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In situ recovery of copper sulfide ores: Alternative process schemes for bioleaching application

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ABSTRACT

There is a growing interest in exploring the application of bioleaching for treating copper sulfide ores of decreasing grade and located at larger depth by in situ recovery (ISR) for its potential savings in ore extraction, crushing, grinding and the avoidance of tailings. As copper sulfide ores are usually present in well consolidated rocks a crucial aspect for ISR to be successful is to increase the ore permeability in order to allow a good access of solution to the valuable metal values. However, in bioleaching an additional critical aspect is to guarantee an adequate supply of oxygen, the final electron acceptor in the reaction chain. Two alternative schemes to solve this issue are here characterized and compared using process simulation.

One approach considers pre-treating the rock with hydrofracturing and/or confined blasting in order to create a network of cracks adequate for pumping the pressurized leaching solution into the ore bed in a saturated flow regime. In this scheme oxygen needs to be added in an external bioreactor where ferric iron is generated by bacterial oxidation of ferrous iron. A second approach considers pre-treating the ore by application of sublevel stopping techniques with partial removal of the rock to be able to irrigate the solution into the ore bed under an unsaturated flow regime. In this scheme oxygen can be directly supplied into the ore bed enabling in situ generation of ferric iron by the oxidative action of microorganisms present in the ore.

The influence of irrigation rate, leaching solution concentration, bacterial population and ore bed dimensions on copper recovery and bioreactor requirements was assessed for these two process schemes. Some economic aspects of these two alternatives are discussed.

1. Introduction

In-situ recovery (ISR) offers the possibility of treating ore bodies with an approach radically different to conventional mining. In ISR metal values can be recovered from the rock by direct dissolution with leaching solutions which are supplied to the ore body and then pumped out for further processing of the dissolved metals (Sinclair and Thompson, 2015; Seredkin et al., 2016). ISR could enable to recover the metal values without the need for ore extraction, crushing or grinding, minimizing energy consumption, Capex and Opex in the process (Batterham and Robinson, 2019). In addition, production of tailings is avoided and landscape disturbance is minimized.

However, a crucial aspect for ISR to be successful is to have the ore permeability necessary to achieve a good access of solution to the valuable metals (Sinclair and Thompson, 2015; Märten, 2019). Application of ISR to copper extraction has been until now restricted to acid leaching of oxidized copper ore bodies which are naturally fractured and have good permeability, enabling good copper recoveries at low operating costs (Thoreau, 1998; M3 Engineering, 2013; M3 Engineering, 2017). However, copper sulfide ores are normally located at greater depths and within a more consolidated rock, then its recovery by ISR will very likely require some type of pre-treatment of the rock for permeability improvement. Main options suggested for permeability stimulation technologies include hydraulic fracturing (up to 100 MPa), acidizing (to dissolve minerals and open path-ways), thermal fracturing (cold water injection), confined and free-face blasting (BIOMore, 2018; Bahamóndez et al., 2016).

Dissolution of sulfide ores requires oxidative leaching conditions, then ISR can be conducted by applying bacterial leaching, a technology which is established in the copper industry for the treatment of copper sulfide ores in heaps and dumps (Ghorbani et al., 2016; Petersen, 2016). Therefore, the choice of the permeability stimulation approach which

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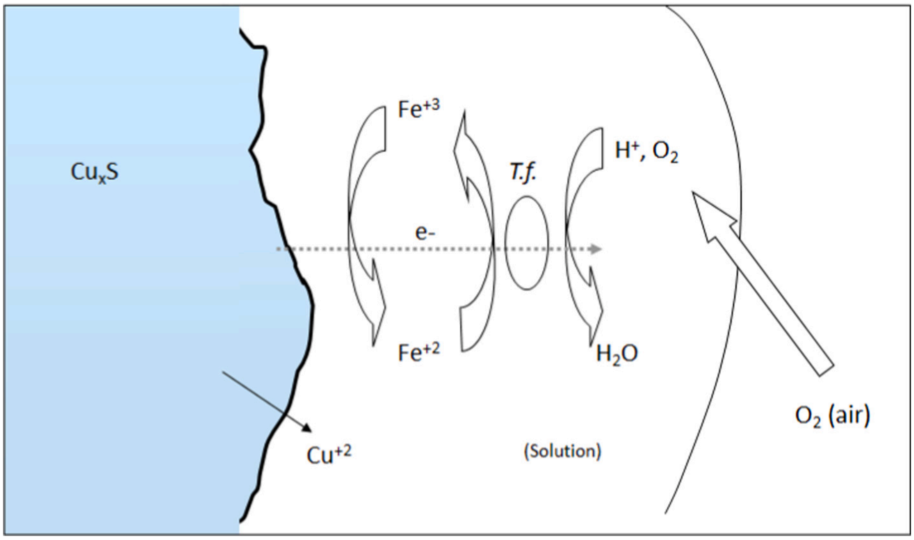

Fig. 1. Scheme showing the interaction of main chemical and biologically catalyzed reactions in bioleaching.

defines the leaching circuit, the efficiency of copper recovery and the process economics (operation size, capex, opex), needs to take into account the fundamental aspects of the complex chemical and biological phenomena involved in bioleaching. A basic reaction scheme of bacterial leaching of copper sulfides is shown in Fig. 1. Copper sulfides dissolves under the oxidative action of Fe^{+3}, which removes electrons from the sulfide while being reduced to Fe^{+2}. Simultaneously, Fe^{+2} is reoxidized to Fe^{+3} by transferring electrons to dissolved oxygen under the catalytic action of leaching microorganisms (Boon et al., 1999; Vargas et al., 2014). The population of microorganism in an ore bed is mainly constituted by planktonic cells present in stagnant solution zones and cells attached to ore particles (Govender et al., 2015). Good circulation of air is required to supply the oxygen necessary as final electron acceptor and the carbon dioxide necessary as carbon source for bacterial growth (Petersen and Dixon, 2007; Marín et al., 2017).

The global reactions for ferric leaching of copper sulfides for the case of chalcopyrite and covellite are:

$$CuFeS_2 + 4Fe^{+3} \rightarrow Cu^{+2} + 5Fe^{+2} + 2S^0 \quad (1)$$

$$CuS + 2Fe^{+3} \rightarrow Cu^{+2} + 2Fe^{+2} + S^0 \quad (2)$$

and for oxidation of ferrous iron oxidation:

$$2Fe^{+2} + ½\,O_2 + 2H^+ \rightarrow 2Fe^{+3} + H_2O \quad (3)$$

The stoichiometry of the global reaction is for each case:

$$CuFeS_2 + O_2 + 4H^+ \rightarrow Cu^{+2} + Fe^{+2} + 2S^0 + 2H_2O \quad (4)$$

$$CuS + ½\,O_2 + 2H^+ \rightarrow Cu^{+2} + H_2O \quad (5)$$

Solution:

$$\frac{dV_i}{dt} = F_{i-1} - F_i \quad (\,m^3/day\,) \quad (6)$$

which shows than oxygen is the only consumed oxidant. As dissolved oxygen acts as the final electron acceptor for copper sulfide dissolution to efficiently occur is critical to have an adequate rate of oxygen transfer from air into the leaching solution. Therefore, when selecting the permeability stimulation approach for ISR application of bioleaching, apart from considering the requirements for good circulation of leaching solutions inside the ore body it is also critical to define the scheme in which oxygen will be incorporated into the solution circuit.

There are currently two main proposed schemes for developing ISR bioleaching which include quite different approaches for supplying oxygen into the process. One approach (see Fig. 2-a) is pumping the pressurized leaching solution under saturated flow regime through a crack network built in the ore body with a combination of hydrofracturing and confined blasting (Johnson, 2015; Biomore, 2018; Richter et al., 2018). As cracks and voids in the rock are completely filled with the leaching solution this process scheme prevents direct incorporation of oxygen to regenerate ferric iron by bacterial oxidation of ferrous ions into the ore body. This is due to the limited solubility of O_2 in water which is 8 ppm (at 25 °C, 1 bar). Therefore, in this process scheme the required ferric iron needs to be produced in an external bioreactor and then pumped with the leaching solution into the ore body, an approach usually referred to as indirect bioleaching, IBL (Carranza et al., 1993; Pakostova et al., 2017).

An alternative approach for developing ISR bioleaching is to form an ore bed with sufficient permeability to operate as a trickle-bed (see Fig. 2-b). In this scheme, solution is irrigated at the top of a well aerated ore bed so that copper sulfides can be leached by ferric iron generated in-situ by the oxidative action of the bacterial population present in the ore. This type of configuration can be achieved by free-face blasting enabled by partial removal of the ore by sub-level stopping, according to the proposed technology of in situ mining through leaching (ISM) (Iriarte, 2015; Bahamóndez et al., 2016). In this configuration a fraction of the ore is removed through galleries and the drawbell ensures an efficient collection of the loaded copper solution at the ore column base.

The purpose of this work is to conduct a preliminary comparative assessment of implementing bioleaching using these two different approaches for oxygen supply. Modelling has proved to give a valuable insight to guide engineers in selecting alternative bioleaching approaches (Petersen, 2010). Accordingly, a simplified model was here developed to analyze the impact of the different aeration approach on the pattern of biooxidation of the ore bed and the efficiency of copper extraction. Model results also enabled a preliminary comparison of some economic aspects of these technologies.

2. Methodology

2.1. Modelled bioleaching schemes

This is a simplified model aimed at obtaining an initial comparison of copper leaching patterns and copper recoveries under two different ISR bioleaching process schemes, indirect bioleaching (IBL) and in situ mining through leaching (ISM). Accordingly, only the kinetics of two main reactions were considered: ferric leaching of a copper sulfide ore mainly composed by chalcopyrite (Eq. 1) and bacterial oxidation of

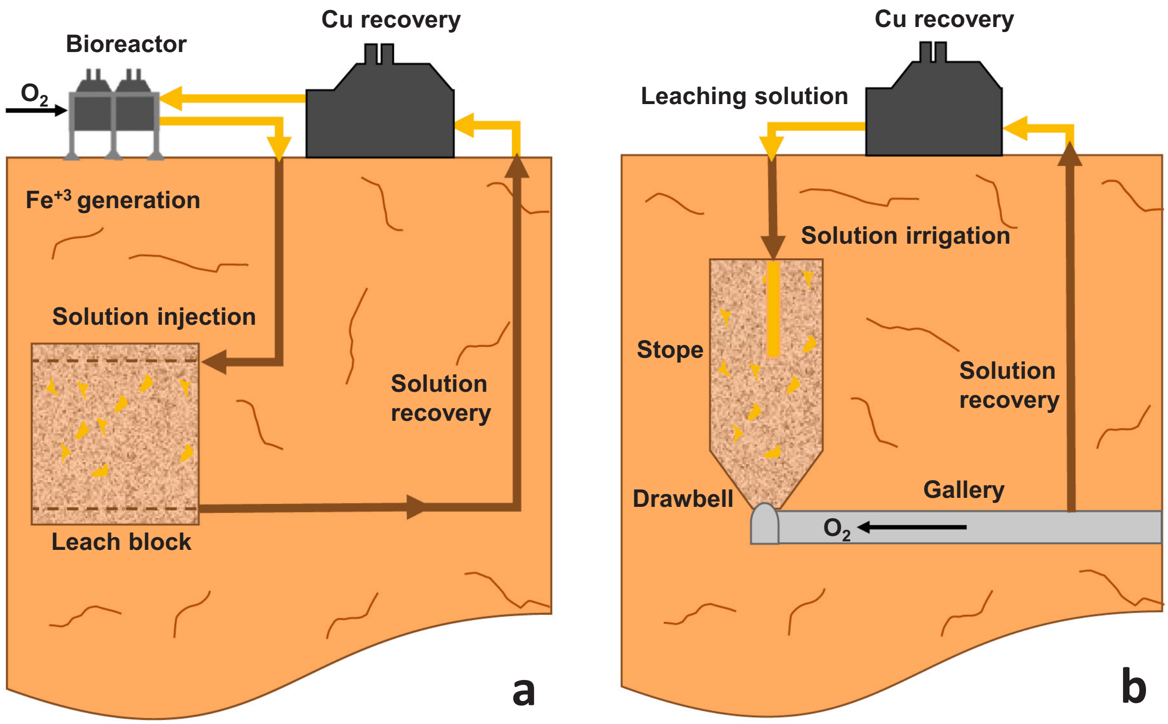

Fig. 2. Schemes of ISR bioleaching using two different approaches for oxygen addition into the process. a) Indirect bioleaching of a fractured ore block with ferric iron generated in an external aerated bioreactor; b) direct bioleaching of a high permeability aerated ore bed produced by sub level stopping techniques.

ferrous iron (Eq. 3). The kinetic expressions for these two reactions are described in the next section. The effect of direct action by bacteria attached to copper sulfides was neglected as in copper ores most of the copper sulfides are imbedded in the silicate matrix far from the reach of microorganisms (Watling et al., 2014).

Simulations were conducted for bioleaching of a buried 20 m height ore bed with 50 × 50 m surface area, composed by copper sulfide ore particles of 5 cm average diameter. This particle size range is achievable in underground copper mining with the application of high-energy ring blasting designs (Cebrían et al., 2017). For comparison purposes ore particle sizes were assumed to be 5 cm diameter in both process scheme models.

Simulations were conducted for two irrigation rates, 1 and 5 L/h-m^2: the first value is in the range of irrigation rates reported when pumping leaching solutions into a leach block pre-conditioned by hydrofracturing and/or confined blasting (Biomore, 2018). The second value is in the range used in the irrigation of heap and dump leaching operations (Ghorbani et al., 2016).

The leaching solution in the whole circuit is assumed to operate in the pH range 1.5–2.5, which is adequate for an efficient bacterial activity (Plumb et al., 2008). Accordingly, the concentration of ferric iron in solution was assumed to be 3 g/L which is about the maximum concentration permitted for a system controlled by precipitation of jarosites when operating in this pH range (Ahonen and Tuovinen, 1993; Leahy and Schwarz, 2009).

In process scheme 1, indirect bioleaching (IBL), the ore bed porosity is assumed to be completely filled with the leaching solution and leaching of copper sulfides occurred just with the 3 g/L of ferric contained in the incoming leaching solution produced in an external bioreactor (Pakostova et al., 2017; Biomore, 2018). In this case there is not ferrous iron oxidation inside the ore bed, then in the model the concentration of bacteria was considered as $C_x = 0$C-mol/L.

In process scheme 2, in-situ mining (ISM), the ore bed porosity was sufficient for air to circulate and keep an adequate supply of oxygen and carbon dioxide across the whole ore bed column. This is a situation reached in heap bioleaching when air is blown through the base at flows over 6 L/min m^2 (Lizama, 2001). Therefore, Fe^{+3} was continuously regenerated by bacteria present along the ore bed by biooxidation of the ferrous iron produced by ferric leaching of the copper sulfides. Two different values of bacterial populations were used for the calculations in this case: $C_x = 0.005$ and 0.05C-mol/L, values which are in the range of those determined in previous bioleaching studies of pyrite is stirred tanks with *Acidithiobacillus ferrooxidans* (Boon et al., 1999). This bacterial population range guarantees an efficient oxidative activity but without the risk of inhibition which has been observed at very high microorganisms concentrations (Okereke and Stevens, 1991). The bacterial population was assumed to be constant during leaching time and homogeneously distributed along the ore bed. Two cases were considered in this process scheme: a) The incoming leaching solution contained 3 g/L Fe^{+3}, assuming that was also produced in an external bioreactor; b) The incoming solution contained 3 g/L Fe^{+2}, which assumes that the system operates without external bioreactor and the incoming leaching solution is simply the raffinate recirculated from SX.

2.2. Dynamic mass balance

To simulate the bioleaching of copper sulfide ores a mass balance model for the ore column was developed, considering ferric leaching of copper sulfides and ferric iron regeneration by biooxidation of ferrous ions. This mathematical model involves the mass balances for the irrigation solution, copper in aqueous and solid phases, ferric and ferrous ions in solution, along the height of the column and with respect to time (dynamic mass balance model). In this model, the column ore was discretized in order to solve the mass balance of each chemical component in an *i* vertical volume width or ore column volume width (CVW), according to the schematic representation shown in Fig. 3.

The mass balance results for each CVW determines the input data for the mass balance of the lower CVW. Therefore, the results of the global mass balance at the bottom of the ore column is the integration of the mass balances in each volume of the column. The mass balance

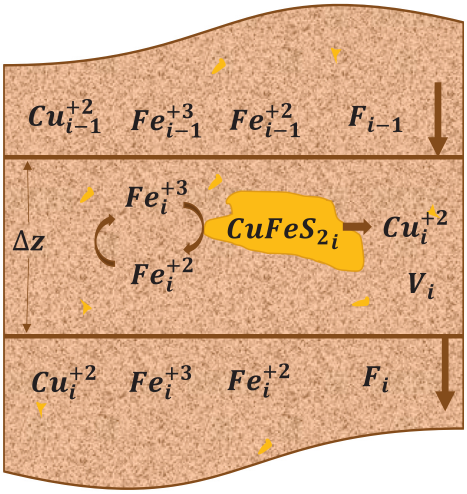

Fig. 3. Scheme of the mass balance in a fraction of the ore column. Cu^{+2}, Fe^{+2}, and Fe^{+3} and F corresponds to concentration of copper (g/L), ferric ion (g/L), ferrous ion (g/L) and solution flow (m^3/s) respectively. Sub-indexes *i-1*, and *i* correspond to values inlet and drained streams of the analyzed discrete leaching solution section V_i in CWV.

equations used in the model are the following five equations:

Chalcopyrite in solid phase:

$$\frac{dmCP_i}{dt} = -r_{CP_i} \quad (\text{ Ton CP/day }) \tag{7}$$

Copper in aqueous phase:

$$[Cu^{+2}]_i \cdot \frac{dV_i}{dt} + V_i \cdot \frac{d\,[Cu^{+2}]_i}{dt} = F_{i-1} \cdot [Cu^{+2}]_{i-1} - F_i \cdot [Cu^{+2}]_i + r_{{Cu^{+2}}_i} \quad (\text{ Ton Cu}^{+2}\text{/day }) \tag{8}$$

Ferric ion in aqueous phase:

$$[Fe^{+3}]_i \cdot \frac{dV_i}{dt} + V_i \cdot \frac{d\,[Fe^{+3}]_i}{dt} = F_{i-1} \cdot [Fe^{+3}]_{i-1} - F_i \cdot [Fe^{+3}]_i + r^{bio}_{{Fe^{+2}}_i} \cdot V_i - r_{{Fe^{+3}}_i} \quad (\text{Ton Fe}^{+3}\text{/day }) \tag{9}$$

Ferrous ion in aqueous phase:

$$[Fe^{+2}]_i \cdot \frac{dV_i}{dt} + V_i \cdot \frac{d\,[Fe^{+2}]_i}{dt} = F_{i-1} \cdot [Fe^{+2}]_{i-1} - F_i \cdot [Fe^{+2}]_i - r^{bio}_{{Fe^{+2}}_i} \cdot V_i + r_{{Fe^{+3}}_i} \quad (\text{ Ton Fe}^{+2}\text{/day }) \tag{10}$$

where *Vi* is the volume of the solution contained in the *i* CVW (solution inventory), m^3; F_i is the solution flow drained from the *i* CVW, m^3/s; $F_{i\text{-}1}$ is the inlet flow of the CVW *i* (which also corresponds to the solution drained from the CVW *i-1*), m^3/h; for each dissolved metal $[Cu^{+2}]$, $[Fe^{+2}]$, and $[Fe^{+3}]$ the sub-indexes *i-1* and *i* refers to the inlet and drained concentrations of the *i* CVW, g/L; mCP$_i$ is the mass of chalcopyrite contained in the ore of the *i* CVW, kg; $r_{CP\ i}$ is the kinetic rate of chalcopyrite dissolution from the ore in the *i* CVW, kg/s; $r_{Fe+3,i}$ is the kinetic rate of ferric ion reduction in the *i* CVW, kg/ m^{3}s; $r_{Fe+2,i}$ is the kinetic rate of ferrous ion oxidation in the *i* CVW, kg/ m^{3}s; $r_{Cu}{}^{+2}$ is the kinetic rate of copper ion dissolution in the *i* CVW, kg/ m^{3}s; *t* is the time, s. Each mentioned kinetic rate reaction will be explained in the next section.

The dynamic model of the ore column is given by a set of partial differential equation system to explain each vertical component variation. This model is simplified using a conventional "method of lines", where a set of (*N* x 5) ordinary differential equation (Eq. 6 to 10) to simulate each concentration for each time. Those were based on a discretization of *N* elements of the length axis resulting in each *i* CVW (Evans, 2010). This model was solved in the software MATLAB with the integrator solver ODE45.

2.3. Kinetic equations

The kinetics of ferric leaching of a copper ore containing 0.5% Cu mainly as chalcopyrite was determined in experiments conducted with single size ore particles in batch flooded columns under iso pH and iso *Eh* conditions, according to a methodology previously described (Vargas and Rojas, 2017; Muñoz et al., 2019). Results confirmed that the kinetics of ferric leaching of the chalcopyrite ore particles was well described according to the following equation (Vargas, 2010):

$$\frac{\text{t}}{\tau} = \left(1 - 3(1 - X_{CP})^{\frac{2}{3}} + 2(1 - X_{CP})\right) \tag{11}$$

in which X$_{\text{CP}}$ is the degree of conversion of chalcopyrite, t is leaching time and τ is the leaching time necessary for full conversion of chalcopyrite. Eq. (11) corresponds to the kinetic expression of the unreacted core model with diffusion control (Bartlett, 1997; Levenspiel, 1999). In the present context this behavior corresponds to control by diffusion of soluble species through the gangue matrix in which copper sulfides are imbedded, a mechanism also identified by other authors in ferric leaching of copper sulfide ores (Córdoba et al., 2008; Abhilash et al., 2013; Ferrier et al., 2016).

For using in the dynamic mass balance eq. (11) was written in differential form as:

$$r_{CP_i} = \frac{mCP_0}{\tau_i}\left(2 - 2 \cdot \left(1 - \frac{mCP_0 - mCP_i}{mCP_0}\right)^{-\frac{1}{3}}\right)^{-1} \quad (\text{ Ton CP/day }) \tag{12}$$

with $X_{CP} = (mCP_0 - mCP_i)/mCP_0$, where mCP_O is the initial mass of chalcopyrite in the *i* CVW and mCP_i the mass of chalcopyrite in that volume at any time t = t. τ_i is the value of τ in the *i* CVW given by the expression:

$$\tau_i = k_{ore}\,\frac{D_p^2}{[Fe^{+3}]_i} \qquad (\text{day}) \tag{13}$$

where D_p is the ore particle diameter, $[Fe^{+3}]_i$ is the concentration of ferric iron in the i CVW at time t, and k_{ore} is a constant. From experimental results the reaction time τ for leaching 5 cm diameter chalcopyrite ore particles in a solution with 3 g/L Fe^{+3} was estimated to be 15.99 years and k_{ore} as 700.36 day-g/cm^2-L (Vargas, 2010).

The rate of copper dissolution and ferric iron consumption are given by the expressions:

$$r_{{Cu^{+2}}_i} = -r_{CPi}\,\frac{MW_{Cu}}{MW_{CP}} \quad (\text{ Ton Cu}^{+2}\text{/day }) \tag{14}$$

$$r_{{Fe^{+3}}_i} = r_{CPi}\ \nu\,\frac{MW_{Fe}}{MW_{CP}} \quad (\text{ Ton Fe}^{+3}\text{/day }) \tag{15}$$

where each reaction rate is proportional to the leaching kinetic ore rate r_{CPi} multiplied by the stoichiometric coefficient ν ($\nu=4$ for chalcopyrite) and molecular weights as described the Eq. 1.

On the other hand, the kinetics of bacterial ferrous iron oxidation is represented according to the following equation (Boon et al., 1999):

$$-\,r^{\,bio}_{Fe^{+2}} = \frac{{q_{Fe^{+2}}}^{max} C_x}{1 + K\frac{[Fe^{+3}]_i}{[Fe^{+2}]_i}} \quad (\text{ Ton Fe}^{+2}\text{/L} - \text{day}) \tag{16}$$

where ${q_{Fe+2}}^{max}$ and K are kinetic parameters and C_x is the bacterial population in C-mol/L. For the case of biooxidation of ferrous ions with *A. ferrooxidans*, constants in Eq. 11 are: $K = 0.05$, ${q_{Fe^{+2}}}^{max} = 0.0043$ Ton Fe^{+2}/C-mol-day (Boon et al., 1999).

The set of parameters used in this work to simulate the bioleaching

Table 1

Detailed parameters used in the model.

Parameter	Value
Discretized elements	100
Ore column height	20 m
Ore bed area	50 m × 50 m
Average ore particle diameter	5 cm
Irrigation Fe^{+3} concentration	0–3 g/L
Irrigation rate	1–5 L/h-m^2
Copper grade	0.5%
Ore bed humidity: initial/drain/dynamic	3 / 9 / 15%
Apparent density	1.5 Ton/m^3

process are shown in Table 1. Model results include profiles of ferric iron concentration and solution Eh obtained along the ore column at different leaching times. Solution Eh was calculated using the Nernst equation: $Eh = 0.77 + 0.0591 \log [Fe^{+3}]/[Fe^{+2}]$. Curves of copper recoveries versus leaching time were calculated from the integration of copper dissolved in the leaching solution exiting at the ore column base.

3. Results

Fig. 4 shows results of the evolution of Fe^{+3} ion concentration and *Eh* profiles along the column height for bioleaching of the chalcopyrite ore with an irrigation rate of 1 L/h-m^2 for three different situations. The case with $C_x = 0$ C-mol/L corresponds to the situation when there is no bacterial oxidation along the column height and the copper sulfides are leached just by the ferric generated in the external bioreactor. The cases with $C_x = 0.005$ and 0.05 C-mol/L correspond to well aerated ore beds containing different populations of active microorganisms. Fig. 5 shows the curves of copper recovery corresponding to each bioleaching condition included in Fig. 4.

Results in Fig. 4-a for $C_x = 0$ C-mol/L show that the concentration of Fe^{+3} in the leaching solution rapidly decays as it flows down the ore bed. These concentration profiles indicate that when there is not biooxidation of ferrous ion inside the ore, the ore column behaves as a two-zone reactor: an upper zone where ferric leaching of copper sulfides occurs, which ends at the point where Fe^{+3} concentration is depleted and a lower zone where the concentration of Fe^{+3} is zero and there is not ferric leaching. However, the limit between the upper and the lower zone behaves as a moving boundary: as the concentration and reactivity of copper sulfides contained in the upper zone decreases, the ore leaching rate decays, the concentration of Fe^{+3} reaches further down in the ore column and the upper reacting zone is extended. This process continues up to the time when solutions with Fe^{+3} concentration over zero reaches the ore bed base, and all the ore column becomes part of the reactive zone, which is achieved after about 4000 days. Depletion of Fe^{+3} concentration is congruent with the *Eh* profiles established along the column height during the operation with $C_x = 0$ C-mol, which shows that values adequate values for copper sulfide oxidation, i.e. over 0.7 V, are only reached in the upper reactive zone (Fig. 4-b).

Results in Fig. 4 for the cases when $C_x \neq 0$, show how regeneration of Fe^{+3} by bacterial oxidation of ferrous iron reduces the rate of decay of Fe^{+3} concentration and *Eh* along the ore column. In the case of bioleaching with $C_x = 0.005$ C-mol/L the ore column still behaves as a two-zone reactor, however duration of this regime is drastically reduced with respect to the case with $C_x = 0$ C-mol/L and after 400 days the Eh is over 0.7 V practically along the whole column height. When the bacterial population is raised up to 0.05 C-mol/L, Fe^{+3} is regenerated much more rapidly and practically from the start of the operation the whole ore bed is at *Eh* values over 0.7 V/NHE and under efficient ferric leaching.

Results in Fig. 5 show that, as expected from profiles in Fig. 4, activating bacterial oxidation of ferrous iron inside the ore bed by adequate oxygenation results in a notorious increase in the rate of copper recovery. For instance, the time necessary to leach 90% of copper in the case of $C_x = 0.05$ C-mol/L is about 3300 days, while in the same leaching time only 45% of copper recovery can be achieved with indirect bioleaching. The linearity of the copper recovery curve in this last case indicates that in this situation copper leaching rate is to a great extent controlled by the rate of ferric iron supply with the pumped solution into the ore column.

The additional copper obtained when passing from $C_x = 0$ to $C_x = 0.05$ C-mol/L corresponds to chalcopyrite leached by the ferric iron internally generated by continuous biooxidation of ferrous iron produced during ferric leaching of this sulfide according to Eq. 1. The biological oxidation of ferrous iron along the column with $C_x = 0.05$ C-mol/L is very efficient as it is able to maintain a *Eh* profile with values over 0.7 V/NHE along the whole ore column. This implies that bacterial ferrous iron oxidation activity is sufficiently fast to produce the required ferric iron so that copper dissolution becomes now partially controlled by the kinetics of leaching of the copper ore (Vargas et al., 2014). This is also evident from the parabolic form of the copper recovery curve for $C_x = 0.05$ C-mol/L (Fig. 5).

Figs. 6 and 7 show simulation results of ferric concentration/*Eh* profiles and copper recovery curves, respectively, in conditions similar to those in Figs. 4 and 5 but for an irrigation rate of 5 L/h-m^2. In the case of $C_x = 0$ C-mol/L this increase in the irrigation rate results in a significant increase in the profiles of ferric iron concentration and solution *Eh* along the ore column (Fig. 6). In fact, the duration of the two-zones pattern is significantly reduced and after 300 days *Eh* values over 0.7 V/NHE are established practically all along the ore column. These profile changes results in a significant improvement in the rate of copper leaching for $C_x = 0$ C-mol/L, which now for 3300 days of leaching increases up to 85%. It is important to outline that now the copper recovery curve obtained at 5 L/h-m^2 has parabolic shape wich indicating that copper leaching rate is now partially controlled by the kinetic of ferric leaching of the copper ore.

In the case of $C_x \neq 0$ the increase in the irrigation rate to 5 L/h-m^2 contributes to further enhance the profiles of ferric iron concentration and *Eh* in solution along the ore column (Fig. 6). However, results in Fig. 7 show that the increase in irrigation rate result only in a marginal gain in copper recovery with respect to the case of irrigation with 1 L/h-m^2. This is because when bacteria is active in the aerated ore the increase in ferric iron supply associated to the increase in irrigation rate is not too relevant as most of the required ferric iron is in fact biologically generated along the ore column.

Results of copper leaching rate for bioleaching of well aerated ore columns with $C_x = 0.05$ C-mol/L fed with 1 L/h-m^2 of a leaching solution containing only 3 g/L Fe^{+2} are shown in Fig. 8. This represents the situation when the ore bed is directly irrigated with the recirculated raffinate. Curves of copper recovery for leaching with 1 L/h-m^2 of a solution containing 3 g/L Fe^{+3} for the case of $C_x = 0$ and $C_x = 0.05$ C-mol/L are also plotted in this figure for the sake of comparison. Results show that when the aerated ore bed is irrigated with a raffinate containing only ferrous iron the rate of copper recovery still improves significantly with respect to the case of indirect bioleaching, being nearly as efficient as when using the 3 g/L ferric solution produced in the external bioreactor. This demonstrates that this process scheme bioleaching can operate efficiently without an external bioreactor.

4. Discussion

4.1. Influence of oxygen supply scheme

Simulation results presented in this work show that copper leaching patterns for ISR bioleaching under the two oxygenation schemes present very different characteristics. Naturally, the differences in behavior between these both approaches will depend on the specific characteristics of the ore to be treated and need to be assessed in each case.

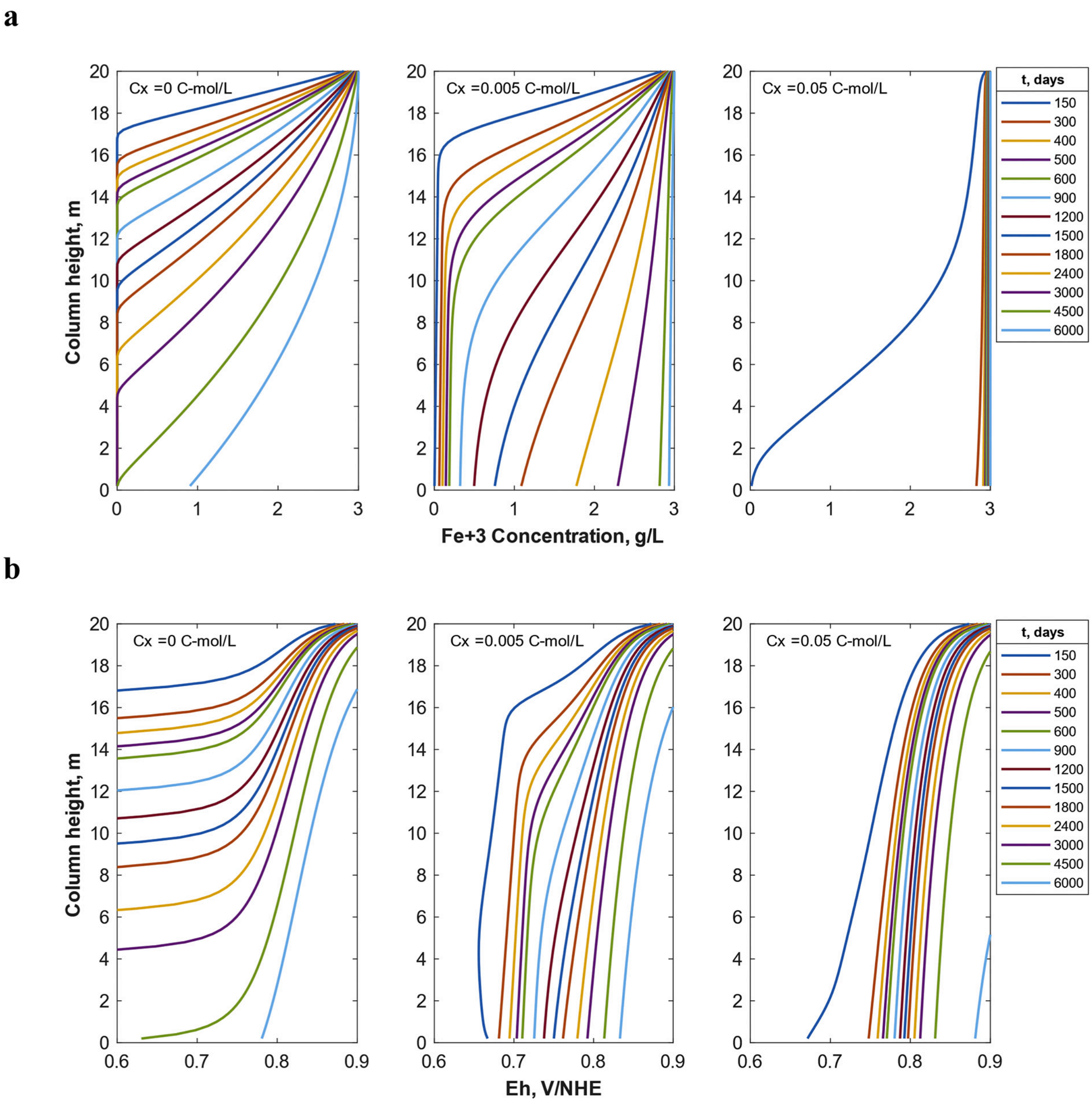

Fig. 4. Profiles of ferric ion concentration and solution Eh inside the ore bed at different leaching times for various levels of bacterial population. Irrigation rate of 1 L/h-m^2, 3 g/L Fe^{+3}. a) Fe^{+3} concentration; b) solution Eh, V/NHE.

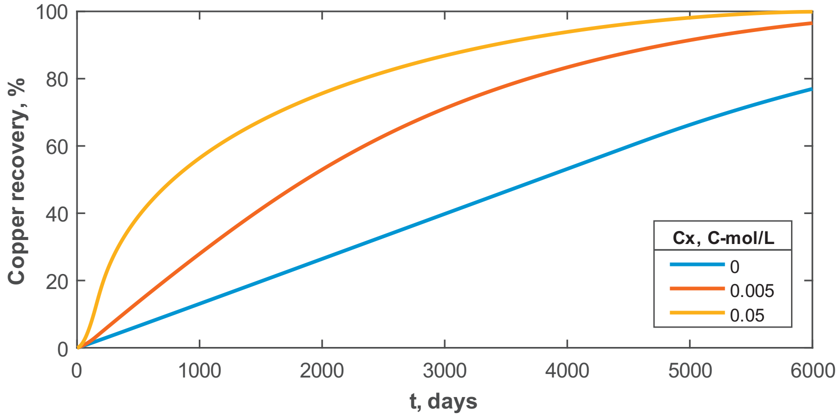

Fig. 5. Copper recovery curves for various levels of bacterial population. Irrigation rate: 1 L/h-m^2, 3 g/L Fe^{+3}.

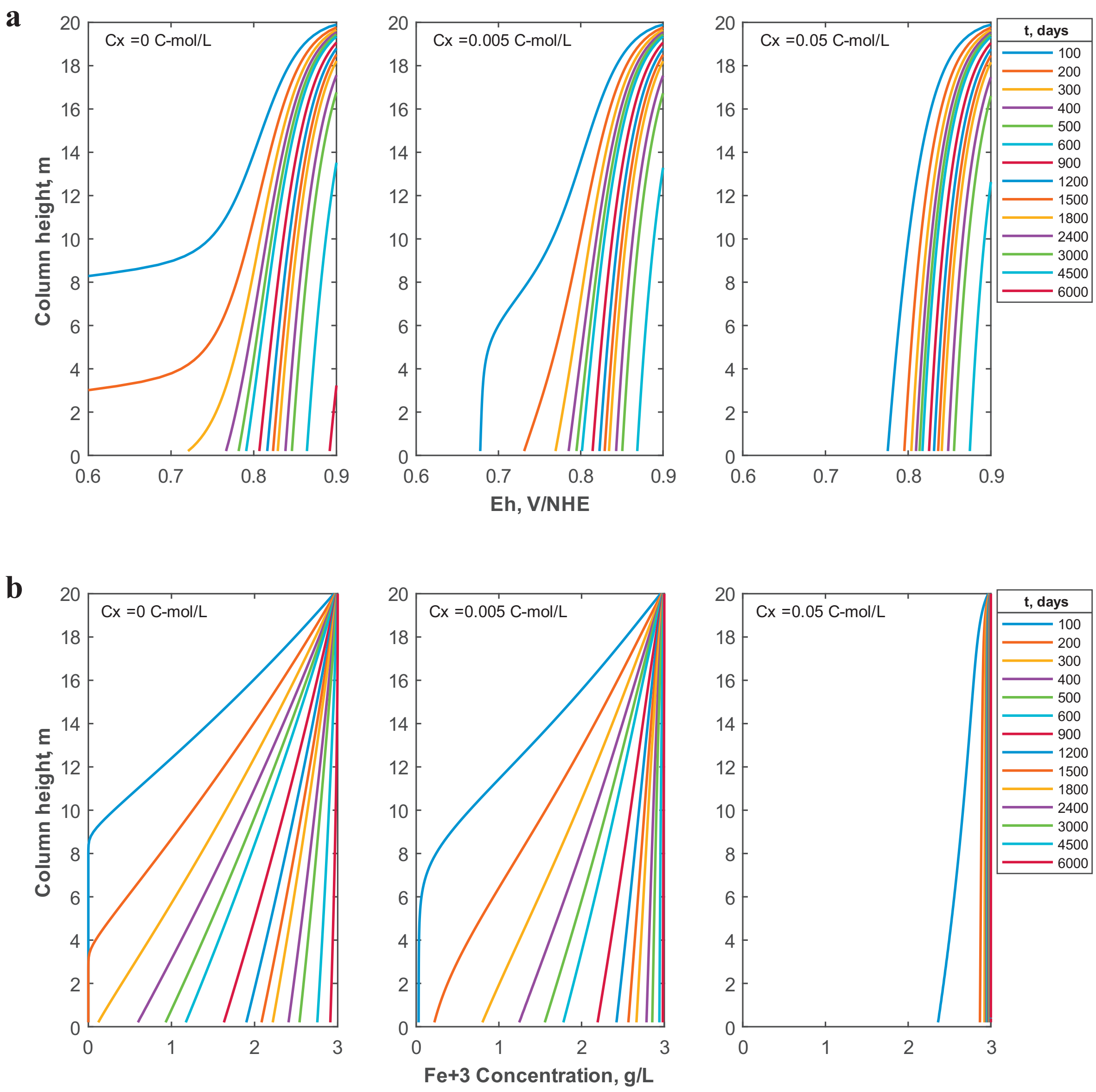

Fig. 6. Profiles of ferric ion concentration and solution Eh inside the ore bed at different leaching times for various levels of bacterial population. Irrigation rate of 5 L/h-m^2, 3 g/L Fe^{+3}. **a)** ferric iron concentration; **b)** solution Eh/NHE.

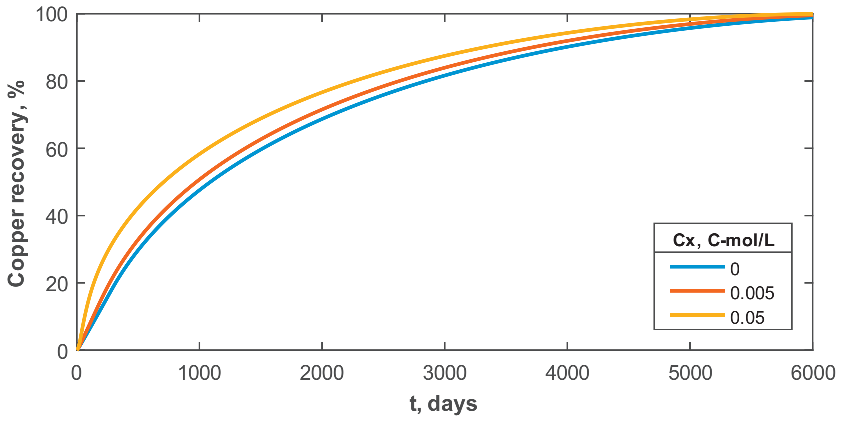

Fig. 7. Copper recovery for various levels of bacterial population. Irrigation rate: 5 L/h-m^2, 3 g/L Fe^{+3}.

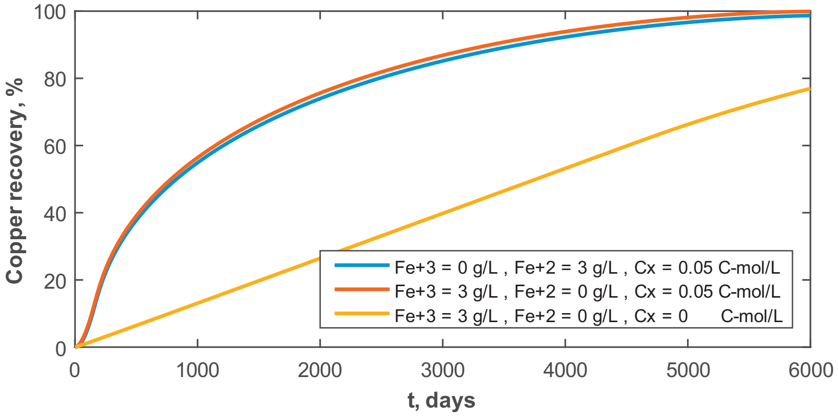

Fig. 8. Comparison of influence of Fe^{+3} concentration and bacterial population on copper recovery when leaching with 1 L/h-m^2.

However, the modelling exercise conducted here already outlines the great relevance that the selected scheme of oxygen supply can have on the rate of copper leaching, the degree of final recovery, the design of the leaching circuit and the relevance of selecting an ore pre-conditioning methodology.

For comparative purposes simulations were conducted for both process schemes with an ore bed of similar height, 20 m. This height is within the dimension range typically found in bioleaching of copper sulfide ores in heaps or dumps (Ghorbani et al., 2016). In addition, an ore bed with these dimensions can be also normally produced applying the sub level stopping techniques (Iriarte, 2015). However, simulation results with an irrigation rate of 1 L/h-m^2 showed that operating with such a large ore bed height it is not too efficient in the case of indirect bioleaching. Ferric iron concentration in the fed leaching solution decreases too fast and becomes practically depleted within a few meters, therefore ferric leaching of copper sulfide would only occur in a narrow zone located at the top of the ore bed. Simulation results showed that increasing the irrigation rate to 5 L/h-m^2 would improve this situation, much higher ferric iron concentration profiles can be established along the ore column and copper efficiencies could be improved. However, available reports of tests of indirect bioleaching of copper ores blocks fractured with confined blasting indicate that application of irrigation rates over 1 L/h-m^2 is not feasible (BIOMore, 2018). Further improvements in the ore permeability achieved with this approach would be very beneficial.

Alternatively, to improve copper leaching rate indirect bioleaching can operate with a lower ore bed height so that Fe^{+3} concentration is maintained at an adequate value along the whole ore bed height. From results of ferric iron profiles for an irrigation rate of 1 L/h-m^2, Fig. 4, to have an effective ferric indirect bioleaching of copper sulfides it appears advisable to operate with much smaller ore bed heights, in the range of 2–3 m, in which an adequate Fe^{+3} concentration profile can be established from the start. In that case if, for instance, indirect bioleaching were conducted with ore beds of 2 m, then 10 ore beds of that size should be simultaneously bioleached to approach the copper recovery performance obtained from bioleaching of a single 20 m height of a well aerated ore bed treated with the ISM approach.

4.2. Bioreactor requirements

In indirect bioleaching the pressurized leaching solution is pumped under a saturated flow regime into the fractured ore and there is no access to oxygen for internal regeneration of ferric iron. Therefore, all the ferric iron required for copper sulfides dissolution needs to be produced in an external bioreactor. The volume of this reactor has to be designed according to the amount of ferric iron needed to extract the copper from the ore. The hydraulic retention times (HRT) for a solution with 50 mM Fe, 2.79 g/L, are between 5 and 33 h (Pakostova et al., 2017). HTR is the time required for microorganisms to oxidize Fe^{+2} to Fe^{+3}. In the present case, if ISL is applied to leach simultaneously 10 ore blocks of 2 m height and 50 × 50 m area with an irrigation rate of 1 L/h-m^2, the required flow is 25,000 L/h. Assuming for HRT a value of 10 h, the volume of the required bioreactor is 250 m^3. For a production plant aimed at producing 50.000 Ton of copper per year, this will require a bioreactor of approximately 33.250 m^3, which is questionable for industrial application.

On the other hand, simulations shown in Fig. 8 showed that copper bioleaching in an aerated ore bed fed with raffinate solutions containing only 3 g/L of ferrous iron reaches efficiencies comparable to those obtained when fed with a solution coming from the bioreactor. In other words, when operating with the ISM scheme the external bioreactor becomes unnecessary, which implies an important saving in investment and operating cost with respect to the IBL approach.

In the ISM approach copper bioleaching rate will be very dependable on the population of active bacteria present in the ore bed, therefore it is important to secure an efficient inoculation procedure in this case. Following the standard heap leaching plant practice, the ore incorporated into the leaching circuit will be inoculated with the microorganisms present in the raffinate recirculated from the SX plant (Pradhan et al., 2008). However, as a fraction of bacteria contained in the pregnant leaching (PLS) is eliminated during contact with the organic phase in the SX unit, it is also advisable to directly recirculate a fraction of the PLS which normally contains a large concentration of planktonic bacteria. Initial inoculation of the ore with bacteria generated in an ad hoc auxiliary bioreactor could be also be considered as a possibility.

In addition, as important as the presence of an adequate bacterial population the ISM scheme also requires an adequate supply of oxygen, which is the final electron acceptor in the bioleaching process. The supply of carbon dioxide contained in the air is also critical as a carbon source for bacterial growth (Petersen and Dixon, 2007; Marín et al., 2017). Modelling calculations conducted in this work assumed an adequate air flow along the ore column so that neither oxygen nor carbon dioxide supply were limiting factors of ferrous iron oxidation. To reach these ideal conditions an adequate aeration systems should be incorporated in the ISM design. Current efficient heap bioleaching operations incorporates air into the ore bed through the heap base with the help of and adequate system of piping and blowers, pumping of air flows in the range 5–10 L/m^2 min guarantees an adequate oxygen concentration profile along the ore column height (Lizama, 2001). In the ISM mining work configuration good aeration could be first approached by direct air blowing through the drawbells located at the ore column base (see Fig. 2-b). Alternatively, air could be supplied by direct blowing into the ore bed through piping inserted from galleries located next to the ore bed surface.

4.3. Economic considerations

Simulation results reported in this work have shown that bioleaching of a well aerated ore bed notably improves the efficiency of copper recovery with respect to the indirect bioleaching approach. However, being able to run an in-situ bioleaching operation with well aerated conditions demands formation of an ore bed with porosity sufficient to establish a trickle bed regime. This can be attained with sublevel stopping techniques in which the ore bed is made combining free-face blasting with removal of a fraction of the ore (Bahamóndez et al., 2016; Iriarte, 2015). However, this approach will imply additional operation costs related to building of galleries and hauling of a fraction of the ore. With the modelling results obtained in this work it is now possible to assess whether the extra mining cost required to preparing a well aerated ore bed is justified by the bioleaching efficiency increase.

The following simplified cost calculation illustrates the potential economic advantage of this approach: a) bioleaching of 1000 Ton of a copper ore with 0.5% Cu present as chalcopyrite by indirect bioleaching results in 45% recovery after 3300 days (Fig. 5a, $C_x = 0$ C-mol/L). With a copper price of USD 5754/Ton (USD 2.6/lb) the recovered copper amounts to USD 12.947; b) bioleaching of the same ore under aerated conditions increases copper recovery to 90% after 3300 days (Fig. 5a, $C_x = 0.05$ C-mol/L), which increases the output to USD 25.893. The permeability increase necessary to produce an ore bed with good aeration requires removal of 20% of sterile mineral (200 Ton) which for a 300 m depth ore body has a cost of USD 7/Ton (Iriarte, 2015). This reduces the economic output of this approach to USD 24.493. However, the shifting from indirect bioleaching to bioleaching in a well aerated ore bed still results in an 89% increase in the economic output.

As mentioned above in the discussion, copper recovery curves in IBL could compete with those obtained in bioleaching of a well aerated 20 m height ore bed, if ISL is simultaneously conducted in 10 ore blocks of 2 m height. This approach, however, will imply a significant additional cost associated to piping, pumping, ore bed preparation, etc., which needs to be evaluated.

The economic estimation carried-out in this study has been based on the main aspects of a cash flow (main incomes determined by copper production and main operational costs determined by the mining works required). Particularly, the degradation of extractant by micro-organisms presence could reduce the solvent extraction efficiency if the extractant concentration is kept at a defined value dependent on the copper concentration in the PLS. However, the solvent extraction plants can increase the extractant concentration in the organic phase in order to avoid an efficiency decrease. This change determines an increase of the initial inventory of extractant (capex) and the organic reposition (opex).

It is relevant to mention that this economic approach has not considered the capex and opex saving related to the reduction of SX, wells and pipes installations, due to the decrease of the overall raffinate solution promoted by a faster kinetic of the ISM case. On the other hand, the increase of capital and operational costs of the additional copper production in the ISM, and the possible detrimental impact of extractant degradation in solvent extraction by the presence of microorganisms have not be included. These considerations must be taken into account in a detailed economic estimation for both options.

4.4. Complementary aspects

Implementing ISR bioleaching with the in situ mining scheme requires extraction of a fraction of the ore to be able to form an ore bed with porosity adequate to operate in a trickle bed. This approach implies in practice a trade off with respect to the standard ISR practiced in uranium and copper oxides, in which none of the ore is extracted. However, the ISM approach still imply a significant reduction in the extraction cost, a drastic reduction in energy consumption due to elimination of crushing and grinding, and elimination of tailings. In this process scheme it is important to minimize the mining cost, which implies to minimize the fraction of extracted ore. This fraction will be defined by the particular relation between porosity and permeability which is highly dependent on the particle size distribution of the blasted ore and ore lithology, and needs to be investigated for each specific ore.

ISM application can also help to reduce the environmental risks usually associated to ISR implementation. Operating ISR in an unsaturated regime by irrigating solutions at atmospheric pressure prevents leakage of solutions through natural rock faults or cracks produced during blasting. These phenomena is more likely to occur when leaching with highly pressurized solutions. In addition, the mining work associated to the implementation of partial sub-level stopping forms a drawbell at the base of the ore column which can help to collect leaching solutions exiting from the ore column base. These two aspects will contribute to improve solution containment, which a critical aspect for ISR to be accepted at industrial scale.

5. Conclusions

It has been demonstrated that the efficiency of copper recovery and process economics when bioleaching is conducted in an ISR context is to a great extent determined by the scheme selected to reach adequate oxygen supply. The analysis and comparison of two process schemes to approach this issue was based on process modelling and can be summarized as follows:

IBL: when leaching solution is pumped through the fractured mineralized rock under a saturated flow regime, it is not possible to supply oxygen directly into the ore bed. In this case, oxygen is added in an external bioreactor in which bacterial oxidation of ferrous iron generates the ferric iron required in the process. In this approach copper leaching rate tends to be controlled by the rate of ferric iron supply from the bioreactor, then bioleaching needs to be conducted in ore beds not higher than 2–3 m. This approach implies lower ore pre-conditioning cost, but its application will require large irrigation areas and a significant investment in an external bioreactor.

ISM: when the leaching solution is irrigated in an ore bed with permeability adequate to operate in an unsaturated flow regime, oxygen can be directly supplied into the ore bed to generate ferric iron in situ by bacterial oxidation of ferrous iron. With this approach there is good availability of ferric iron along the whole ore bed and copper bioleaching can be efficiently conducted in 20 m heights ore beds. This approach requires a larger ore pretreatment cost related to application of sub level stopping and removal of a fraction of the ore. However, its application will require a much lower irrigation area and the investment in an external bioreactor becomes unnecessary.

Further modelling and economic analysis of these alternatives should be conducted incorporating concrete data from specific mine sites where application of ISR bioleaching is an attractive alternative.

Declaration of Competing Interest

None.

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