000 years shifting between arid and hyper-arid periods [48]. Accordingly, fluvial run-off is minimal and erosion rates are extremely low ranging from 0.2 to 0.4 m Ma^{-1} [49]. Therefore, more environmentally friendly forms of copper extraction should be sought in Chilean mining, providing water reuse, such as hydrometallurgical processes used in the country today.

Leaching processes include several stages. First, the ore (chalcocite) is crushed until it reaches a size under 1 in [14]. Then, the crushed ore is transported to the pile, having a height between 4 to 10 m [50]. Finally, the ore is irrigated by a leaching solution distributed by sprinklers or drip emitters, flowing down through the heap by gravity [14]. At the end of the process, cupric ions are obtained together with other ions dissolved in the PLS (Pregnant Liquid Solution), which is deposited in leaching pools, and subsequently advanced to the solvent extraction stage [51].

In this work, an analytical model for estimation of copper recovery from chalcocite in the heap leaching process is derived~~.~~ Creation of analytical models (theoretical and/or empirical) representing dynamics of mining processes such as heap leaching are of vital importance for study of the process performance at the operational level [52], since such models can support development, verification, testing and application of new specialized technologies related to process innovation, different modes of operation, or operational efficiency. This work presents the theoretical framework supporting the analytical model for copper recovery estimation, fundamentals of the uncertainty analysis and the model optimization process followed by application of the optimized analytical model, the uncertainty analysis, and discussion of the model results.

2. MATERIALS AND METHODS

2. 1. Chalcocite Heap Leaching

Heap leaching data at the operational level were recovered from a mine with the copper ore grade of 0.6 % approximately, located in the Antofagasta region, Chile. Samples of copper recovery were recorded for a period of two years approximately, in processes with different levels of the factors: heap height (300 - 840 cm), particle size (15 - 33 mm), porosity (1 -5.5), effective diffusivity of the solute within the particle pores (0.06 - 0.108 cm^2 day^{-1}), superficial velocity of leaching flow (9 - 54 cm day^{-1}) and chloride concentrations (20 - 50 g dm^{-3}).

2. 2. Analytical models for heap leaching

There are several copper recovery models in literature [53,54], while the analytical model used in this work is given by Eq. (1) [55–58], which is based on the hypothesis that the leaching process could be modelled by using a system of first-order differential equation (1).

$$\frac{\partial y}{\partial \tau} = -k_\tau e^{n_\tau} \tag{1}$$

where y is a dynamic quantity, such as concentration or recovery R_τ, k_τ is the kinetic constant and n_τ is the order of the reaction and τ represent a time scale that depends on the phenomenon to model. To solve Eq. (1), an initial condition is required, introducing a delay parameter ω. Then, the general solution for this problem is known, as $n_\tau = 1$, and the solution is given by the Eq. (2).

$$R_\tau = R_\tau^\infty(1 - e^{-k_\tau(\tau-\omega)}) \tag{2}$$

R_τ^∞ is the maximum expected recovery depending on the experimental conditions, and ω is a factor of reaction delay (associated with the activation time; generally, this period is minimal or is considered as 0). Dixon and Hendrix [59–61] considered that the leaching process occurs at different scales of size and time with participation of different phenomena [58]. It is possible to represent these phenomena by using Eq. (2) in conjunction with expressions associated with the particle properties and the heap height in the leaching process. At the particle level τ (see Eq. 3), the authors considered that the process was dominated by the porosity ε_0 of the feeding material, the effective diffusivity of solute within the particle pores D_{Ae}, particle size (radius, r) and t is time.

$$\tau = \frac{D_{\mathrm{Ae}} t}{\varepsilon_0 r^2} \tag{3}$$

At the bulk level θ, the authors considered that the heap is porous, formed by particles through which the leaching solution flows at a constant rate. Recovery can be defined based on the heap height as is presented in Eq. (4).

$$\theta = \frac{\mu_{\mathrm{s}} t}{\varepsilon_{\mathrm{b}} Z} \tag{4}$$

Where μ_{s} is the superficial velocity of the leaching flow, ε_{b} is the volumetric fraction of the leaching solution in the bed and Z is the pile height. Eq. (2) could be rewritten to include both dependences of the reaction.

Then, considering the evident proportional relation between the copper recovery from secondary sulfides and chloride concentration [20,26,27,62,63], the term δ^ρ is incorporated into the analytical model as factors of both scales, as shown in Equations (5) and (6). The term δ^{ρ_i} (chloride concentration, c_{Cl}) is defined as the potency of the fraction of the sampled chloride concentration (x_i) over the average concentration (x) raised to a mathematical adjustment constant ρ_i, where i are the particle levels and heap height.

$$R_\tau = R_\tau^\infty \left(1 - e^{-k_\tau \delta^{\rho_1} \left(\frac{D_{\mathrm{Ae}}}{\varepsilon_0 r^2} t - \hat{\omega} \right)} \right) \tag{5}$$

$$R_\theta = R_\theta^\infty \left(1 - e^{-k_\theta \delta^{\rho_2} \left(\frac{\mu_{\mathrm{s}}}{\varepsilon_{\mathrm{b}} Z} t - \omega \right)} \right) \tag{6}$$

Including both scales in an aggregate model, Mellado *et al*. [58] assumed that the total recovery is the sum of both recoveries (, $R^\infty = R_\tau + R_\theta$, see Eq. 7), which shows asymptotic behaviour over time.

$$R = R^\infty \left(1 - \lambda e^{-k_\theta \delta^{\rho_2} \left(\frac{\mu_{\mathrm{s}}}{\varepsilon_{\mathrm{b}} Z} t - \omega \right)} - (1-\lambda) e^{-k_\tau \delta^{\rho_1} \left(\frac{D_{\mathrm{Ae}}}{\varepsilon_0 r^2} t - \hat{\omega} \right)} \right) \tag{7}$$

where $\hat{\omega}$ represents the delay on the scale of τ, and its relation to ω is given by Eq. (8) [58], and λ represents the kinetic weight factor. The analytical model for R^∞ used by Mellado *et al*. [58] is presented by Eq. (9).

$$\hat{\omega}=\frac{D_{\mathrm{Ae}}}{\varepsilon_0 r^2}\frac{\varepsilon_{\mathrm{b}}Z}{\mu_{\mathrm{s}}}\omega \tag{8}$$

$$R^{\infty}=\frac{\alpha}{Z^{\gamma}+\beta} \tag{9}$$

Where α, γ and β are mathematical adjustment coefficients, and Z is the heap height. Finally, the model for copper heap leaching for copper sulfide minerals is given by Eq. (10).

$$R=\frac{\alpha}{Z^{\gamma}+\beta}\left(1-\lambda e^{-k_{\theta}\delta^{\rho_2}\frac{\mu_{\mathrm{s}}}{\varepsilon_{\mathrm{b}}Z}\left(t-\frac{\varepsilon_{\mathrm{b}}Z}{\mu_{\mathrm{s}}}\omega\right)}-\left(1-\lambda\right)e^{-k_{\tau}\delta^{\rho_1}\frac{D_{\mathrm{Ae}}}{\varepsilon_0 r^2}\left(t-\frac{\varepsilon_{\mathrm{b}}Z}{\mu_{\mathrm{s}}}\omega\right)}\right) \tag{10}$$

2. 3. Uncertainty analysis

The uncertainly analysis (UA) determines the uncertainty of output variables due to the uncertainty of input variables [64]. It is generally performed by using the probability theory [65], where uncertainty is represented by probability distribution functions (PDF) and can be realized in four steps. First, the PDF type and the uncertainty magnitude for each input variable are determined, *i.e.* the input uncertainty is characterized. Second, for each input variable, a sample of the PDF is generated. Third, output variable values are determined for each element sampled. Finally, the results are analysed by using graphs, descriptive statistics, and statistical tests to characterize the behaviour of the output variables.

When the input variables have epistemic uncertainties, the uncertainty can be represented by a uniform distribution. Design and operation variables present this type of uncertainty. When the input variables have stochastic uncertainties, normal distribution is generally used to represent this type of uncertainty [66].

2. 4. Optimization of the experimental model

A multivariate function of seven independent variables and one dependent variable is defined from an inverse exponential model, a statistical analysis, and the multiple regression adjustment is presented in Eq. (11).

$R(X) = f(X)$ (11)

Formalizing the optimization model, the objective is to maximize copper recovery considering the range of sampled values as domain of the input variables [67] expressed in Eq. (12).

Max $\{R(X)\}$ (12)

The operational constraints for the n independent variables are shown in Eq. 13:

$x_i^{\min} \leq x_i \leq x_i^{\max}\ \forall\ i \in X \mid X = \{x_1, x_2..., x_n\}$ (13)

Considering the nature of the analytical model developed, it is proposed to optimize it using the Lagrange multipliers technique, which provides determination of the optimal values of a multivariate function when there are one or more restrictions on the input parameters.

3. RESULTS AND DISCUSSIONS

3. 1. Analysis of the effects of main independent variables

Analysis of the data generated by the factorial model, also used for the fit of the analytical model presented by Eq. (7), indicated only four factors that have main effects on the response variable: the heap height, superficial velocity of leaching flow and chloride concentration. It is corroborated that the superficial velocity of leaching flow in the bed is the variable with the greatest impact (of the analyzed variables) on the copper recovery as shown in Figure 1.

Figure 2 shows that copper recovery increases as superficial velocity of lixiviant flow and chloride concentration are increased, while decreases at higher heap heights.

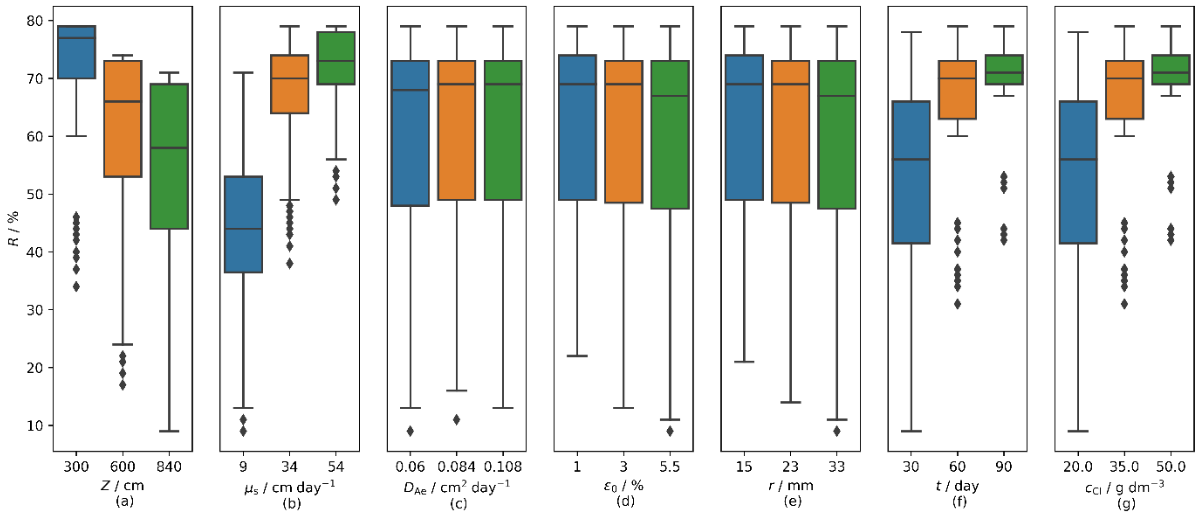

Figure 1. Main effects of independent variables heap height Z (a), superficial velocity of lixiviant flow μ_s (b), effective diffusivity D_{Ae} (c), porosity e ε_0 (d), particle ratio r (e), leaching time t (f) and Cl concentration c_{Cl} (g), in copper extraction R from sulfide minerals

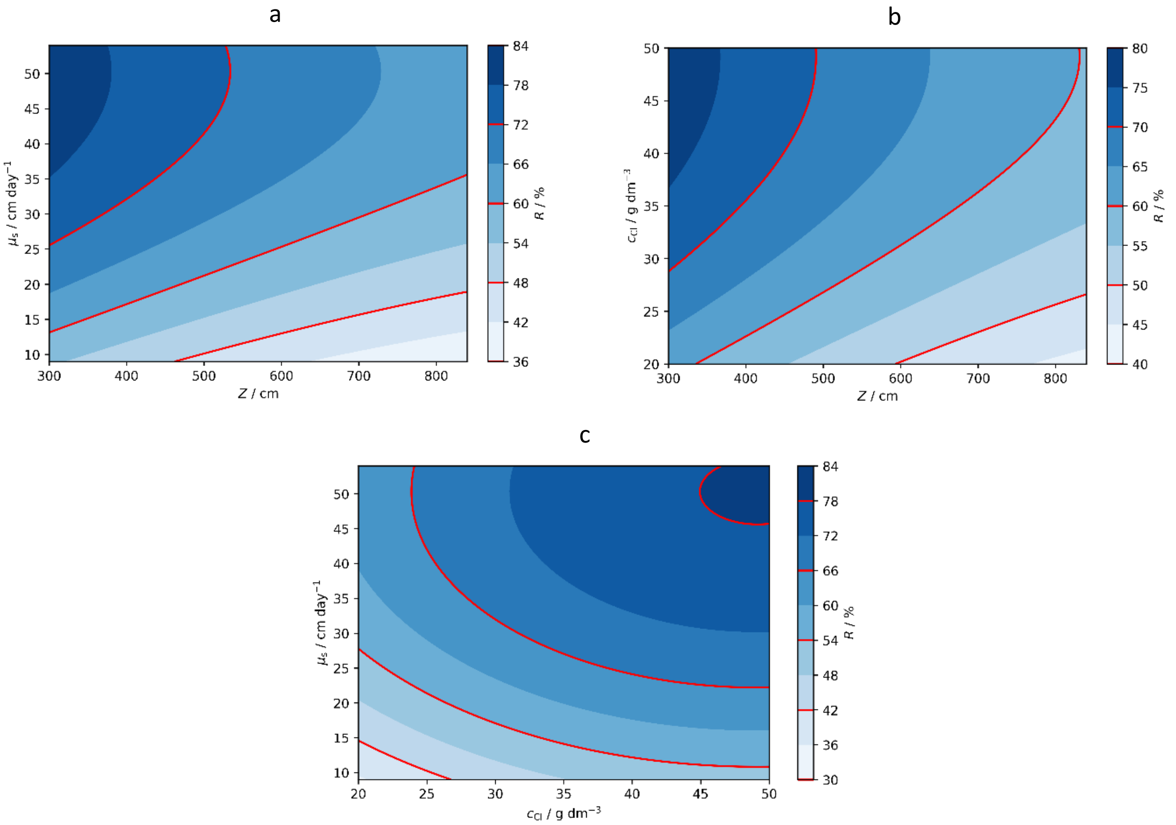

Figure 2. Contour plot of copper recovery versus the heap height and superficial velocity (a); heap height and chloride concentration (b); and, chloride concentration and superficial velocity (c).

3. 2. Uncertainty analysis

Eq. (10) included the copper recovery dependence on the following operational variables: leaching time, particle size, heap height, particle porosity, superficial velocity of the leaching flow and effective diffusivity of the solute through particle pores. A proper distribution function to represent epistemic uncertainties is the uniform PDF, taking the values of x_1, x_2..., x_n, as the central tendency values of the parameters p_1, p_2..., p_n, respectively. The sensitivity analysis was performed 3 times for leaching times of 30, 60 and 90 days (see Fig. 3).

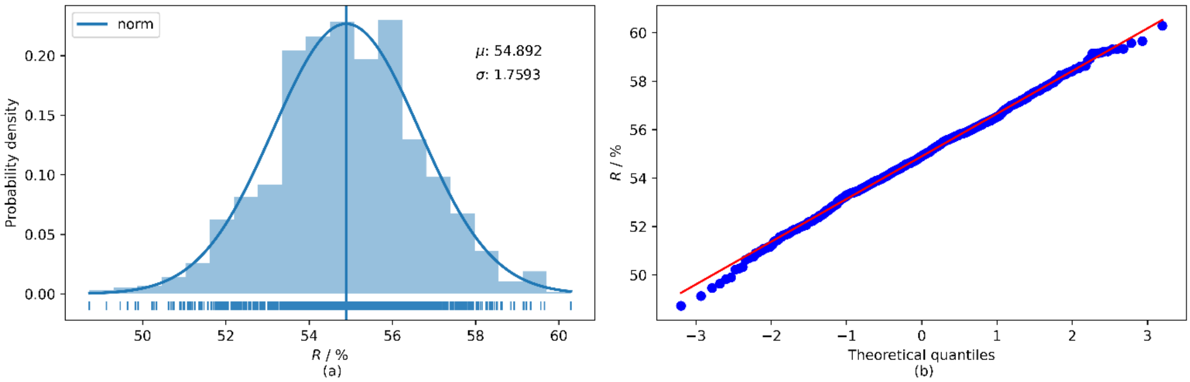

Figure 3. Probability density (a) and normal Q-Q plot (b) of UA at 30 days of leaching

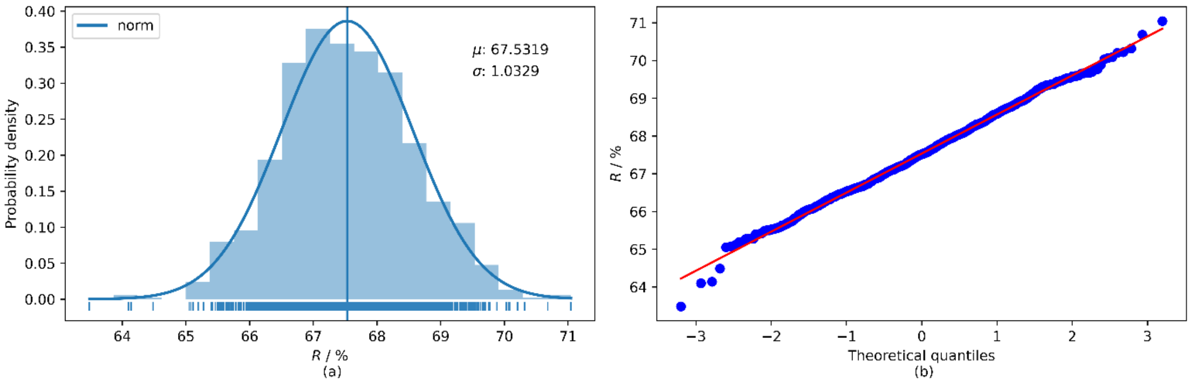

Figure 4. Probability density (a) and normal Q-Q plot (b) of UA at 60 days of leaching

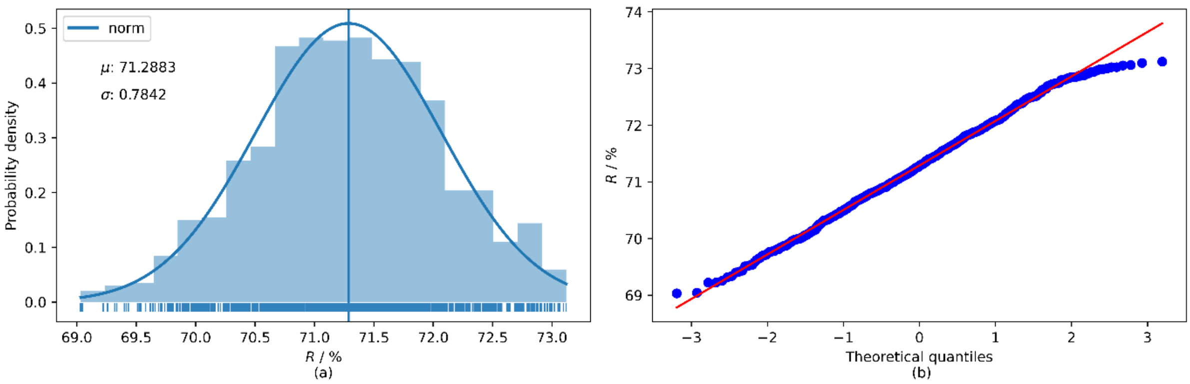

Figure 5. Probability density (a) and normal Q-Q plot (b) of UA at 90 days of leaching

UA shows that leaching time affects the kinetic uncertainty of the heap leaching phase. Histograms show that uncertainty in the input variables produces lower uncertainty in recovery as the leaching time is increased from 30 to 90 days. The normal distribution plots (Q-Q plot) indicate that copper recovery normally behaves for all investigated leaching times. The recovery presents a normal PDF with averages of 54.89 ± 1.76, 67.53 ± 1.03, and 71.29 ± 0.78 %. On the other hand, the normal probability plot indicates that for the leaching time of 90 days the recovery has a tail that deviates from the normal behaviour. The change in the recovery behaviour as a function of the time factor is due to the tendency to asymptotic behaviour.

3. 3. Analytical model adjustment

The fit of the analytical model developed by Mellado *et al.* [57] by optimization algorithms [67] indicates that the copper recovery from sulfide minerals can be explained by Eq. (14), where the volumetric fraction of the solution in the bed is assumed as $\varepsilon_b = 0.015$, while the delay of the reaction is assumed as $\omega = 1$.

$$R=\frac{138.83}{Z^{0.042}+0.038}\left(1-0.705\,e^{-0.027\delta^{1.81}\frac{\mu_s}{0.015Z}\left(t-\frac{0.015Z}{\mu_s}\right)}-0.295\,e^{-2.3\delta^{2.081}\frac{D_{Ae}}{\varepsilon_0 r^2}\left(t-\frac{0.015Z}{\mu_s}\right)}\right) \quad (14)$$

The analytical model presented by this equation is validated by the goodness-of-fit statistics Mean Absolute Error (MAD), Mean Squared Error (MSE) and Mean Absolute Percent Error (MAPE), with values of 1.147×10^{-2}, 2.475×10^{-4} and 0.793 %, respectively. The error statistics indicates that the fitted model explains the system under the set of sampled values. The Sensitivity analysis of the dependent variables that model the copper recovery for low, medium, and high levels operational conditions, check again that the variables that influence the copper recovery are the heap height (see Fig. 6a), chloride concentration (see Fig. 6b), and superficial velocity of lixiviant flow (see Fig. 6c). The impact of the other variables at different levels is considered are negligible (see Figures 6d, 6e, and 6f).

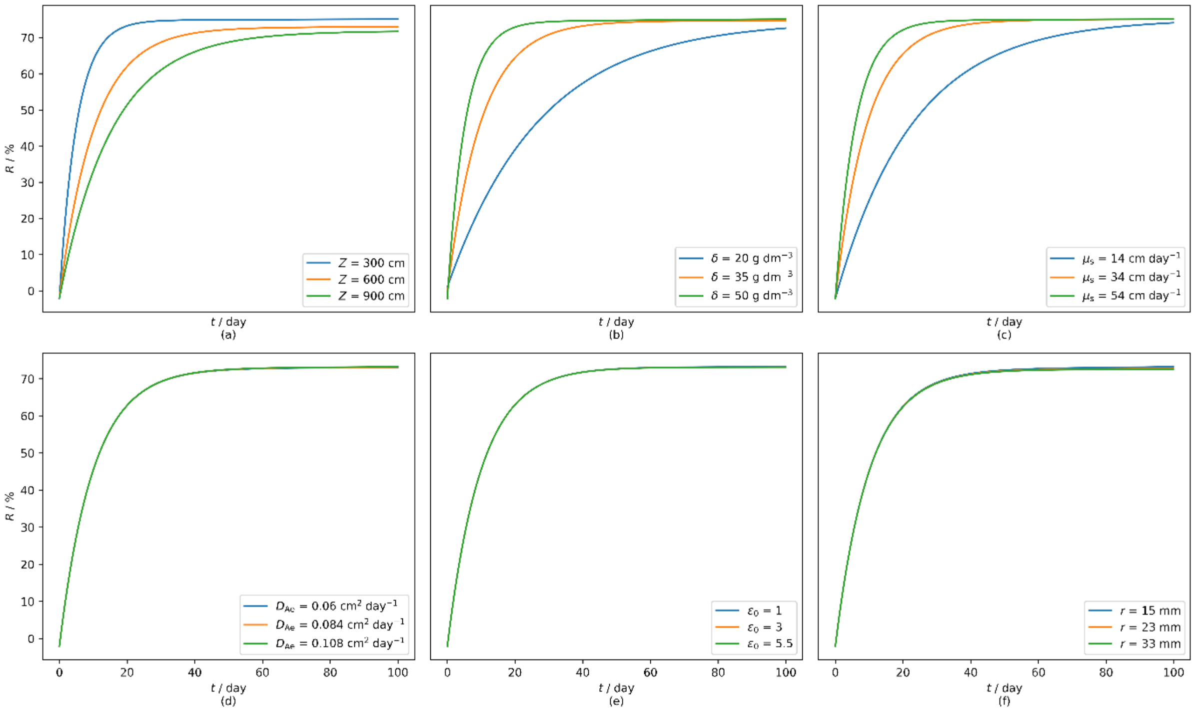

Figure 6. Sensitivity analysis of copper recovery for low, medium, and high levels of the factors: heap height (a), chloride concentration (b), superficial velocity of lixiviant flow (c), effective diffusivity within particle pores (d), porosity (e), and particle size (f)

Finally, comparison of the theoretical results in the literature and industrial heap processes, shows that despite the fact that the heap height is inversely proportional to the recovery, the heights of industrial heaps are at high levels. The increase in the height of commercial heaps is due to economic efficiency, which is the function of the available surface area [14]. The factors that influence the process kinetics the most are the percolation rate and chloride concentration as the leaching agent, of which, the percolation rate is directly related with the heap height and its permeability [51]. Also, the time factor has a strong impact on the copper recovery, being initially rapid recovery and showing asymptotic behaviour as time increases.

The current low ore grades reduce profitability of other recovery technologies due to requirements of greater comminution, temperature [68], or operating times. Those variables may change depending on the working material and the recovery standards of a mining company [66] severely impacting the projected profits. Therefore, mathematical models that provide optimization of the process would be an added value to the study and improvement of ore recovery in industrial contexts.

3. 4. Optimization of the analytical model

Optimization of the analytical model adjusted in the previous section for the set of sampled values was performed by using the Python library "SciPy Optimize" (Version 3.7.0). This library provides several methods to minimize/maximize objective functions subject to constraints.

Table 1 presents the operational restrictions associated with the independent variables in the form of lower and upper limit values. Optimal values for each variable are also presented.

The graphical analysis of the copper recovery response surface (see Fig. 7), model the recovery over time in the form of an inverse exponential function tending to become asymptotic between 80 and 100 days of leaching.

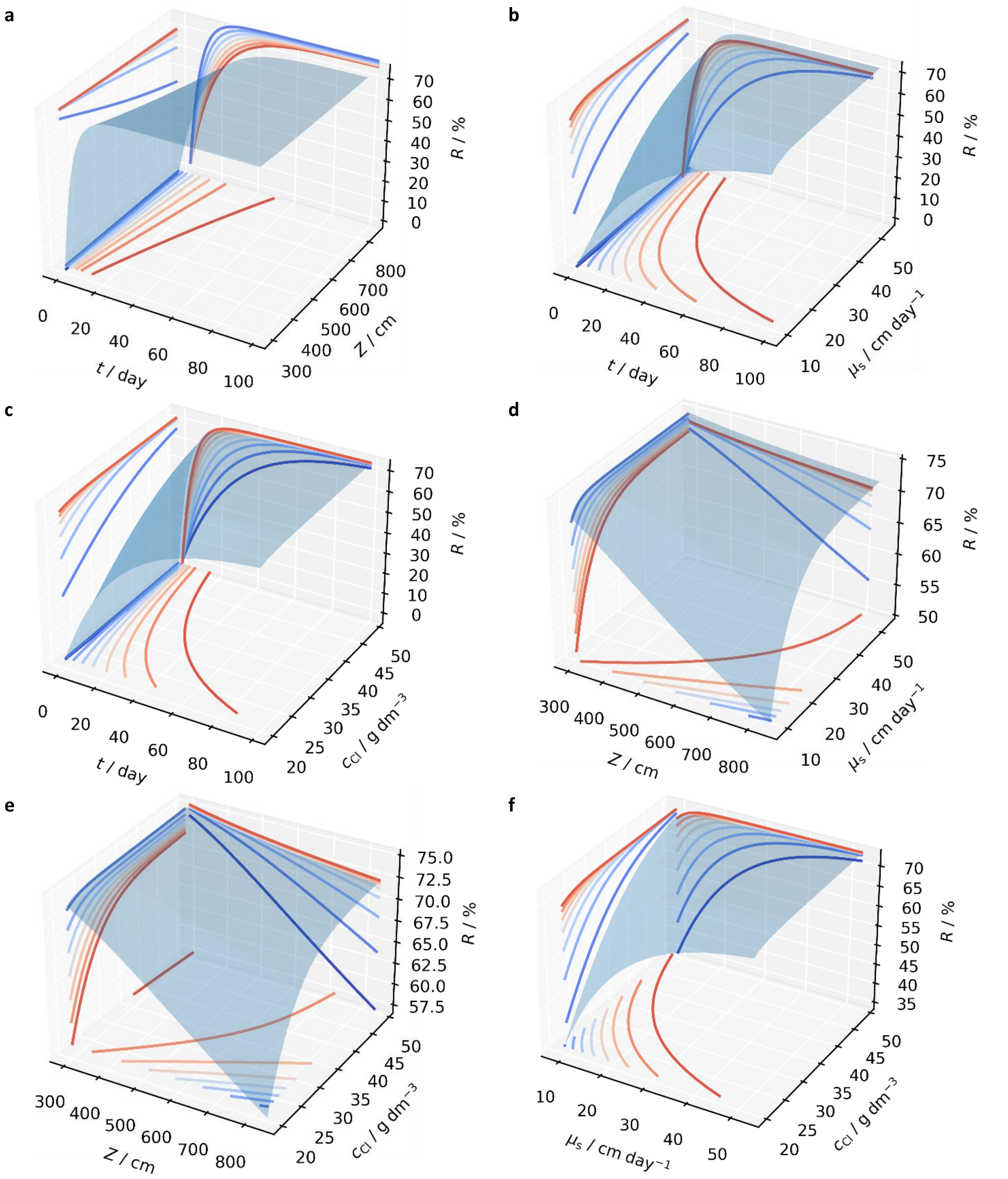

Figure 7. Response surface of copper recovery from sulfide minerals versus: time and the heap height (a); time and the superficial velocity of the leaching flow (b); time and the chloride concentration (c); heap height and the superficial velocity (d); heap height and the chloride concentration (e); superficial velocity and the chloride concentration (f)

Table 1 Limits and optimal values of the independent variables

Variable	Lower limit	Upper limit	Optimal value
Z / cm	300	900	900
μ_s/ cm^3 cm^{-2} d^{-1}	9	54	54
D_{Ae}/ cm^3 cm^{-1} d^{-1}	0.06	0.108	0.108
ε_0 / %	1	5.5	1
r / mm	15	33	15
t / day	0	90	90
c_{Cl}/ g dm^{-3}	20	50	50
R / %	-	-	72.12

This value for leaching time is common in hydrometallurgical processes in the Chilean mining industry. On the other hand, at the lower heap height, a greater recovery is observed, which is due to the improvement in the efficiency of the percolation of the leaching flow through the heap. And finally, additional surface plots in Figure 7 model the dynamics of response variable as functions of significant independent variables.

Additionally, future works could incorporate machine learning techniques for process modelling, simulation and optimization [69]. Also, integration of the model presented here along with discrete events simulation models, (*e.g.* [63,70]), aimed to optimize the mineral recovery, while incorporating the feeding mineralogical variation, different process operation modes by variation of reagents or the levels of the variables and/or other operational parameters, has the potential to add value to the study of leaching dynamics of sulfide copper minerals.

4. CONCLUSIONS

The present investigation presents the results of an analytical model of copper extraction from a sulfide mineral (chalcocite) as a system of first-order differential equations through an inverse exponential function. The main findings in this study are summarized below.

The behavior of heap leaching process of copper sulfide minerals (secondary sulfides), like chalcocite, can be modelled as a system of first-order differential equations, which is validated by the goodness-of-fit statistics.

Particle size, porosity, and effective diffusivity of the solute within the particle pores are not as significant in the copper extraction, as is leaching time, heap height, superficial velocity of the leaching flow and chloride concentration in the leaching solution.

The best result predicted by optimizing the generated analytical model would be obtained by working at high chloride concentration and a high leaching flow rate.

On the other hand, the fit of this type of analytical models can be extended to other variable levels or factors, such as inclusion of different leaching agents. The model would be modified then according to the kinetics that describe or dominate the operation.

Generation of analytical models to represent complex processes, such as mineral leaching, has the potential to be used for analysis, generalization, and optimization tasks, since these models capture the essence of the modelled process and could be used to predict the response under operational conditions, identifying the conditions that maximize the aggregate process productivity.

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Razvoj analitičkog modela za iskorišćavanje bakra iz sekundarnih sulfida u hloridnim medijima u industrijskom okruženju

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(Stručni rad)

Izvod

U multivarijantnoj analizi, model predviđanja je matematičko/statistički model koji povezuje skup nezavisnih varijabli sa zavisnim ili promenljivim varijablama. Ovaj rad prezentuje opisni model koji objašnjava iskorišćavanje bakra iz sekundarnih sulfidnih minerala (halkocita) uzimajući u obzir efekte vremena, visine jalovišta, površinske brzine ispiranja, koncentracije hlorida, veličine čestica, poroznosti i efektivne difuzije rastvorene supstance unutar pora čestice. Izluživanje bakra se zatim modeluje sistemom diferencijalnih jednačina prvog reda. Rezultati su pokazali da su visina jalovišta i površinska brzina toka ispiranja najkritičnije nezavisne varijable, dok su ostale od manjeg uticaja u primenjenim uslovima rada. U ovoj studiji dobijeni su reprezentativni parametri podešavanja, tako da se model može koristiti za istraživanje izluživanja bakra u hloridnim medijima, kao deo proširenog lanca prerade bakra.

Ključne reči: ekstrakcija bakra, fenomenološko modelovanje, luženje hlorida, modelovanje, hidrometalurgija