Mining with microbes

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As early as 166 AD, biotechnology was applied to the extraction of metals from ores in the copper mines of Cyprus, and in 1928 in Kennecott, USA, 'dump leaching' – the use of microorganisms to extract copper from low grade mine waste material – was conducted on commercial scale. It was not until 1947 that Colmer and Hinkle [1] demonstrated the role that microorganisms play in the oxidation of mineral sulfides for the release of metals in solution. Currently, 20% of annual global copper production results largely through the bioleaching of chalcocite (Cu_2S). Many other metals, such as gold, cobalt, nickel, uranium and zinc are also being produced through bioleaching technology. Today, biotechnology is used to improve the environmental outcomes in a range of mining operations such as the use of sulfate-reducing bioreactors for the treatment of acid mine drainage (AMD), and heterotrophic and chemolithotrophic biofilm reactors for the degradation of cyanide products from gold processing and for the destruction of organic wastes such as oxalate from Bayer liquors during alumina production.

The major focus of current biotechnological research and development in the minerals industry is the commercial application of heap bioleaching for production of copper from chalcopyrite ($CuFeS_2$) in low grade ores. Low grade ores cannot be economically concentrated by flotation for the production of copper by conventional processing methods, such as pyrometallurgical methods. This goal is driven by the diminishing resource base of other types of copper ores and the huge untapped chalcopyrite resource.

On the surface, heap bioleaching seems a relatively simple process. Ore is mined, crushed to typically about a size of 1–3 cm, agglomerated with acid to initiate a low pH environment and compact the 'fines', and stacked to a height of about 10 m on an impermeable geotechnical membrane. During construction aeration piping is implanted within the heap. In some cases, heaps contain a multiple number of stacked 10 m high 'lifts'. Once built, irrigation of the surface of the heap with acidic solution (often at pH 1.8) is conducted. The solution permeates through the heap and aeration is supplied to promote aerobic conditions for the microbial oxidation of iron and sulfur. As copper is leached from the ore and dissolved in the leach acid, it is collected on the geotechnical membrane, after which the copper is extracted through a combination of solvent extraction and electrowinning. Heap bioleach operations probably represent the largest bioreactors in commercial use (Figure 1) and are of such a scale that only course control of the operation is possible.

MICRO-FACT

Microorganisms are the most abundant representatives of all three domains of cellular life on earth – Bacteria, Archaea, and Eucarya.

Bioleaching of mineral sufides is a mixture of abiotic and microbially catalysed reactions that involve iron and sulfur and occur between pH values from around 0.3 to 3.5. For the bioleaching of chalcopyrite, the process commences with the oxidation of the sulfide by ferric ions to release copper in solution (reaction 1).

$$CuFeS_2 + 4Fe^{3+} \xrightarrow{abiotic} Cu^{2+} + 5Fe^{2+} + 2S^0 \quad [1]$$

Microbes catalyse the reoxidation of the ferrous ion to ferric (reaction 2), which regenerates the major reactive oxidant in the leaching process, and sulfur to sulfuric acid (reaction 3), which also serves to acid leach some copper (reaction 4). The primary role of the microoganisms is to generate the leaching agents in reactions 2 and 3.

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{microorganisms} 4Fe^{3+} + 2H_2O \quad [2]$$

$$2S^0 + 2H_2O + 3O_2 \xrightarrow{microorganisms} 2SO_4^{2-} + 4H^+ \quad [3]$$

$$CuFeS_2 + 4H^+ + O_2 \xrightarrow{abiotic} Cu^{2+} + Fe^{2+} + 2H_2O + S^0 \quad [4]$$

There are currently no economic operations that employ heap bioleach technology for the recovery of copper from low grade chalcopyrite ores. Chalcopyrite heap bioleaching is a very slow process, taking up to five years to recover 20 – 40% of the copper values compared with the heap bioleaching of chalcocite, which gives an 80 – 90% copper recovery in three to five years.

The difference with the bioleaching of chalcopyrite when compared with chalcocite (Cu_2S) bioleaching is that after an initial and rapid phase of copper recovery, the bioleaching process slows rapidly. This reduction of the rate of copper release coincides with the precipitation of jarosite ($MFe_3(SO_4)_2(OH)_6$ on the surface of the chalcopyrite crystals [2], in which M is a monovalent cation; reaction [5].

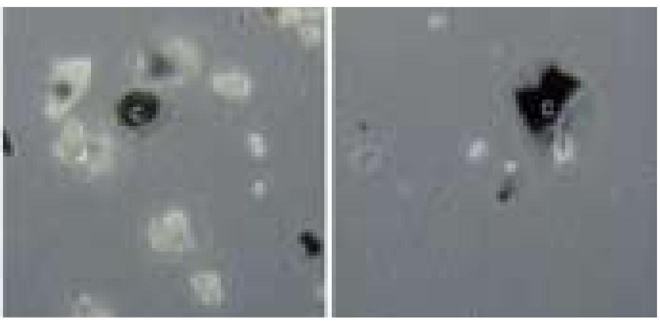
$$3Fe^{3+} + 2SO_4^{2-} + 6H_2O + M^+ \longrightarrow MFe_3(SO_4)_2(OH)_6 + 6H+ \quad [5]$$

Figure 1. Multiple 10m 'lifts' of chalcocite ore at the Monywa copper heap bioleach operation of the Myanmar Ivanhoe Copper Company, showing leach liquor rich in iron and copper draining from the heaps. These operations represent some of the largest commercial bioreactors in use.

In laboratory cultures, rapid bioleaching of chalcopyrite can be achieved using cultures of thermophilic Archaea such as *Acidianus brierleyi*. The higher temperature increases reaction rates and may increase the rate of diffusion of the leaching agents to the chalcopyrite crystal even in the presence of jarosite precipitates. It may also be the case that rapid chalcopyrite leaching is enhanced by longer initial periods of lower redox conditions in batch cultures of *Acidianus brierleyi* [3], as chalcopyrite does leach more readily at potentials of 420 mV (pt vs Ag, AgCl) than at 600 mV [4]. Another method to increase the dissolution rate of copper from chalcopyrite is to leach at extremely low pH values, down to 0.3. Recent bioprospecting attempts have yielded a new organism, *Acidianus sulfidivorans*, that can bioleach chalcopyrite very rapidly at ultra low pH values [5]. At these low pH values, jarosite tends not to form as the iron remains in solution (see Figure 2).

Development of high temperature heap bioleaching of low grade chalcopyrite ores that takes advantage of the special properties of hyperthermophiles is problematic. The oxidation of mineral sulfides is an exothermic reaction; 2,578 and 2,883 kJ mol^{-1} for pyrite and chalcopyrite, respectively [6]. Experience with chalcocite heaps has shown that the heaps, which are generally not inoculated, heat rapidly over a number of days to over 60°C, although these temperatures are not sustained [7].

Figure 2 Growth of *Acidianus sulfidivorans* on chalcopyrite (c) at pH 1.8 (left) and 0.8 (right) showing different levels of jarosite (j) precipitation.



An examination of the microbial ecology of these heaps has shown that the heaps are colonised by mesophilic and moderately thermophilic Bacteria and Archaea [8], but the development and proliferation of populations of thermophilic Archaea in uninoculated heaps of mineral sulfide ores has not been demonstrated.

Some indication of the temperature constraints on the microbial populations in these heaps may be obtained by examining the relationship between temperature and iron oxidation rate, through the application of Ratkowsky plots, for the types of organisms commonly encountered in commercial heap bioleach operations (Figure 3).

Succession of microbial populations is required for successful high temperature heap bioleaching of low grade ore. At

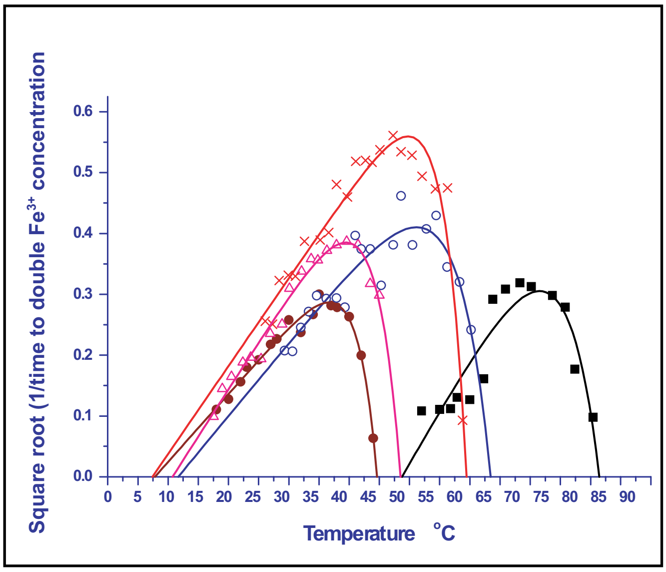


Figure 3 Ratkowsky plots showing the relationship of temperature to the oxidation of iron for a range of common bioleaching organisms: *Leptospirillum ferrooxidans* (closed circles), *Leptospirillum ferriphilum* (triangles), *Acidimicrobium ferrooxidans* (crosses), *Sulfobacillus thermosulfidooxidans* (open circles) and *Acidanus brierleyi* (squares). (Reprinted from Franzmann *et al,* 2005 [9], copyright 2005, with permission from Elsevier).

MICRO-FACT

Psychrophilic microorganisms have recently been suggested to be able to metabolise, albeit at very low rates at temperatures down to -196°C.

heap start-up mineral sulfide ores at ambient temperature would naturally contain mixed populations of mesophilic and moderately thermophilic microbes, as both the mesophiles and moderate thermophiles have similar minimal temperatures for growth (Tmin); the temperature at which the left-hand side of the Ratkowsky plots intersect the temperature axis, generally between 7 – 12°C. As the heap temperatures increase during the initial phases of mineral sulfide bioleaching, the physiological temperature operating window for these organisms allows growth until they reach their maximal temperatures for growth (Tmax), which vary from 45 – 64°C. Once heap temperatures increase to above the Tmax of the moderate thermophiles, unless thermophiles are present in number in the population, microbial growth and activity, regeneration of leaching agents, and the heat generation through sulfide oxidation stops. The heap would then be expected to cool. This happens in practice [7].

As suggested by Rawlings [10] "one would predict that the microbes required for processes that operate at 60°C or higher are unlikely to be found ubiquitously in mineral environments and would therefore need to be deliberately introduced". Cultures of thermophilic iron and sulfur oxidising microorganisms have only been sourced from geothermal environments such as volcanoes, hot springs and combusting coal seams.

The importance of inoculation for thermophilic heap bioleaching has not permeated the industry as yet, but the practicality of inoculation of low-grade chalcopyrite heaps is being investigated by a number of mineral processing companies. Inoculation of thermophiles into heaps for the biooxidation of refractory sulfide ores prior to gold extraction has been practiced by Newmont Mining Corporation at Gold Quarry mine in Nevada, USA, for an ore with a relatively high sulfide-S head grade of 1.67% [11]. Temperatures in the heap did reach stable thermophilic temperatures at a depth of 12 m in the heap, but the majority of the heap remained in the mesophilic to moderately thermophilic temperature range. Economically, successful heap bioleaching of copper from low-grade chalcopyrite ores will require a good understanding of the microbial ecology of these environments and how that ecology is controlled by heap conditions such as mineral composition, irrigation rates, aeration, heat conservation methods, and other physicochemical variables.

Studying the microbial ecology of large heap bioleach operations is not a trivial undertaking. It is our experience, and the experience of others [12], that the extraction of DNA from microbes associated with acidic mineral sulfide materials is problematic. Cell numbers are often low and cells can be strongly bound to the mineral surface. Acid conditions may degrade DNA in the extraction process, but buffering of the material to higher pH may cause precipitation of metals that can not only interfere with the DNA extraction but also reduce the quality of the DNA, which will impact on subsequent manipulations such as PCR. Few studies on the molecular ecology of commercial heap bioleaching operations have been reported, perhaps because of difficulty of conducting the studies and also for reasons of commercial confidentiality. Two exceptions were studies of heaps in Chile [13] and Myanmar [8]. The size of heaps and the gradients and heterogeneity within them challenge our ability to describe the many ecological niches within the heap environment. There is much research to be undertaken if we are to develop an understanding of the microbial ecology of heap bioleach operations, but with this understanding will come the potential to optimise the biotechnology of heap bioleaching.

MICRO-FACT

The first complete genome sequence of an organism, 1.8 million base pairs for Haemophilus influenzae, *was published in 1995.*

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