



Biological and chemical control in copper bioleaching processes: When inoculation would be of any benefit?



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ABSTRACT

Bioleaching of secondary and low-grade copper ores in heaps and dumps today is a well-established technology. However, there is still a strong need to improve the copper leaching rates and recoveries currently reached at plant level in order to improve the economics and broaden the range of application of this technology. In this context, it is important to be able to define the factors which are controlling the rate of copper leaching in different process configurations and at different stages during the operation. This work presents a conceptual mathematical model which can help to define when a bioleaching process is controlled by biological, chemical, or transport phenomena. The model is based on the kinetic analysis of the electrochemical aspects of the microbiological and chemical sub-processes involved in bioleaching. It will facilitate collaboration among biologists, metallurgists and process engineers in the search for innovative developments in the field.

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1. Introduction

Bioleaching of secondary and low-grade copper ores in heaps and dumps today is a well-established technology (Gericke et al., 2009; Watling, 2006). However, there is still a strong need to improve the copper leaching rates and copper recoveries currently reached at plant level in order to improve the economics and broaden the range of application of this technology (Brierley, 2009). In particular, it is of high relevance to improve this technology in regard to chalcopyrite leaching, a sulfide that predominates in the copper deposits but is refractory to bioleaching (Brierley and Brierley, 2001).

In this context, there are too many expectations about the potential impact that an improvement of the oxidative activity of leaching microorganisms could have on increasing the copper leaching rate and total copper recovery in bioleaching attempted either through inoculation, adaptation or consortia diversity (Demergasso et al., 2010; Gericke, 2012; Hunter and Williams, 2002; Morales and Badilla, 2010; Rawlings, 2005; Rawlings and Johnson, 2007; Valenzuela et al., 2006). However, to define when inoculation or other forms of improving microbial activity would be of any benefit for the efficiency of the process is not a microbiological problem only, but a process engineering one. In order to answer this, a global analysis of the bioleaching process is required, pondering simultaneously biological and chemical aspects.

To approach this problem in a scientific form it is necessary to count with conceptual tools which enable to elucidate which are the factors that control copper leaching rates under different process configurations and various operating conditions. In principle, it can be stated that a bioleaching process is biologically controlled when an enhancement of the oxidative activity of the microorganisms, either through inoculation or adaptation or consortia optimization, results in a net increase of the rate of copper leaching. However, to clearly define when this situation is achieved it is necessary to develop a conceptual model in terms of the kinetics of the fundamental processes involved.

This work proposes a conceptual model which can help to elucidate when a bioleaching process is controlled either by biological or chemical phenomena. The model, mathematically simple but scientifically well-grounded, is based on the kinetics analysis of the electrochemical aspects of the fundamental biological and chemical sub-processes involved in the bioleaching of mineral sulfides.

2. Conceptual analysis

The analysis is focused on the electrochemical aspects of the so called indirect bacterial action which is based on the regeneration of ferric ion by oxidation of ferrous ion under the catalytic activity of leaching microorganism (Hansford and Vargas, 2001). It is well-accepted that in many circumstances this is the fundamental catalytic activity of microorganisms in the bioleaching of sulfide minerals (Rawlings, 2005). In bioleaching there can also be an influence of other types of bacterial activity, such as their catalytic influence on the oxidation of reduced sulfur compounds and elemental sulfur

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(Rojas-Chapana and Tributsch, 2001). These aspects, however, will not be considered at this initial stage.

Indirect bacterial action is based on the interaction of the three following semi-reactions:



In reaction (3) MS represents the generic sulfide of a divalent metal. The value of the electrochemical potential of each of these semi-reactions is given by the following Nernst equations, respectively:

$$E_{\text{O}_2/\text{H}_2\text{O}} = +1.229 + \frac{RT}{4F} \ln [\text{H}^+]^4 p_{\text{O}_2} \quad (4)$$

$$E_{\text{Fe}^{+3}/\text{Fe}^{+2}} = +0.77 + \frac{RT}{F} \ln \left[\frac{\text{Fe}^{+3}}{\text{Fe}^{+2}} \right] \quad (5)$$

$$E_{\text{M}^{+2}/\text{MS}} = E_{\text{M}^{+2}/\text{MS}}^0 + \frac{RT}{2F} \ln [\text{M}^{+2}]. \quad (6)$$

The value of the standard potential $E_{\text{M}^{+2}/\text{MS}}^0$ varies for the different sulfides in the range of 0.34–0.63 V/NHE (Hiskey and Wadsworth, 1981; Chmielewski and Kaleta, 2011). In these equations it has been assumed that the activities of solid compounds MS and S^0 are equal to the unity, and the activities of ions in solutions have been approximated to their respective molar concentrations. Semi-reactions (1), (2) and (3) are represented in the potential scale in Fig. 1-a, arranged according to the value of their respective standard electrochemical potentials. Electron transfer between the components of these semi-reactions is triggered by the differences between their respective potentials, following the equation which rules the spontaneity of electrochemical reactions, $\Delta G = -nF\Delta E$. Accordingly, as $E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0 > E_{\text{M}^{+2}/\text{MS}}^0$, MS is anodically dissolved in the presence of Fe^{+3} and spontaneously transfers electrons to this ion, which is reduced to Fe^{+2} . Simultaneously, as $E_{\text{O}_2/\text{H}_2\text{O}}^0 > E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0$, Fe^{+2} oxidizes to Fe^{+3} in the presence of dissolved oxygen and spontaneously transfers electrons to this element which is reduced to water. In this context, the $\text{Fe}^{+3}/\text{Fe}^{+2}$ couple acts as an intermediate electron acceptor which simultaneously receives electrons from MS and transfers these electrons to oxygen. Oxygen then only acts as the final acceptor of electrons released from the sulfide. Thermodynamically, as $E_{\text{O}_2/\text{H}_2\text{O}}^0 > E_{\text{M}^{+2}/\text{MS}}^0$, MS could also transfer electrons directly to oxygen. However, the kinetics of this electron flow pattern in which oxygen acts as a direct leaching agent is not too important in ambient conditions and does not need to be considered in the present analysis.

The complete flow electron pattern between semi-reactions (1), (2) and (3) is shown in the schemes in Fig. 1-a and -b. Leaching microorganisms catalyze the oxidation of ferrous iron with oxygen with enzymes located on the cell wall. This catalytic action is the key aspect in the bioleaching process as it contributes to greatly enhance the rate of electrons transfer from the sulfide to the final electron acceptor, oxygen. Leaching microorganisms biologically remove electrons from Fe(II) through a series of electron carriers from the outer membrane to the cytoplasm where they reduce oxygen to water consuming protons in the process (Holmes and Bonnefoy, 2007).

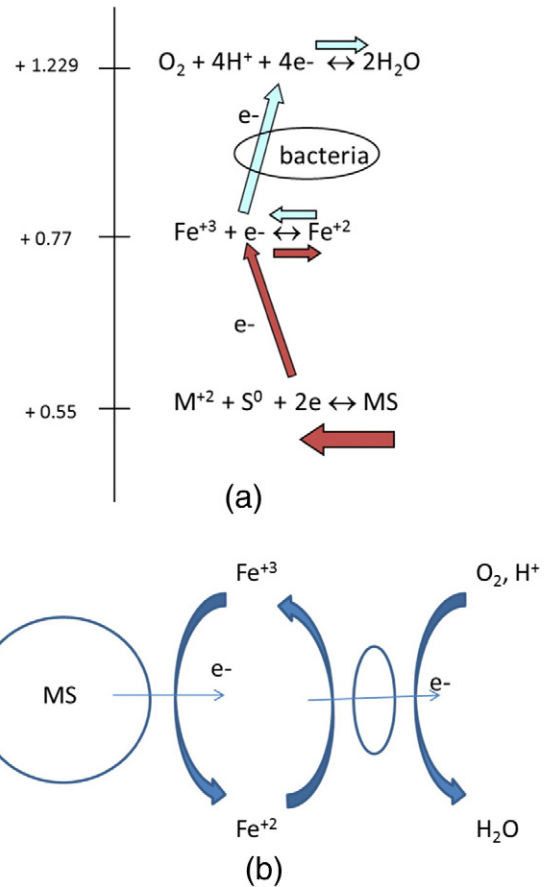
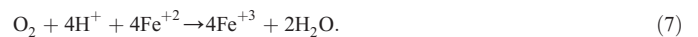


Fig. 1. a) Semireactions involved in the mechanism of indirect action represented in the potential scale; b) Pattern of transfer of electrons from the sulfide to dissolved oxygen, the final electron acceptor.

From the kinetic theory of electrochemical reactions it is expected that the rate of transfer of electrons between compounds of two semi-reactions will increase with an increase of the ΔE between the semi-reactions. Accordingly, the rate of electron transfer from MS to Fe^{+3} will increase when $|E_{\text{Fe}^{+3}/\text{Fe}^{+2}} - E_{\text{M}^{+2}/\text{MS}}|$ increases. Similarly, the rate of electron transfer from Fe^{+2} to O_2 will increase when $|E_{\text{O}_2/\text{H}_2\text{O}} - E_{\text{Fe}^{+3}/\text{Fe}^{+2}}|$ increases. Then, it becomes evident that the ferric/ferrous iron ratio plays a key role in the bioleaching kinetics as its value influences the rate of the two fundamental chemical and biological processes here involved. For a given value of $[\text{M}^{+2}]$, $[\text{H}^+]$ and p_{O_2} , an increase in the ferric/ferrous iron ratio will increase the rate of MS oxidation, but will decrease the rate of bacterial oxidation of Fe^{+2} , while the opposite will occur when the ferric/ferrous iron ratio decreases. Then, to understand in depth the global kinetics of bioleaching it is now necessary to define precisely how the variation of the ferric/ferrous iron ratio affects the kinetics of these two processes.

Combining semi-reactions (1) and (2), the reaction of oxidation of Fe^{+2} with O_2 can be written as:



The dependence of the kinetics of this reaction on the ferric/ferrous iron ratio, which occurs under the catalytic action of leaching microorganisms, has been characterized by several authors (Boon, 1995; Boon et al., 1999; Meruane et al., 2002). The following expression can be

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