Biotechnology and mineral processing: Fundaments of bacterial leaching processes

Biotecnología y procesamiento de minerales:
Fundamentos de la lixiviación bacteriana

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Bacterial leaching is recognized nowdays as an alternative or complementary process for the recovery of metals from medium grade ores, low grade ores and concentrates. There are also new promising applications of this technology such as coal biodesulfurization and toxic metal cleanup. Recent progress in genetic engineering promises both to revolutionize the existing biohydrometallurgical processes and to speed-up the adoption of new processes at industrial scale. However, the development of bacterial leaching processes requires the integration of the work of different disciplines (metallurgy, chemical, biochemical and electrochemical engineering, geology, microbiology, molecular biology and genetic engineering). The most important aspects of the process are addressed with special emphasis on the rate limiting steps in the recovery of copper from ores in either dumps, heaps and other in-place mineral processing operations.

With the continuing decline of the high and average grade mineral reserves worldwide and in order to employ the existing resources to the greatest extent, it is necessary to implement technologies that not only work economically but whose lower investment and operating costs allow that small and medium-scale mineral processing operations become feasible. In the case of copper, these processes are based on the dissolution of the various copper-bearing minerals present in the ore, followed by the recovery of the metal from solutions through cementation and/or solvent extraction/electrowinning processes.

Copper ores contain nearly always a mixture of oxide and sulfide minerals. Oxide minerals are easily solubilized by just acid solutions whereas sulfide minerals are solubilized only in the presence of strong oxidizing conditions in which bacteria plays a crucial role. Because of the inherently favourable economics of bacterial leaching processes (potentially around on third the capital requirements of the conventional flotation/smelting/refining processes and about 25-40% reduction in the operating costs) it is being increasingly applied worldwide, in particular for the recovery of copper from low-grade sulfide ores which are otherwise wasted. Depending upon the characteristics of the deposit and the ore, the technology is applied in different ways: heap leaching, dump leaching and in-place mineral processing operations (see for example the review of Murr, 1980). This technology is also applied to the recovery of other metals such as gold (by bacterial oxidation of refractory gold concentrates), uranium, lead, zinc and cadmium.
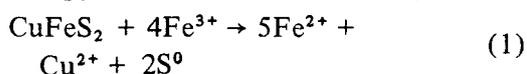
STOICHIOMETRY OF THE LEACHING PROCESS

The ore mineral composition varies continuosly during leaching, since oxide species are completely dissolved during the early stages of the process. Sulfide species are gradually leached, being the secondary sulfide minerals depleted first, and from a practical point of view, the most important characteristic of copper-
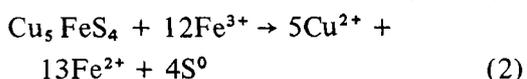
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bearing ores is the nature of the sulfide species present. The overall bioleaching rate increases in the series primary sulfides < secondary sulfides < oxides. The most refractory mineral for the bioleaching process is chalcopyrite, which, on the other hand, is the most abundant. Although there are many nonstoichiometric compounds formed on the surface of these sulfide minerals during leaching, the overall stoichiometry for the reactions that take place under the normal pH and oxidation potencial (E_h) conditions that occurs in the bioleaching processes, can be summarized as:
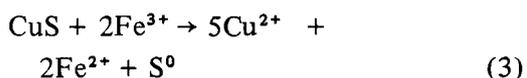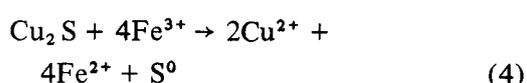
Chalcopyrite (Dutrizac *et al.*, 1969)

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

Bornite (Dutrizac and Mac Donald, 1974)

$$Cu_5FeS_4 + 12Fe^{3+} \rightarrow 5Cu^{2+} + 13Fe^{2+} + 4S^0 \tag{2}$$

Covellite (Dutrizac and Mac Donald, 1974)

$$CuS + 2Fe^{3+} \rightarrow 5Cu^{2+} + 2Fe^{2+} + S^0 \tag{3}$$

Chalcocite (Dutrizac and Mac Donald, 1974)

$$Cu_2S + 4Fe^{3+} \rightarrow 2Cu^{2+} + 4Fe^{2+} + S^0 \tag{4}$$

These reactions require a pH and E_h of the leaching solutions in the range of 1.5-4 and 400-600 mV, respectively.

Iron is always present in the ore normaly as pyrite, which plays a crucial role in the process both as a source of iron for the chemical oxidation of the sulfide minerals as well as enhancing the initial rate of leaching, via galvanic interactions by associations of pyrite with the sulfide minerals. Pyrite is dissolved according to (Garrels and Thompson, 1960):

$$FeS_2 + 8H_2O + 14Fe^{3+} \rightarrow 15Fe^{2+} + + 2SO_4^{2-} + 16H^+ \tag{5}$$
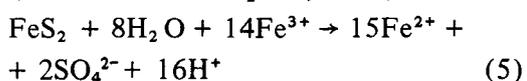
The chemistry of the solution is quite complex, and there are a large number of homogeneous reactions taking place in the leach liquor. The total amount
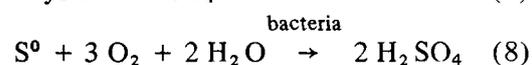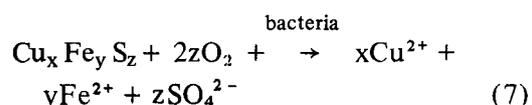
of copper dissolved without precipitation is highest if high Fe^{3+} concentrations are used. High H_2SO_4 concentrations are beneficial whereas high Fe^{2+} concentrations are detrimental because of their influences on the precipitation equilibria (Liddell and Bautista, 1981). Iron from leach solutions has a tendency to precipitate in the presence of NH_4^+, K^+, Na^+ or even H^+ into various kinds of jarosites compounds. These compounds, under certain conditions, can prevent bacterial attachment onto the surface of minerals as well as being able to permanently seal the ore body being leached.

THE ROLE OF THE BACTERIA

Thiobacillus ferrooxidans is one of the most important microorganisms involved in the bioleaching process. The catalytic role of bacteria in the bioleaching process involves at least two different mechanisms: indirect and direct leaching effects. Indirect leaching entails oxidation of the minerals by ferric iron produced by the bacterial oxidation of the soluble ferrous iron that is present in the bioleaching solutions. On the other hand, the direct leaching effect proceeds through the direct interaction of bacteria with the surface of the sulfide minerals, or with the elemental sulfur or other sulfur-containing compounds that are formed on the surface of the mineral particles during leaching. Thus, the overall stiochiometry for the bacterial oxidation of ferrous iron (indirect effect) is:

$$2Fe^{+2} + O_2 + 2H^+ \xrightarrow{\text{bacteria}} 2Fe^{+3} + H_2O \tag{6}$$
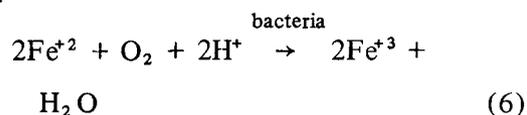
whereas, for the direct oxidation of sulfide minerals and sulfur by bacteria, the overall stoichiometry of the process is:

$$Cu_xFe_yS_z + 2zO_2 + \xrightarrow{\text{bacteria}} xCu^{2+} + yFe^{2+} + zSO_4^{2-} \tag{7}$$

$$S^0 + 3O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2H_2SO_4 \tag{8}$$

There are contradictory indications for the so called direct effect in bioleaching.

Fig. 1 shows a Scanning Electro Micrograph picture of the surface of a pyrite cristal after leaching in the presence of bacteria, and in which cells of *Thiobacillus ferrooxidans* are clearly seen on the surface. In fact, it appears that some of them are actually growing on the surface, suggested by the fact that they are dividing (indicated by the arrows in Fig. 1). In a culture containing a sulfide mineral, soluble iron and bacteria, there are two different populations: the metabolically active and replicating cells that are attached to the insoluble substrate and the free, unabsorbed cells, that are utilizing the soluble substrate as the sole energy source (ferrous iron). As it has been demonstrated elsewhere (Espejo *et al.,* 1988) *Thiobacillus ferrooxidans* cells are able to simultaneously oxidize elemental sulfur and ferrous iron for growing. Therefore, the attached cells (as those shown in Fig. 1), although being physically attached to the surface, can use the electrons from the oxidation of ferrous iron, sulfur and other sulfur-containing compounds as their energy source for growth.

Fig. 1: SEM of cells of *Thiobacillus ferroxidans* attached onto the surface of pyrite.

It is very difficult to study separately the direct oxidation mechanism from the indirect mechanism in the bioleaching of sulfide minerals, since under practical conditions, the presence of iron interferes with both the kinetics of leaching and bacterial growth. In the case of elemental sulfur oxidation in iron free leaching solutions (Espejo *et al.,* 1988; Herrera *et al.,* 1989b), the only energy source for bacterial growth available is sulfur and the sulfur oxidation compound formed during leaching. Therefore, the leaching process involves the direct bacterial oxidation of sulfur. In the case of bioleaching of chalcopyrite, it has been shown that an important fraction of the total bacteria generated during leaching remains attached to the chalcopyrite surface. Bacterial growth, in this instance, can be well explained in terms of the utilization of both the total iron (as ferrous iron) and sulfur oxidized in the system (Vargas *et al.,* 1990). Much work is still needed in order to have a better understanding of the direct bioleaching mechanism of sulfide minerals, since it represents one way of increasing leaching rates.

From a practical point of view, at the typical process conditions found in the laboratory (no oxygen, carbon dioxide or any other nutrient limitation), the potentials for the direct and indirect bacterial action are normally fully utilized by the existing cells, the kinetics of the process being controlled only by the intrinsic kinetics of the mineral dissolution. However, the conditions of bioleaching processes at industrial scale are quite different in comparison to those found in the laboratory. As an illustration of this, total iron oxidizing bacteria counts in the laboratory are in the order of 10^{7-8} cells/ml, whereas, in industrial dumps, this value could be as low as 10^3 cells/ml.

Physical characterization of a dump or a heap indicates that there are large differences both spacially and with time in the environmental conditions throughout the ore body. In particular, the differences in pH, temperature, oxygen and carbon dioxide concentrations, determine the activity and type of microorganisms present in the system. Normally, aerobic, mesophillic organisms predominate near the surface, whereas anaerobic low-oxygen requiring organisms will prevail deep in the heaps or dumps. Not all the microorganisms

present in the bioleaching process are involved in metal oxidation, and a significant fraction could compete with the leaching microorganisms for limiting nutrients, thus reducing the rate of metal dissolution.

The fact that there are such big differences in the performance of bioleaching processes on the laboratory-scale and the industrial-scale, presents a unique opportunity for biotechnologysts. Better strains are required, capable of supporting higher environmental changes without decreasing their activity, higher toxic metal resistances, higher sulfide oxidation activity, etc. Factors such as survivability of laboratory strains in industrial heaps and dumps are key issues to be solved before these genetically modified microorganisms can be succesfully introduced to the industrial practice.

BIOLEACHING OF SULFIDE ORES

Fig. 2 shows typical metal recovery vs. time curves for a given ore processed in different bioleaching reactors. Curve (a) represents the behaviour of the liberated minerals of the ore in a shake flask, (b) the leaching behaviour in laboratory-scale percolator, (c) in pilot-plant column, (d) industrial scale heaps and (e) in industrial dumps. The large differences in the leaching rates and overall metal recovery among these bioleaching reacting systems, are due to the nature of the rate limiting steps that control the process. The main task, from the point of view of process design and development, is to optimize design parameters and process operating conditions in order to have the highest possible recovery and leaching rates. The dissolution and transfer of the metal ions from the surface of the ore (or a concentrate particle) to the bulk of the leaching solution and out of the ore body can be better understood through microscopic balances of the various steps involved in the bioleaching process: bacterial growth, chemical reactions, diffusion and mass transfer resistances both within the ore particle and throughout the ore body.
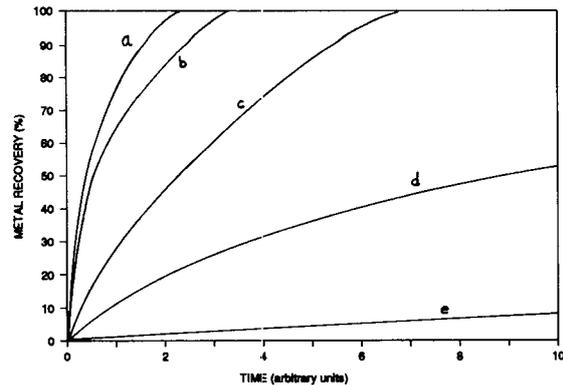

Fig. 2: Effect of the type of bioleaching reacting system on the metall recovery and leaching rates, curves (a) shake-flask using liberated minerals; (b) air-lift packed bed percolator, (c) pilot-scale laboratory columns; (d) industrial heap; (e) industrial scale dumps.

Bacterial growth and oxidation rates

Experimental determinations of bacteria numbers in bioleaching of sulfide minerals and ores suggests that the activities of both attached and free bacteria are relevant to the leaching process. Since both populations are growing using primarely the same substrate (ferrous iron), the specific bacterial growth rate can be assumed to be essentially the same for free and attached cells (Espejo *et al.*, 1988). Therefore, tha variation of the number of attached bacteria per unit volume of the ore bed of can be expressed as:

$$\frac{dX'}{dt} + v_z \frac{A(1-\epsilon_L)}{\epsilon_S} \frac{dX'}{dV} =$$

$$= \mu^* X'^* (1-\epsilon_L) + K_{ads}^* X^* (X_{sat}-X')^*$$

$$(1-\epsilon_L) - K_{des}^* X'^* (1-\epsilon_L) \qquad (9)$$

and the variation of bacteria in solution as:

$$v_z \frac{AdX}{dV} = \epsilon_s^* X^* \mu - K_{ads}^*$$

$$X^* (X_{SAT}-X')(1-\epsilon_L) + K_{des}^*$$

$$X^* (1-\epsilon_L) \qquad (10)$$

In Equation 10, ϵ_L and ϵ_s represent the packed bed void fraction and liquid volume fraction, A the surface area normal to the liquid flow, X' the concentration of attached cells per unit volume of ore, μ the specific bacterial growth rate, X the con-

centration of bacteria in solution, whereas K_{ads} and K_{des} represents the absorption and desorption constants for bacteria attachment and X_{sat} the saturation concentration of bacteria attached to the surface of ore particles.

The total number of bacteria per unit volume of solution at any point of the leaching bed that are involved in the oxidative process can be then written as:

$$X_T = X + \frac{(1-\epsilon_L)}{\epsilon_s} X' \qquad (11)$$

The rate of ferrous iron oxidation is related to the total bacterial growth rate through a Monod equation such as:

$$-R_{Fe}{}^{+2} = -V_z \frac{dFe^{+2}}{dt} = -\frac{V_z}{Y} \frac{dX_T}{dt} \qquad (12)$$

where Y is the bacterial yield and X_T is the total bacterial population present in the column. The specific bacterial growth rate μ can be related to the maximum rate μ_{max} through a Michaelis-Menten type of mechanism and the dependence of the bacterial specific growth rate with pH and dissolved oxygen levels and the following expression can be derived for the rate of microbial ferrous iron oxidation:

$$-R_{Fe+2\,L} = \mu_{max} \frac{\epsilon_s}{Y} X + X \frac{(1-\epsilon_L)}{\epsilon_s} *$$

$$\frac{(Fe^{+2}L)}{(K + (Fe^{+2}L))} F_1 * F_2 \qquad (13)$$

where the factor F1 accounts for the dependence of $\mu_{máx}$ on the pH of the leaching solution (Ingledew, 1982) and F2 takes into account the dependence of μ_{max} to the dissolved oxygen concentration, being an inhibitory term which becomes significant when dissolved oxygen levels in the solution are low (below 1 ppm). K represents the bacterial saturation constant.

Mineral dissolution rates

Considering the shrinking core model including external and internal mass transfer resistances (Braun et al., 1974; Madsen et al., 1975), the rate of leaching of the

sulfide minerals contained in an ore particle can be stated as:

$$-R_{CuFeS2} = \frac{4\pi r_i^2}{\phi_{io}} *$$

$$\frac{(Fe^{+3} L)}{\left[\frac{1}{G\beta} + \frac{\sigma}{D_{eff}} \frac{r_i}{r_{io}} (r_{io} - r_i) + \frac{1}{K_c} \left[\frac{r_i}{r_{io}} \right]^2 \right]} \qquad (14)$$

in which r_{io} and r_i are the particle radius and reaction front radius respectively, ϕ_{io} the particle shape factor, G the overall grade of the ore, β the true mineral oxidation kinetic constant, σ a stoichiometric factor, D_{eff} the effective diffusion coefficient in the solid and k_c the mass transfer coefficient of ferric ion in the liquid film surrounding the ore particle. Generally speaking, the first term in the denominator of Equation (14) represents the chemical reaction kinetics resistance, the second the diffusion resistance for the mass flux of ions through porous structure of the gangue and the last term, the mass transfer resistance in the liquid-solid interphase. In the case of mixed mineral ore, the effect of the progressive change of the ore composition in the kinetic factor β must be also taken into account through the utilization of an instantaneous grade coefficient to take into account the mineralogical composition and changes during the leaching process.

Mass transfer in the flowing phases

The mass balance for the chemical species i present in the system is represented by the continuity equation:

$$\frac{\delta (\epsilon_s C_i)}{\delta t} + A v_z \frac{\delta C_i}{\delta V} - A \frac{\delta}{\delta V}$$

$$D_{ai} \frac{\delta C_i}{\delta V} = \Sigma R_i \qquad (15)$$

where ϵ_s is the liquid volume fraction (volume of solution per unit volume of packed bed), C_i concentration of species

i in solution, v_z superficial liquid velocity and D_{ai} the axial dispersion coefficient of species i. ΣR_i is the net rate of mass change of the species i by production or consumption through chemical and biochemical reactions and/or transport from or into another phase per unit volume of packing.

Equation 15 is applied to oxygen balance in the gas phase as well as to oxygen, ferrous ion, ferric ion, sulfate and cupric ions and hydrogen ion mass balances in the liquid phase.

Mineral behaviour in bioleaching processes

Based on the computational solution of the previously described set of differential equations, Fig. 3 shows the effect of the ore composition on the copper recovery and leaching rates for chalcocite, covellite, bornite and chalcopyrite-bearing ores, under the most favourable process conditions, *i.e.*, when the bioleaching process is carried out in a laboratory air-lifted packed-bed percolator. These are the most abundant copper-bearing sulfide minerals and it can be seen that there are large differences in the behaviour of these minerals in the bioleaching process. Chalcocite is the most amenable mineral to bioleaching, and recoveries of about 90 to 99% are obtained after only 1 to 2 days of processing whereas for chalcopyrite, leaching periods of about 9 to 12 months are required to obtain the same overall recovery. Of course, this large difference
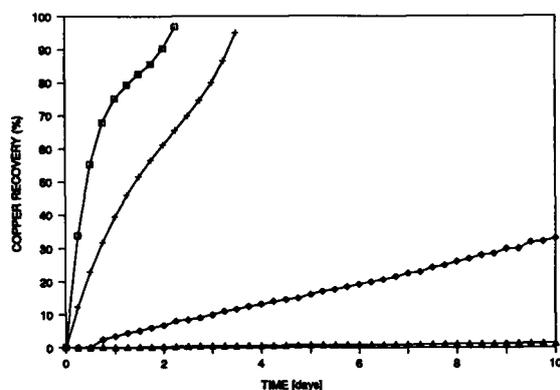

Fig. 3: Copper recovery and bioleaching rates of the most common sulfide minerals, (a) chalcocite; (b) covellite; (c) bornite, and (d) chalcopyrite.

in the bioleaching behaviour has a great effect on the economics of the processes, and the technology is best applied to recover copper from secondary sulfide minerals (chalcocite and covellite) containing ores.

Bioleaching of low grade sulfide ores

Low grade sulfide ores are leached in dumps or other in-place operations, since the metal content in the ore is such that it is not possible to cover the cost involved in mining, crushing and transport of the ore required by more efficient mineral processing technologies such as heap bioleaching or flotation/smelting processes. From a practical point of view, the most important parameters of the process are the particle size distribution of the ore, liquid and gaseous flow rates and iron concentration in the inlet solutions.

As it has been demonstrated elsewhere (Herrera *et al.*, 1989) for the bioleaching of low grade chalcopyritic ores, the microbial effect on the overall leaching rate is mainly related to the bacterial oxidation of ferrous to ferric iron, both by bacteria which is free in solution, and that attached onto the surface of the ore particles. Fig. 4 shows a computer model prediction (Castillo *et al.*, 1988) of the leaching of an ore containing 0.5% w of soluble copper, 2% w insoluble copper (containing 70% w chalcocite and 30% chalcopyrite), in the presence (curve a) and absence (curve b) of leaching microorganisms in a heap. These results clearly illustrate the role of bacteria in the process, inspite of the physical limitations, and both copper recovery and leaching rates are largely enhanced in the presence of bacteria.

It is very important to speed-up the rate of copper dissolution in industrial bioleaching operations. However, it is apparent from the present work that there are a large number of factors that affect metal recoveries and leaching rates under industrial bioleaching conditions. Efforts have been made to study the physical, chemical and biological factors on heap and dump leaching, through laboratory studies and field testing. Today, it can be
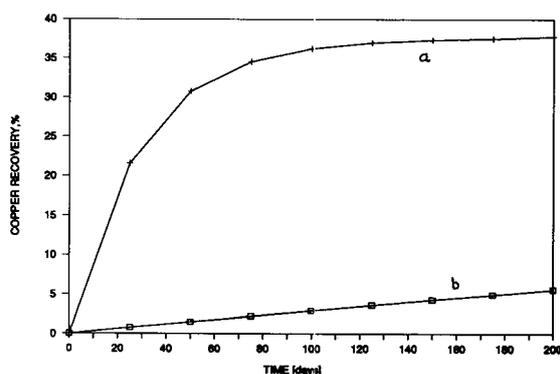
Fig. 4: Effect of the presence (curve a) and absence (curve b) of leaching microorganisms in a heap bioleaching operation.

estimated that 5 to 10% of all Chilean copper production results from bacterial leaching of low and medium grade sulfide ores in heap and dump leaching operations. Other countries such as Australia, Canada, United States, South Africa and Zimbawe are also involved in bioleaching, making it a worldwide multi-billion-dollar a year business. This is one of the most important applications of biotechnology nowadays.

CONCLUSIONS

Bioleaching of sulfide ores is a very complex phenomena, involving physical, chemical and biological aspects, all of which are to be considered together in order to understand and apply bioleaching processes. There are large differences between the performance of the process under controlled conditions (such as those found in the laboratory) and those of industrial bioleaching operations. However, progress in the near future in this area is most likely to come from improvements in heap and dump design and operation to allow a better control of the biological variables of the process, rather than the utilization of genetically improved microorganisms.

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