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Application of bioleaching to copper mining in Chile

Juan Carlos Gentina[1] ✉ · Fernando Acevedo[1]

1 Pontificia Universidad Católica de Valparaíso, Facultad de Ingeniería, Escuela de Ingeniería Bioquímica, Valparaíso, Chile

✉ Corresponding author: jgentina@ucv.cl
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Abstract

Background: Bioleaching of minerals is a process that allows the treatment of insoluble sulphides and insoluble oxides via hydrometallurgy, as opposed to the more traditional technology of pyrometallurgy. Bioleaching presents several technological, environmental and economic advantages as compared with pyrometallurgy, as well as some limitations.
Results: In this work a general panorama of copper mining and biomining, the influence of the most relevant operating variables and their present and future situation in Chile are presented and discussed.
Conclusions: Today, Chile plays an important role in the development and commercial application of bioleaching to copper ores. This background information allows predicting a brilliant future for this technology in Chile, as has been forecasted in the last years.

Keywords: dumps, heap leaching, hydrometallurgy, leaching microorganisms, pyrometallurgy.

INTRODUCTION

Bioleaching of minerals is the oxidative selective solubilization of mineral species mediated by the action of microorganisms. Different alternative names are also used, such a bacterial leaching, microbial leaching, and biooxidation, all of them part of what is known as biohydrometallurgy or biomining. This process allows the treatment of insoluble sulphides and insoluble oxides via hydrometallurgy, as opposed to the more traditional technology of pyrometallurgy. Bioleaching presents the following advantages as compared with pyrometallurgy: simple and low cost equipments, apt for treating low grade or waste ores, low energy requirement, and no atmospheric contamination. Its main disadvantages are low reaction rates and productivities, requirement of extensive grounds, and current inadequacy for treating primary sulphides.

Chile plays an important role in the development and application of bioleaching of copper ores, and in the following sections a general panorama of the past, present and future of this technology in Chilean mines is presented, together with a discussion of the main variables involved in the process.

Overview of current copper mining

Copper has been used by man since ancient times. It is thought that already in the Stone Age, over 90,000 years ago, copper had domestic, hunting and war applications. In those days copper was found in elemental state with relative abundance, but around 5,300 BC smelting began to be used to obtain the metal from ores. Since then, the applications and the production of copper have increased steadily so this industry has reached in our days a high degree of technological sophistication (Sutulov, 1978; Domic-Mihovilovic, 2001).

Today copper is abundantly found in nature in sulphide and oxidized ores. Examples of these ores are listed in Table 1. Oxides are easily dissolved in acid and, from the resulting solution, metallic copper can be recovered by cementation with scrap iron or by solvent extraction and electrowinning. On the other hand, copper sulphides are almost insoluble in acid, so metal recovery from these ores requires a previous stage of flotation concentration followed by smelting at high temperatures. In smelting, sulphides are oxidized to SO_2 and cupric and cuprous ions are reduced to the elemental metal. The crude metal obtained in the furnaces must be refined by dissolution in acid and electrowinning.

Table 1. Common copper ores (Gaines et al. 1997).

	Mineral	Formula
Oxides	Cuprite	Cu_2O
	Tenorite	CuO
	Malachite	$CuCO_3$ x $Cu(OH)_2$
	Chrysocolla	$CuSiO_3$ x $2H_2O$
	Atacamite	$CuCl_2$ x $3Cu(OH)_2$
Sulfides	Chalcocite	Cu_2S
	Covellite	CuS
	Chalcopyrite	$CuFeS_2$
	Bornite	Cu_3FeS_3
	Enargite	Cu_3AsS_4
	Tennantite	Cu_3AsS_3

Not long ago ores used to contain 5% copper or more, but nowadays most ore grades have diminish to less than 1%. Very low-grade ores (0.6% or less) are abundant in nature, but currently their processing by smelting in most cases is not economical. So in order to obtain copper from them alternative technologies, such as bioleaching, must be employed.

Although copper reserves and production are widely distributed around the world, no more than 15 countries contribute with over 90% of the total production. Among these, Chile occupies a privileged position with one third of the total world production as can be seen in Table 2. It is worth noting that currently Chile produces over three times more copper than the second world producer, USA. With respect to reserves the situation is similar, Chile having over 30% of them. It is important to notice that the introduction of new technologies can increase the reserves of a specific country. For instance, according to a former executive vice-president of CODELCO, Chile will increase its reserves up to 50% when primary sulphides and very low-grade ores could be economically benefited by bioleaching (Villarzú, 2003).

Table 2. World and Chilean copper production (thousand tonnes/year) (Cochilco, 2012).

	Chile	World	% Chilean production
2002	4580.6	13,565.4	33.8
2003	4904.2	13,653.0	35.9
2004	5412.5	14,681.0	36.9
2005	5320.5	15,150.2	35.1
2006	5360.8	15,180.6	35.3
2007	5557.0	15,548.0	35.7
2008	5327.6	15,695.0	33.9
2009	5394.4	15,881.9	34.0
2010	5418.9	16,134.4	33.6
2011	5262.8	16,248.4	32.4

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Nominal prices of copper are quite variable according to the world economical situation and the market demand. In the present decade copper price has been rather high, on the range of US$3.5-3.8 per pound.

Processing of copper minerals by bioleaching

Bioleaching of copper has occurred naturally since many centuries ago. Indications exist that during the Roman Empire copper was recovered from acidic waters. It seems that the first large-scale utilization of bioleached copper occurred in Río Tinto, Spain, back in the XVIII century. But the rational technical exploitation of this phenomenon is relatively recent and goes back to the isolation and characterization of leaching bacteria in the period 1947-1953, and the understanding of the role that these bacteria play in dissolving metals (Colmer and Hinkle, 1947; Temple and Colmer, 1951; Temple and Delchamps, 1953).

Early application of bioleaching to copper mining centred in its recovery from dumps (Gentina and Acevedo, 1985; Acevedo, 2002). This is a low technology process and renders low productivities and recoveries. Nevertheless, dump bioleaching is economical, mainly because it recovers copper otherwise wasted with very modest investment and operation costs. A step in the direction of using a more refined technology is the use of heaps which are intentionally designed and erected so to facilitate the different complex transfer phenomena and reactions involved. Also some use of *in-situ* bioleaching has been reported as shown in Table 3 and discussed by O'Gorman et al. 2004).

Table 3. Some early commercial bioleaching operations (Gentina and Acevedo, 1985).

Mine	Configuration	Total copper %	Production (tonne/year)
Duval (USA)	dump	0.15 - 0.20	2,500
Bluebird (USA)	heap	0.5	6,800
Degtyansky (URSS)	dump/ in-situ	-	900
Kosaka (Japan)	in-situ	0.15 - 0.25	800
Río Tinto (Spain)	dump	variable	8,000
Cananea (Mexico)	dump/ in-situ	variable	9,000
St. Domingo (Portugal)	in-situ	unknown	670

Back in the sixties and seventies, several interesting projects were conducted in order to develop a scalable bioleaching technology. One of them was developed in Australia in the period from 1964 to 1968. Bench scale columns were first used with ore crushed to 0.5 inches. Then, heaps of 360,000 tons were installed, one for oxides and one for sulphides. This was a very early attempt when not much was known about the process, so the results were modest but interesting (Allman and Harris, 1969). Heaps of 100,000 to 500,000 tons of mixed copper minerals containing mostly oxides and some sulphides (chalcopyrite, covellite, bornite, enargite) were in operation in 1965 in western United States, with an estimated annual production of 250,000 tons of copper (Evans and Sheffer, 1968). Perhaps the first important attempt to evaluate copper heap bioleaching technology in a developing country was the pilot operation established in Toromocho, Peru, in the mid seventies. Heaps and dumps of 10,000 to 36,000 tons of ore with 0.4% Cu were installed and operated for several months. Although productivities and recoveries were lower than expected, the economic evaluation of a plant processing 6,250 ton mineral per month gave a high internal rate of return (Zegarra, 1979; Warhust, 1985). Some early commercial operations of copper bioleaching of low-grade ores are shown in Table 3.

Currently, heaps are widely used in the large-scale bioleaching of copper. They are employed for processing low-grade ores non apt for concentration and smelting or as an alternative to smelting when the overall economy of the process is favourable. This can be the case for secondary minerals such as covellite and chalcosite; primary minerals such as chalcopyrite and enargite are currently not treated economically in heaps (Crundwell, 2005). Heaps were originally 100 to 300 m long with a height of 3 to

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6 m (Zárate, 1994), but in more recent bioleaching plants sizes have been scaled to up to 4000 m long and more (Anonymous, 2004; Demergasso, 2008). The leached liquor is purified and concentrated by solvent extraction and fine copper is recovered by electrowinning. Figure 1 shows a block diagram of a typical installation while Table 4 lists some commercial operations.

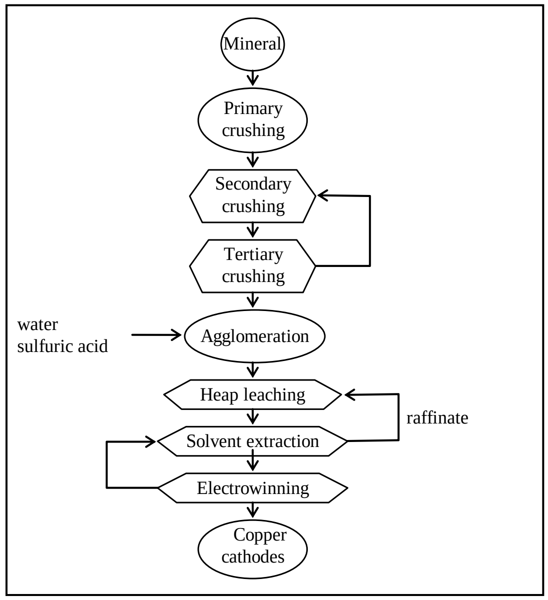

Fig. 1 Block diagram of a typical copper heap bioleaching process (Acevedo et al. 1993).

Many operating factors have strong influence on the performance of heaps as will be discussed in the next section. Among them, curing and agglomeration are crucial for a satisfactory operation. Curing consists in the addition of concentrated sulphuric acid to the crushed ore to provide an adequate moisture content allowing a fast and efficient conditioning of the gangue. Agglomeration of the fine solids with the coarser fraction results in a homogeneous heap of high porosity facilitating the down flow of liquid and up flow of gasses (Acevedo et al. 1993; Domic-Mihovilovic, 2007). The fundamentals and recent advances in heap bioleaching have been reviewed by Bustos (2005), Watling (2006), Petersen and Dixon (2007a), Petersen and Dixon (2007b) and Brierley (2008).

Table 4. Commercial applications of copper heap bioleaching. Adapted and modified from Olson et al. 2003 and Domic-Mihovilovic, 2007.

Plant	Period of operation
Lo Aguirre, Chile	1982-2001
Cerro Colorado, Chile	1993-present
Quebrada Blanca, Chile	1994-present
La Escondida, Chile	2006-present
Andacollo, Chile	1996-present
Dos Amigos, Chile	1996-present
Ivan-Zar, Chile	1994-present
Zaldivar, Chile	1998-present
Cerro Verde, Peru	1998-present
Gunpowder's Mammoth, Australia	1991-present
Mt. Leyson, Australia	1992-1997
Girilambone, Australia	1993-2004
Equatorial Tonopah, USA	2001-2002
S&K Copper, Myanmar	1998-present

Although the performance of heaps is satisfactory, they are not very efficient reactors from a kinetic point of view because of their heterogeneity and difficulties in establishing proper control systems for important variables such as temperature, pH, dissolved oxygen concentration, dissolved carbon dioxide concentration and others (Acevedo, 2000). Considering this situation, it would be desirable to use other types of reactors for bioleaching that allow for a more stringent control of the reactions; however, this would be difficult because of the large volume of ores involved in copper mining. The situation in gold mining is different because of the much smaller volumes involved. In fact, continuous stirred tank reactors (CSTR) are successfully used in the pretreatment of refractory gold concentrates. Since several decades ago, it has been postulated that bioleaching of copper concentrates in CSTR could be possible considering that concentration reduces the volume 25 to 35 times (McElroy and Bruynesteyn, 1978; Groudev, 1986; Acevedo et al. 1998). The kinetic and engineering fundamentals of the design of CSTRs for bioleaching have been addressed by several authors (Gormely and Brannion, 1989; Greenhalgh and Ritchie, 1999; Harvey et al. 1999; Acevedo, 2000; Rossi, 2001; Roger Morin, 2007; Acevedo and Gentina, 2007). Other reactor configurations such as bubbling columns, airlift columns, percolation columns, Pachuca tanks and rotary reactors have been studied (Murr and Brierley, 1978; Atkins et al. 1986; Acevedo et al. 1998; Loi et al. 1995; Acevedo et al. 1999; Rossi, 2001; Giaveno et al. 2007).

Although at present bioleaching of copper concentrates in CSTRs is still not an industrial reality, the important pilot plant project developed in the Chuquicamata mine of CODELCO-Chile with the technical assistance of BHP Billiton starting in 1997 is worth mentioning. This large pilot facility had a capacity of 200 tons concentrate/day with a yearly production of 20,000 tons of copper. This process, named BioCop™, was based in the experience of BHP Billiton with its Biox™ process in the biooxidation of gold concentrates. To the authors' knowledge, this is the first successful project in the large-scale bioleaching of copper concentrates in CSTRs. After several years of operation, the project was shut down more for economical than for technical reasons (Morales, 2005; Clark et al. 2006; Batty and Rorke, 2006).

Influence of operating factors on bioleaching of copper

As said before, bioleaching is an operation where the metal sulphides are extracted from the mineral with the contribution of microbial cells that are chemolithotrophic and grow at pH as low as 1.0. The most studied microorganism has been *Thiobacillus ferrooxidans*, today renamed *Acidithiobacillus ferrooxidans* (Kelly and Wood, 2000), but it is well established that many different genus and species participate actively in the bioleaching process (Norris, 2007; Schippers, 2007). Table 5 shows some examples of bioleaching microorganisms grouped according to their optimal growth temperature.

Table 5. Example of microorganisms with different growth temperature.

Mesophilic range	Thermophilic range	Hyperthermophilic range
Acidithiobacillus albertensis	*Acidimicrobium ferrooxidans*	*Acidianus brierleyi*
Acidithiobacillus ferrooxidans	*Acidithiobacillus caldus*	*Metallosphaera sedula*
Acidithiobacillus thiooxidans	*Sulfobacillus acidophilus*	*Sulfolobus acidocaldarius*
Leptospirillum ferrooxidans	*Sulfobacillus thermosulfidooxidans*	*Sulfolobus acidophilus*
Leptospirillum ferriphilum	*Sulfobacillus thermotolerans*	*Sulfolobus metallicus*
Thiobacillus prosperus	*Ferroplasma acidiphilum*	*Sulfolobus thermosulfidooxidans*

These cells utilize reduced iron and/or reduced sulphur as energy sources oxidizing them, an action that contributes to bioleach the mineral. Ferric iron oxidizes the mineral sulphide liberating the metal into solution. The reduced sulphur compounds generated during the ferric iron attack are further oxidized by cells to sulphate, helping to keep the low pH required for cell activity and ferric iron action. Finally, the reduced iron generated during mineral attack is re-oxidized by the microorganisms. Two ways of sulphide ores oxidation chain has been proposed according to the nature of the mineral

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species (Schippers and Sand, 1999; Sand et al. 2001; Schippers, 2004; Rohwerder and Sand, 2007). Species like pyrite, molybdenite and tungstenite are oxidized by the so-called thiosulphate pathway while sphalerite, chalcopyrite, arsenopyrite and galena are oxidized via polysulphide pathway.

This indirect mechanism (in opposition to an enzymatic direct mechanism) of sulphur moiety oxidation of heavy metals sulphides is considered the only relevant mechanism. It can happen in contact and non-contact ways (Sand et al. 2001; Tributsch, 2001; Rawlings, 2002; Rohwerder et al. 2003). The first one is accomplished by planktonic cells and the latter by cells attached to the mineral surface. The extracellular polymeric substances (EPS) play an important role in cell attachment (Sand et al. 1995; Gehrke et al. 1998).

Copper bioleaching is influenced by a number of factors that, in addition to the operation conditions, play an important role: the mineral, the microbial participants and the operating system. All these elements are relevant to assess the technical and economical feasibility of a bioleaching process for treating copper sulphides.

Mineral

Both mineral species and ore composition and structure affect the rate and extension of the copper extraction by bioleaching from reduced sulphur compounds. For instance, the secondary copper minerals are easier to bioleach than the primary ones. In fact, the industrial bioleaching processes of copper ores are currently focused almost exclusively on secondary type minerals. Table 6 lists the more common primary and secondary copper minerals. Being the primary copper sulphides by far the most abundant in nature, to find the economical way of processing these minerals through bioleaching has became a challenge to researchers, both at the scientific and technological levels. In this way, it is not also necessary to find the way to speed up extraction kinetics, but also to improve the extent of copper recovery, being characteristics of these minerals the incomplete copper extraction (40 to 60%) at normal bioleaching conditions (Rossi, 1990; Acevedo et al. 1998; Córdoba et al. 2008a).

Table 6. Common copper sulphide minerals.

Primary copper mineral		Secondary copper mineral	
Mineral	Chemical formula	Mineral	Chemical formula
Chalcopyrite	$CuFeS_2$	Chalcocite	Cu_2S
Enargite	Cu_3AsS_4	Covellite	CuS
		Bornite	Cu_5FeS_4

The highest ore copper content is normally around 3-4%, which means that bioleaching takes place in the presence of a high percentage of materials that vary widely from one ore deposit to another. Some of these materials can interfere with the process inhibiting the microbial activity or modifying the required acidity of the leach liquor. Particle ores can differ also in their component distribution, being probable in some cases that the mineral species becomes mainly exposed at the particle surface after milling facilitating bioleaching, or, in other cases, the mineral grains may allocate inside the particle making the contact with the leaching solution difficult. These situations directly affect the kinetics and yield of copper extraction.

Particle size

Particle size is a key factor since smallest particles contribute directly to improve bioleaching kinetics, but at the same time grinding is a highly energy demanding operation having a strong impact in the economy of the whole process. Nevertheless, the range of particle size is defined by the bioleaching operation mode. Dump leaching, one of the earliest way of bioleaching, utilizes run-of-mine lumps of several inches in size. Heap leaching, the operation mode used as a standard technology for bioleaching, uses particles of controlled size in the range of half inch. Use of smaller particle sizes is not recommended because bed permeability decreases impairing leach liquor circulation and oxygen and carbon dioxide transfer from air to the liquid phase. At the opposite extreme, bioleaching in stirred tank reactors, which has not been adopted until now as an operation mode for copper recovery for economic reasons, requires particle sizes around 100 µm or less in order to keep them suspended by means of an agitator. As a result, dump leaching operation can take 4 or more years, heap leaching operation times are in the range of 5 to 10 months and less than a month is required for stirred tank reactor (Domic-Mihovilovic, 2001; Bustos, 2005). Of course, operation time is not only determined by particle size but also by different factors related to the prevailing environmental conditions that improve from dump to tank mode of bioleaching operation.

Temperature, ph and Eh

Copper solubilization and microbe activity are strongly influenced by these operation conditions and not necessarily in the same way. Sulphide oxidation rate and microbial activity increases with temperature. However, in the latter case temperature cannot be increased over the optimal microbial growth temperature. Beyond optimal temperature, microbial activity decreases and consequently bioleaching kinetics. In this sense, thermophilic and hyperthermophilic microorganisms are preferred because they can withstand the highest operation temperatures favouring the chemical steps of copper solubilization. This has been demonstrated in several studies at laboratory level, especially in the case of copper extraction from chalcopyrite, where it has been possible to increase significantly both kinetic parameters and percentage of copper extraction. However, care must be taken with respect to oxygen and carbon dioxide transfer from gas to leach liquor. Besides increasing the consumption rate of both gases, as a consequence of a higher bioleaching activity, the driving force acting on the mass transfer rate tends to decrease because the equilibrium saturation concentrations of gases decrease while temperature increases (Hougen et al. 1954).

During bioleaching there are several heat flows that induce changes in the system temperature (Acevedo and Gentina, 2007), being the principals those derived from microbial activity and from chemical oxidation of reduced sulphur minerals. These temperature changes are difficult to control, especially in static mode of operation (dump, *in-situ*, in-place and heap leaching) where wide temperature profiles inside the ore beds are generated affecting in a non-homogeneous way the performance of the bioleaching operation. At microbial level, temperature changes induce certain populations to increase their activity and others to diminish it according to their own range of growth temperature.

Microorganisms involved in bioleaching are acidophilic, being mostly active in the pH range from 1.5 to 3.0. From the point of view of the process, operating pH over 2.0 are not allowed mainly because certain chemical reactions require high proton concentrations as catalyst and also because over that pH the precipitation of jarosites (different types of ferric hydroxides *i.e.* $H(Fe(SO_4)_2 \times 2Fe(OH)_3)$ is abundant and it is known that interferes with the mechanisms of copper extraction. However, pH cannot be allowed to drop down to 1.0-1.5 since the viability of cells would be highly affected. pH tends to change during bioleaching operation mainly as a result of microbial activity, namely ferrous ion and reduced sulphur compounds oxidation. The former case contributes to raise pH while the latter contributes to lower it. A more complex situation occurs when copper is inserted in a basic gangue ore, which causes important proton consumption that in turn requires the addition of sulphuric acid to the bioleaching system.

Again, as in the case of temperature, depending upon the operation mode it will be possible to correct deviations from convenient bioleaching pH. Static bed operations will develop pH profiles affecting in different ways both cell activity and copper extraction. At microenvironment level the pH situation can still be worse since in fixed bed configurations the mass transfer rates are low mainly because of the laminar characteristic of the hydrodynamic regimes. The incoming solutions to the ore body may have the right pH but this does not secure that the pH of the leach liquor film around the ore particles will be the right one.

The importance of the leach solution Eh is well recognized in copper bioleaching operations (Córdoba et al. 2008b; Córdoba et al. 2008c). Eh is a physicochemical condition that changes during a bioleaching operation as a consequence of cell activity. During copper extraction, Eh level is highly dependent on the ferric-ferrous ion ratio, but also depends on other galvanic pairs. Normally at the beginning of a bioleaching operation the leaching solution Eh is around 350 mV and the copper extraction rate becomes important once Eh values get over 450 mV. In this sense, Eh is an important variable to quantify during bioleaching in order to use it as an index to assess the process behaviour.

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Lately, Eh has also been pointed out as an important factor, since there are experimental evidence that extraction of copper from chalcopyrite is better achieved using low Eh than the usual values obtained in normal bioleaching operations where Eh reach values around of 600-700 mV (Gericke et al. 2009).

Oxygen and carbon dioxide

Microorganisms involved in bioleaching operations need molecular oxygen and carbon dioxide to grow and keep viable. The first is used by cells as final electron acceptor of their energetic metabolic pathway. The second is used by cells as unique carbon source. Having both gases a low solubility in water and for extension in leach solution, it is crucial to the process transferring both of them at least at the same rate they are demanded by the microorganisms and, in the case of oxygen, also by the oxidation reactions of sulphide minerals. A shortage of any of them will slow down the whole process and reduce the effectiveness of copper extraction (Cautivo and Gentina, 2009).

The microbial rate of gas consumption depends directly on the number of viable cells and their level of activity. More active cells mean greater demand.

Another important concern related to these gases is the relatively low proportion of the carbon dioxide present in the air with respect to oxygen. In other words, when using air as source of both gases it is very likely to run into a situation where the growth and activity level of the bioleaching microorganisms become limited by the availability of the carbon source (Acevedo and Gentina, 2007). This is so because bioleaching systems are most of the time in a condition where transfer rates are sufficient to satisfy the oxygen demand, but not the carbon dioxide demand. To face this situation the proper solution is to enrich the inflowing air with carbon dioxide, practice whose convenience has been demonstrated at laboratory level in different studies (Bastías and Gentina, 2009; Cautivo and Gentina, 2009; Bastías and Gentina, 2010).

Bioleaching microorganisms

Normally, because of their huge size where it is impossible to control aseptic conditions, commercial heap copper bioleaching operations are carried out using the natural micro flora existing at the ore site, which is advantageous because those cells are supposed to be already adapted to that particular copper ore. However, by doing so, the start-up period may become excessively long because the initial number of microorganisms is not enough to generate significant changes in the system. One practice at industrial level is to use the leach solution of a previous operation containing an acceptable microbial count to irrigate a starting operation, so reducing the start-up period. An important fraction of cells is adhered to the ore particles and a low count of them remains in the liquid phase.

The microbial population is diverse and a large number of bioleaching microorganisms coexist inside the heap including bacteria, archea, mesophiles, thermophiles, etc. (Norris, 2007). In discontinuous operations it has been observed that the relative stratification of the microbial populations change with time, induced by environmental changes as operation proceeds (Demergasso et al. 2009; Mutch et al. 2009). Unfortunately, it is not an easy task to identify the predominant populations (Johnson and Hallberg, 2007). Molecular biology techniques have proven to be more effective than traditional microbiological protocols, but still they are an expensive and complex solution. Another important drawback is the absence of a methodology to determine the biomass present in the bioleaching system, an extremely useful variable to monitor and control the bioprocess performance. To count cells present in the leach liquor is easily done, but the quantification of the biomass adhered to the ore particles in a huge commercial operation is far from possible. Also not possible is to infer total biomass starting from the known number of planktonic cells.

At the present time some industrial operations are using inoculation of specially propagated bioleaching microorganisms with the object of increasing rapidly their number at the start of the bioleaching operation (Du Plessis et al. 2007). This strategy is currently being studied in detail considering the propagation of highly active strains or mixed populations to enrich the natural flora. Although iron and/or sulphur oxidizing microorganisms have a longer lag period than common industrial heterotrophic microorganisms, it is still possible to shorten the natural flora enrichment period considerably and start and early copper extraction. Two inoculation moments have been proposed: one is while leaching heap is being built and the other after the heap has been finished using the percolating liquor. Both have advantages and disadvantages. In the first case inoculation is

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homogeneous, but no culture conditions may exist for a very long period, probably affecting the viability of the cells. In the second case, the inoculated cells immediately find an adequate environment but their distribution is not homogeneous leaving zones inside the heap with none or low cell counts. This phenomenon occurs mainly because of the marked tendency of cells to adhere to ore surfaces decreasing rapidly the cell concentration in the leach solution stream and also because the uneven way the leaching solution percolates through the ore heap.

Bioleaching microorganisms need an energy source, a carbon source and sources of several others elements in order to keep viable and active. Most of their nutritional requirements are found in the mine environment, but some of them, like nitrogen and phosphorous sources, are not frequently found in the amounts required, especially in arid zones. It is known that these ecosystems have existed since many years being able to support microbial activity. Somehow microorganisms find there their essential materials and energy sources to grow, develop and perpetuate until now. However, in bioleaching operations, where a similar environment exists, the presence of many more microorganisms is desirable and enforced in order to accelerate copper extraction. Under those circumstances, the natural way of obtaining sources of elements such as nitrogen and phosphorous may be not enough and constitute a limitation to microbial activity. In this sense, further studies are needed to assess, from an economic perspective, the convenience of adding certain nutrients to the leach solution (Van Hille et al. 2009).

The active presence of bioleaching microorganisms is essential to the copper extraction from sulphur ores, so the careful definition of operation conditions and their monitoring are critical in order to maintain the best condition to support microbial activity in the bioleaching system.

Operation modes

Nowadays, the commercial exploitation of sulphur copper ores by bioleaching is based mainly on the utilization of heaps, a fixed bed operation mode. As said previously, the ore beds need a certain permeability to secure a reasonable percolation rate of the leach liquor and oxygen and carbon dioxide transfer rates. This is done by stacking usually agglomerated (free of fines) and cured particles half inch or more in size (Rossi, 1990; Bustos, 2005).

Since copper content in ores is in the range from 0.5 to 4%, large amount of material has to be treated at industrial level, resulting therefore in heaps of several hundred meters long and wide and several meters high. The leach solution is fed on top, mostly by dripping, and percolates through the ore bed down to the bottom where it is collected, sent to metal recovery by solvent extraction and later recycled to the heap. In this sense the heap has to be seen as a reactor where the combined action of microbial activity and chemical reactions takes place. So the challenge in operating a heap is to maintain the adequate environmental conditions in the entire ore body at any time. However, this system does not allow a strict control on several important operation variables like temperature, pH, and oxygen and carbon dioxide transfer rates. Furthermore, it may occur that poor environmental conditions in certain zones will not support microbial activity at all. All these characteristics configure a situation that certainly may have a negative effect on the productivity of the system.

Using agitated tank bioreactors the situation is the opposite. As also said previously, particle size has to be sufficiently small (usually less than 100 µm) to keep them suspended by mechanical means or by air-lift agitation. Mineral concentrated by flotation meets that particle size requirement. Copper content may increase almost 10 times when the mineral undergoes concentration by flotation procedures, which reduces the amount of material to be processed for copper extraction, representing another advantage of tank over heap bioleaching.

Most important features of an agitated tank bioreactor are the strict control over process variables like temperature and pH, and the adequate characteristics to favor mass and heat transfer operations and mixing. No doubt this configuration maintains operation conditions in a better way than heap bioleaching, allowing higher productivities of copper extraction (Acevedo and Gentina, 1989). However, investment in equipment and operation costs is high enough to make it non-economically feasible until now.

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More work is necessary in order to improve heap performance and/or to reduce costs of agitated tank bioleaching, which will cause an important impact on copper production economy (Du Plessis et al. 2007; Harvey and Bath, 2007; Plumb et al. 2007).

There are other operation modes that are less used at commercial level, like dump leaching or *in-situ* and in-place bioleaching. The last two are performed without moving the ore from its original site and the leach liquor is pumped at high pressure through the ore body (*in-situ*) or percolated through previously fractured ore rocks (in-place). All these operation modes are less productive than heap bioleaching because it is more difficult to obtain minimal conditions to support a reasonable microbial activity.

Present and future situation of copper bioleaching in chile

Heaps were first used for processing low-grade copper oxides replacing the previous technology of vat leaching in which the mineral was flooded with acid solution. The liquor was recycled until it reached the concentration of 30 to 40 g Cu/L necessary for electrowinning. Heaps, together with solvent extraction and electrowinning, was a significant technological and economical advance that made it possible to leach sulphides with the aid of microorganisms (Bustos, 2005; Domic-Mihovilovic, 2007).

During the decade of 1980 Chile made a significant breakthrough in the commercial application of copper sulphides heap leaching, not only of marginal low-grade ores but also as an alternative to the smelting of medium-grade ores. This was possible by the confluence of two important factors: the innovative spirit of Sociedad Minera Pudahuel (Bustos, 2005; Domic-Mihovilovic, 2007) and the advances in bioleaching know-how made in a major multidisciplinary and multiinstitutional research project developed in Chile.

Sociedad Minera Pudahuel in its Lo Aguirre mine located 30 km west of Santiago made an important contribution to bioleaching technology. Their operation is recognized to be the first to successfully use the LX-SX-EW (leaching-solvent extraction-electrowinning) process (Anonymous, 2005). This technology allowed benefiting oxides and sulphides for almost 20 years. Moreover, the technology and experience accumulated in that operation paved the way for several other projects that are currently in operation and several others in advanced design/construction stage. Table 7 shows bioleaching copper operations in Chile. It is worthwhile noticing that not only low-grade ores are being bioleached but also minerals with more than 1% copper.

Table 7. Copper bioleaching in large-size mines in Chile. Adapted from Demergasso, 2008.

Mine	Operator	Production tonne/year	Ore grade %	Period of operation
Lo Aguirre	Sociedad Minera Pudahuel	15,000	1.5	1980-2001
Cerro Colorado	BHP Billiton	130,000	1.0	1993-present
Ivan	Minera Milpo	10,000	2.1	1994-present
Quebrada Blanca	Aur Resources	82,000	0.9	1994-present
Chuquicamata	CODELCO	12,500	0.3	1994-present
Andacollo	Aur Resources	22,500	0.6	1996-present
Dos Amigos	Cemin	10,000	2.5	1996-present
Los Bronces	Anglo-American	46,400	0.45	2006-present
Punta del Cobre	Pucobre S.A.			
Zaldívar	Barrick	147,000	1.4	1998-present
Alliance Copper	CODELCO-BHP Billiton	20,000	concentrate	2004-2005
Escondida	BHP Billiton	750,000	0.3-0.7	2006-present
Spence	BHP Billiton	200,000	1.1	2007-present

The research project mentioned above, funded by the Chilean government and the United Nations Development Program-UNDP, started in 1985 with the participation of scientists and engineers from Chilean universities, research institutes and mining companies. Its activities covered a wide spectrum of topics, from scientific aspects to the operation of small pilot heaps. Its contribution to basic and applied knowledge in the area was recognized by the United Nations Industrial Development Organization-UNIDO (Anonymous, 1987; Badilla-Ohlbaum et al. 1991; Acevedo, 2002).

Current status of Chilean commercial copper bioleaching operations and projects has been extensively reviewed by Domic-Mihovilovic (2007). In this review, details can be found of the operations of Lo Aguirre, Cerro Colorado, Quebrada Blanca, Zaldivar, Ivan, Chuquicamata dumps, Andacollo, Collahuasi, Dos Amigos, BioCOP^{TM} project in Chuquicamata, La Escondida and Spence. To the above-mentioned, the bioleaching operation at El Abra with its LX-SX-EW plant (Anonymous, 2008b) and the heaps at Andina mine (Anonymous, 2007) can be added. In 2009 it was announced that Quebrada Blanca was expanding its LX-SX-EW plant (Anonymous, 2009a; Anonymous, 2009b). Table 7 shows bioleaching operations in large-size mines, while Table 8 lists operations in mid-size mines.

Table 8. Copper bioleaching in mid-size mines in Chile. Adapted from Anonymous, 2012.

Mine	Production tonne/year	Region
Michilla	42,000	Antofagasta
Franke	16,000	Atacama
Tres Valles	9,000	Coquimbo
Cerro Negro	5,000	Valparaíso

Intense research in bioleaching is going on in Chile in the mining companies, universities and research institutions. In 2002 the government established BioSigma, a joint venture between CODELCO and Nippon Mining & Metals. They are currently working in the isolation and modification of leaching microorganisms, developing amenability tests and on-site process monitoring and control (Badilla, 2005; Domic-Mihovilovic, 2007). Also large investments are being made by private companies and CODELCO. The 2007-2011 Chilean mining expansion plans considered the investment of US$ 22,000 million. Esperanza, Nueva Andina, Los Bronces, Collahuasi, Chuquicamata, El Teniente, Alejandro Hales are some of the mines that are currently being installed or expanding their operations (Anonymous, 2008a). Only in 2010 CODELCO planned to invest US$ 1,300 million (Anonymous, 2010). This background information allows predicting a brilliant future for this technology in Chile, as has been forecasted in the last years (Domic-Mihovilovic, 2007; Anonymous, 2008a; Anonymous, 2008b; Anonymous, 2009b; Cochilco, 2009).

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