

## Microbially assisted dissolution of minerals and its use in the mining industry\*

Douglas Eric Rawlings<sup>‡</sup>

Department of Microbiology, University of Stellenbosch, Private Bag X1,  
Stellenbosch 7602, South Africa

*Abstract:* Biomining is currently used successfully for the commercial-scale recovery of metals such as copper, cobalt, and gold from their ores. The mechanism of metal extraction is mainly chemistry-driven and is due to the action of a combination of ferric and hydrogen ions, depending on the type of mineral. These ions are produced by the activity of chemolithotrophic microorganisms that use either iron or sulfur as their energy source and grow in highly acidic conditions. Therefore, metal extraction is a combination of chemistry and microbiology. The mixture of organisms present may vary between processes and is highly dependent on the temperature at which mineral oxidation takes place. In general, relatively low-efficiency dump and heap irrigation processes are used for base metal recovery, while the biooxidation of difficult-to-treat gold-bearing arsenopyrite concentrates is carried out in highly aerated stirred-tank reactors. Bioleaching reactions, the debate as to whether the reactions are direct or indirect, the role of microorganisms, and the types of processes by which metals are extracted from their ores are described. In addition, some new processes under development and the challenges that they present are discussed.

### INTRODUCTION

Biomining is a general term used to describe the use of microorganisms to facilitate the extraction of metals from sulfide or iron-containing ores or concentrates [1]. The metal-solubilization process is due to a combination of chemistry and microbiology: chemistry, because the solubilization of the metal is considered to be mainly a result of the action of ferric iron and/or acid on the mineral, and microbiology, because microorganisms are responsible for producing the ferric iron and acid [2–4]. Since the metal is extracted into water, the process is also known as bioleaching and sometimes as biooxidation (used in the case of gold recovery where the metal remains in the mineral, and, therefore, the term bioleaching is inappropriate) [3].

There are several reasons why the use of microorganisms in mineral extraction is playing an increasing role [5]. One of these is that provided a mineral is amenable to bioleaching, the metal can be economically extracted even if the metal grade of the ore is very low (e.g., the leaching of copper from waste copper dumps [2]). As higher-grade mineral deposits become worked out, there is an increasing need to recover metals from lower-grade minerals. Furthermore, bioleaching is generally more environmentally friendly than many physicochemical metal extraction processes. It is also a natural process, so that wherever an iron- and sulfide-containing mine dump is exposed to rain, metal-laden, acid solutions tend to leach out of the dump and pollute the surrounding environment [6]. Where irrigation of the dump is carried out as a deliberate extraction process, the metal is recovered, the acid is neutralized,

---

\*Plenary lecture presented at the Southern and Eastern Africa Network of Analytical Chemists (SEANAC), Gaborone, Botswana, 7–10 July 2003. Other presentations are published in this issue, pp. 697–888.

<sup>‡</sup>E-mail: der@sun.ac.za; Tel.: +27-21-808 5848; Fax: +27-21-808 5846

the disposal of the solutions is controlled, and the environment is protected. More recently, bioleaching is being used to also recover metals from higher-grade ores as these processes are frequently more economic than alternate methods.

## BRIEF HISTORY

Biomining has a long and interesting history, some of which has been published elsewhere [3], and one example of which is briefly summarized here. The use of microorganisms to extract copper has roots deep in antiquity, although the early miners would not have understood the chemistry or known that microbes were involved. Pre-Romans recovered silver, and the Romans recovered copper from a mineral deposit located in the Seville province of southern Spain. This deposit was later to become the site of the Rio Tinto mine. The Rio Tinto (Red River) obtained its name from the red color imparted to the water by the high concentration of ferric iron present. This dissolved ferric iron is extracted from the mineral deposits located in the hills that are the source of the Rio Tinto by natural microbial activity. From earliest records, the Rio Tinto has been known as a river that has undrinkable water and is devoid of fish. The immense workings of the Rio Tinto mines were rediscovered in 1556 when Fransisco de Mendoza went searching for assets that could help fill the empty coffers of Philip the Second, king of Spain [7]. Villagers from the area explained to Diego Delgado, a priest left behind by Mendoza, that if iron was placed in the river it would disappear. Furthermore, the water had another property that the priest would not commit to paper, but on which he reported to the king in person. Speculation is that he had been shown the electrochemical phenomenon whereby copper is precipitated from solution as the iron dissolves. This gives the appearance of iron being “converted” into copper. This process is known as cementation and is one of the methods by which dissolved copper is recovered from aqueous solutions. What may have made the priest secretive about this phenomenon is that a method for converting one metal to another had long been an objective of alchemists and if iron could be “converted” to copper, could it not also be converted to gold? The irrigation of heaps of copper-containing ore with Rio Tinto water that was loaded with ferric iron resulted in the solubilization of the copper and its extraction into water (see below) in a process that is the reverse of cementation. This biomining process is known as bioleaching.

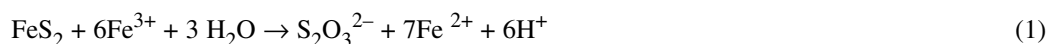
## BIOLEACHING REACTIONS

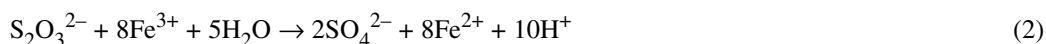
Not all types of mineral are amenable to biologically assisted leaching. In general, the mineral should contain iron or a reduced form of sulfur. Alternately, a mineral lacking in these compounds may be leached if it occurs together with another mineral that contains iron and reduced sulfur, provided that the mineral is subject to attack by ferric iron and/or sulfuric acid.

### Effect of mineral type

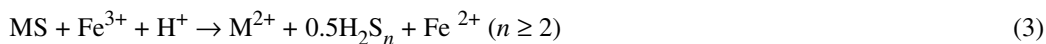
The mineral dissolution reaction is not identical for all metal sulfides. Sand and coworkers [8] have observed that the oxidation of different metal sulfides proceeds via different intermediates. They proposed a **thiosulfate mechanism** for the oxidation of acid-insoluble metal sulfides such as pyrite ( $\text{FeS}_2$ ) and molybdenite ( $\text{MoS}_2$ ), and a **polysulfide mechanism** for acid-soluble metal sulfides such as sphalerite ( $\text{ZnS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), or galena ( $\text{PbS}$ ).

In the thiosulfate mechanism, solubilization is through ferric iron attack on the acid-insoluble metal sulfides, with thiosulfate being the main intermediate and sulfate the main end-product. Using pyrite as an example, the reactions proposed by Schippers and Sand [8] are:





In the case of the polysulfide mechanism, solubilization of the acid-soluble metal sulfide is through a combined attack by ferric iron and protons, with elemental sulfur as the main intermediate. This elemental sulfur is relatively stable, but may be oxidized to sulfate by sulfur-oxidizing microbes (reaction 5 below).



This explains why strictly sulfur-oxidizing bacteria, like *Acidithiobacillus thiooxidans* or *Acidithiobacillus caldus*, are able to leach some metal sulfides, but not others. The ferrous iron produced during the process may also be reoxidized by iron-oxidizing organisms to ferric iron.



The role of the microorganisms in the solubilization of metal sulfides is, therefore, to provide sulfuric acid (reaction 5) for a proton attack and to keep the iron in the oxidized ferric state (reaction 6) for an oxidative attack on the mineral.

## MICROORGANISMS INVOLVED IN MINERAL DECOMPOSITION

### General characteristics

As would be gathered from the above, the most important microbes involved in the biooxidation of minerals are those that are responsible for producing the ferric iron and sulfuric acid required for the bio-leaching reactions. These are the iron- and sulfur-oxidizing chemolithrophic bacteria and archaea [3]. These microbes have a number of features in common that make them especially suitable for their role in mineral solubilization. They grow autotrophically by fixing  $\text{CO}_2$  from the atmosphere, which means that it is not necessary to feed them on an organic carbon source. Unlike most autotrophic organisms that use radiant energy from sunlight, these chemolithotrophs obtain their energy by using either ferrous iron or reduced inorganic sulfur compounds (some use both) as an electron donor, and oxygen as the electron acceptor. From an inorganic chemistry point of view, these organisms use the difference in redox potential between their electron donor redox-couples (e.g.,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{S}^0/\text{SO}_4^{2-}$ ) and their electron acceptor redox-couples (e.g.,  $\text{O}_2/\text{H}_2\text{O}$ ) as their source of energy. As sulfuric acid is produced during the oxidation of inorganic sulfur, these organisms grow in low pH environments. Most mineral biooxidation processes operate at a pH between 1.4 and 1.6. This permits these microbes to make use of the iron cycle as both ferrous and ferric iron are soluble at low pH. Beside ferrous iron serving as the electron donor for iron oxidizers, many of the sulfur-oxidizing organisms are able to use ferric iron in place of oxygen as an electron acceptor [9]. This ability is relevant in nonaerated heap reactors in which oxygen might not penetrate to the bottom of the heap. The modest nutritional requirements of these organisms are provided by the aeration of an iron- and/or sulfur-containing mineral suspension in water or the irrigation of a heap. Small quantities of inorganic fertilizer can be added to ensure that nitrogen, phosphate, potassium, and trace element limitation does not occur. As may be expected, microbes that grow in mineral-rich environments are remarkably tolerant to a wide range of metal ions [10], though there is considerable variation within and between species.

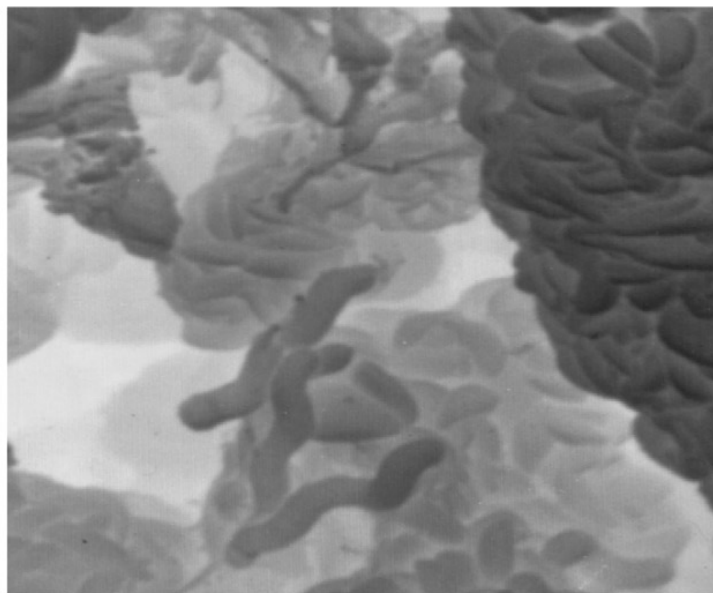
### Types of microorganisms

Bioleaching processes can be carried out at a range of temperatures, and, as would be expected, the iron- and sulfur-oxidizing microbes present differ depending on the temperature range. The types of microbes found in processes that operate from ambient to 40 °C tend to be similar, as are those within the temperature ranges 45–55 °C and 65–80 °C. As will be described later, there are two broad categories of biologically assisted mineral degrading processes. An ore or concentrate is either placed in a heap or dump where it is irrigated, or a finely milled mineral suspension is placed in a stirred tank where it is vigorously aerated. In general, the types of microorganisms found in heap-leaching processes are similar to those found in stirred-tank processes, however, the proportions of the microbes may vary depending on the conditions under which the heaps or tanks are operated [11].

In mineral biooxidation processes that operate at 40 °C or less, the most important microorganisms are believed to be a consortium of gram-negative bacteria. These include the iron- and sulfur-oxidizing *Acidithiobacillus ferrooxidans* (previously, *Thiobacillus ferrooxidans*), the sulfur-oxidizing *Acidithiobacillus thiooxidans* (previously *Thiobacillus thiooxidans*), and *Acidithiobacillus caldus* (previously, *Thiobacillus caldus*), and the iron-oxidizing *Leptospirillum ferrooxidans* and *Leptospirillum ferriphilum* (Fig. 1) [12–16]. In continuous-flow, stirred-tank processes, the steady-state ferric iron concentration is usually high and under such conditions *At. ferrooxidans* appears to be less important than a combination of *Leptospirillum* and *At. thiooxidans* or *At. caldus* [17].

Studies on microorganisms that dominate bioleaching consortia at temperatures of 50 °C, have been less well reported. However, these are believed to include *At. caldus*, some *Leptospirillum* spp, bacteria belonging to the gram-positive genera *Sulfobacillus* and *Acidimicrobium* [18], and frequently members of the archaeal genus, *Ferroplasma* [19].

At temperatures >65 °C, biomining consortia are dominated by archaea rather than bacteria, with species of *Sulfolobus* and *Metallosphaera* being most prominent [20]. Archaea belong to the genus *Acidianus* such as *Ad. ambivalens* or *Ad. infernus* are also capable of growing at high temperature (90 °C for *Ad. infernus*) on reduced sulfur and at low pH. However, the use of these organisms to contribute to industrial bioleaching is not as well established as those that grow at 50 °C or less.



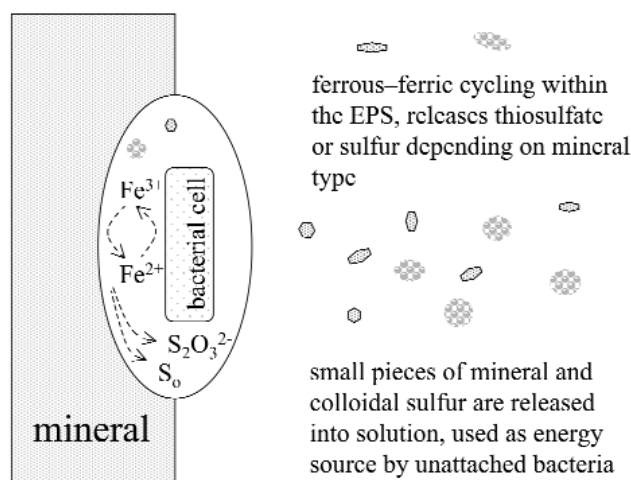
**Fig. 1** A scanning electron microscope photograph illustrating the typical spiral shape of a strain of *Leptospirillum*. Rod-shaped bacteria in different stages of entrapment in a biofilm on ore particles are also visible.

### Are bioleaching reactions direct or indirect?

In 1970, it was reported that *At. ferrooxidans* increased the rate of ferrous iron oxidation by half a million to a million times, compared with the abiotic chemical oxidation of ferrous iron by dissolved oxygen [21]. There has been a long-standing debate concerning whether the microbially assisted biooxidation of minerals is by a so-called “direct” or “indirect” mechanism [22]. In a strict sense, direct attack is viewed as a process by which components within the bacterial membrane interact directly with the metal and sulfide moieties of the mineral by using an enzymatic type of mechanism [3]. In contrast, the indirect mechanism refers to a chemical attack by ferric iron or protons on a mineral sulfide that results in the dissolution of the mineral and the formation of ferrous iron and various forms of sulfur. Iron-oxidizing microbes use the ferrous iron as an electron donor, reoxidizing it to ferric iron, thereby regenerating the reactant. If the role of the microbes is nothing more than their ability to regenerate ferric iron and protons (as shown in eqs. 5 and 6), then the efficiency of biooxidation should be independent of whether the microbes are in contact with the mineral or not.

The direct vs. indirect debate has been confused by a related question that has long exercised people who have studied biologically assisted mineral dissolution. This is, do the microorganisms have an effect on the solubilization of metals from minerals that is greater than simply their ability to produce ferric iron and acid? The reason this has caused confusion is that there is strong evidence that attachment of the microbes does improve the rate of leaching. Furthermore, bacteria like *At. ferrooxidans* [23–25] or *L. ferrooxidans* [26,27] have a strong affinity for mineral surfaces like pyrite to which they rapidly attach. At face value this may appear to indicate that the microbes are attacking the mineral directly. Nevertheless, the overwhelming evidence from a number of studies based on reaction kinetics, reaction stoichiometry, and several other considerations [28], including a recent scanning electron microscope study of mineral surface leaching [29], suggests that the mechanism of mineral solubilization is mostly indirect (physicochemical).

The most efficient leaching reactions take place within the exopolysaccharide (EPS) layer that surrounds the microbial cells, but mainly by the indirect mechanisms described above (Fig. 2). Typically, this EPS is produced only when the cells are growing on a mineral surface and not when growing in solution. The iron-impregnated EPS serves as the “reaction space” where the reactants are concentrated close to the surface of the mineral, thereby facilitating a more efficient chemical attack on



**Fig. 2** Schematic diagram illustrating the indirect leaching reactions believed to take place in the reaction space provided by the exopolysaccharide (EPS) layer that surrounds mineral attached microbial cells. (Based on models presented in [4] and [27].)

the valence bonds of the mineral [30]. Iron species within the EPS layer have been estimated to be approximately 53 g/l, a concentration that can be maintained only by the formation of complexes, possibly with glucuronic acid [8]. In addition, effects such as a local rise in pH close to the mineral surface may assist in bond breaking [31], whereas the rise in pH is so diluted in the bulk solution that it has little effect. This local rise in pH takes place when the ferrous iron produced during mineral dissolution is reoxidized to ferric iron, as shown in reaction 6.

Having said that, the potential for direct enzymatic attack on the mineral does exist. Tributsch and coworkers [27,32] have shown that the amino acid cysteine on its own is able to rapidly oxidize pyrite in the absence of oxygen or bacteria [33]. Free-SH groups from the pyrite react with the sulfhydryl group of cysteine. This thiol-disulfide reaction results in cysteine being consumed by the pyrite with the release of iron-sulfur species. As many proteins and enzymes contain cysteine, the potential for a direct attack on minerals by proteins (enzymes) is obvious. However, based on other studies, the contribution of direct attack must be small.

In summary, the attachment of microorganisms to a mineral surface results in EPS production, and this provides a reaction space that facilitates an increase in the rate of mineral solubilization. This gives the appearance that leaching is direct. However, the most important reactions are indirect (chemical- rather than enzyme/protein-mediated) and chemical turnover (cycling) takes place over the very short distance between the surface of the mineral and the surface of the attached bacterial cell.

## **TYPES OF BIOMINING OPERATIONS**

### **Dump and heap bioleaching**

As described earlier, bioleaching has been taking place for centuries, using what may be considered to be a low-technology process, the irrigation of waste ore dumps [2]. Since the early 1960s, the metal recovery process was made more efficient by the construction and irrigation of especially designed heaps [2,34,35]. When building a heap, agglomerated ore is piled onto an impermeable base and supplied with an efficient leach liquor distribution and collection system. Acidic leaching solution is percolated through the crushed ore, and microbes growing on the surface of the mineral in the heap produce the ferric iron and acid that result in mineral dissolution and metal solubilization. Aeration in such processes can be passive, with air being drawn into the reactor as a result of the flow of liquid, or active, with air blown into the heap through piping installed near the bottom (Fig. 3). Metal-containing leach solutions that drain from the heap are collected and sent for metal recovery [34]. Heap reactors are cheaper to construct and operate and are therefore more suited to the treatment of lower-grade ores. However, compared with tank reactors, heap reactors are more difficult to aerate efficiently, and the undesirable formation of gradients of pH and nutrient levels as well as liquor channeling are difficult to manage. Furthermore, although one can rely on the natural movement of microbes to eventually inoculate the heap, initial rates of bioleaching can be improved by effective heap inoculation, but this is difficult to achieve.



**Fig. 3** Photograph of the copper heap-leaching operation at Cerro Colorado, Chile. Heaps of copper-containing mineral have been stacked, an irrigation system has been placed on top of the heap, and air is blown into the heap from below. The heap has been covered with an insulation thermofilm to reduce heat loss. (Photo courtesy of Rodolfo Reyes via Chris du Plessis.)

### **In situ bioleaching**

In the 1960s, it was discovered that uranium could be recovered by bioleaching, and industrial-scale uranium bioleaching was carried out by spraying stope walls with acid mine drainage and the in situ irrigation of fractured underground ore deposits [36]. This same process has also been applied to certain copper and other ore deposits and can be viewed as a variation of an irrigation-type process [37,38]. In situ bioleaching has the advantage that the ore does not need to be removed from the ground and is usually carried out on the haloes of the low-grade ore that are left behind after the high-grade ores have been removed. It is most economic when old mine workings can be used to access the low-grade deposits.

### **Stirred-tank technology**

Stirred-tank processes use highly aerated, continuous-flow reactors. Finely ground mineral concentrate or ore is added to the first tank together with inorganic nutrients in the form of ammonia- and phosphate-containing fertilizers. The stirred suspension flows through a series of pH- and temperature-controlled aeration tanks in which the mineral decomposition takes place [3,5,39]. Mineral decomposition takes only days in stirred-tank reactors compared with weeks or months in heap reactors. Stirred-tank reactors that operate at 40 and 50 °C have proven to be highly robust, and very little adaptation is required for the treatment of different mineral types [1].

One of the major constraints on the operation of stirred-tank reactors is that the quantity of solids (pulp density) that can be maintained in suspension is limited to about 20 %. At pulp densities >20 %, physical and microbial problems occur. Not only does the liquid become too thick for efficient gas transfer, but also the shear force induced by the impellers causes physical damage to the microbial cells.

This limitation in solids concentration, plus considerably higher capital and running costs than heap reactors has meant that the use of stirred-tank reactors has been restricted to high-value minerals or mineral concentrates [35].

## METALS RECOVERED IN BIOMINING PROCESSES

The metals that are currently being recovered in the greatest tonnages are copper followed by gold. In general, most copper is recovered by the irrigation of heaps and dumps, while most gold is recovered using stirred-tank technology as a pretreatment process.

### Copper leaching

It is difficult to obtain figures of the quantity of copper that is being recovered using bioleaching as new mines continually come on stream and while others reduce or cease operation. Two fairly recent surveys of copper production data have been presented [5], with only a few mines that are common to both sets of data. By way of illustration, many of the largest operations are in Chile with up to 225 000 tonnes of copper being produced per annum in the largest of these (Sociedad Contractual Minera El Abra, Calama). Bioleaching of copper involves the conversion of water-insoluble copper sulfides to water-soluble copper sulfates. Copper-containing minerals such as chalcocite ( $\text{Cu}_2\text{S}$ ) or covellite ( $\text{CuS}$ ) are crushed, acidified with sulfuric acid, and agglomerated in rotating drums to bind fine material to coarser particles before stacking in heaps [34]. The stacked heaps are irrigated with an iron-containing solution (usually recycled spent leach liquor) through a system of pipes laid on or just below the heap surface. The solution percolates through the heap and bacteria growing on the surface of the ore and in solution catalyzes the release of copper. The ferric iron generated by the bacteria plays an important role in the production of copper sulfate.



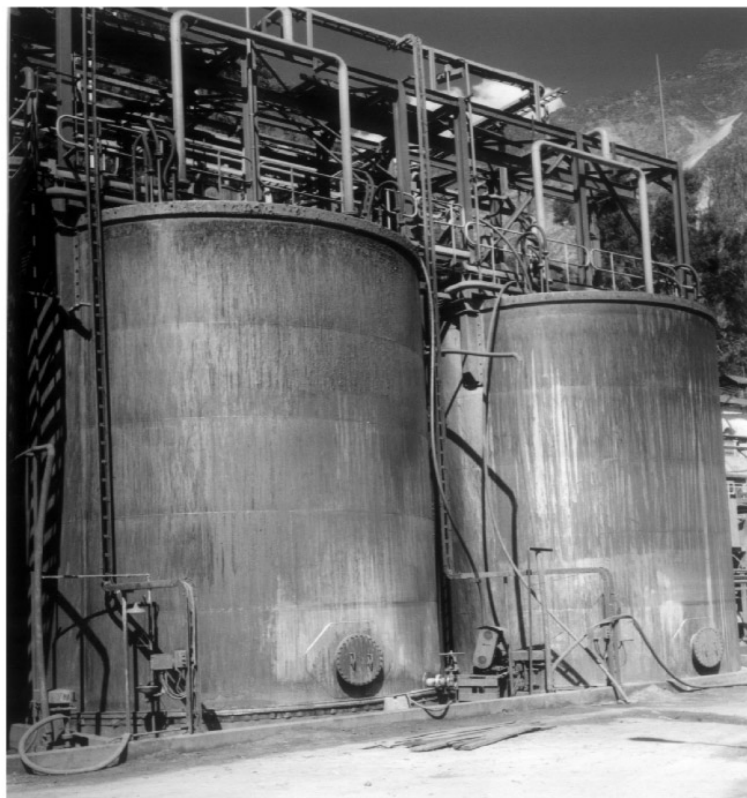
As described before, the ferrous iron and sulfur produced in the above reactions can be re-oxidized by bacteria (see reactions 5 and 6).

The pregnant leach solution containing 1.5 to 6 g/l soluble copper and up to 20 g/l iron is collected and sent to a recovery plant. The most common methods for copper recovery are by precipitation using iron filings (cementation), electrowinning or solvent extraction followed by electrowinning. The latter procedure produces the highest grade of copper [34].

### Gold biooxidation

In the 1980s, a process for the biooxidation of gold-bearing arsenopyrite ores in highly aerated stirred-tank reactors was developed by Gencor, South Africa [40]. This was at the Fairview Mine, Barberton, Mpumalanga and was designed to treat 10 tons of gold-bearing arsenopyrite concentrate per day [39]. Critical to the development of the process was the selection of a bacterial culture that was highly resistant to arsenic. The details of this selection process are described elsewhere. With the successful development of that process, biomining became a significant part of the more sophisticated mineral recovery industry. An illustration of this is that the biooxidation plant built at the Sansu mine in the Ashanti gold fields of Ghana [41] is currently (with the possible exception of some sewage treatment facilities) the largest fermentation plant in the world (960 tons of gold-bearing arsenopyrite concentrate is treated per day in 24 tanks of 1 million litres each). Currently, about 10 commercial stirred-tank biooxidation plants operate in 6 countries using highly controlled fermentation technology (an example

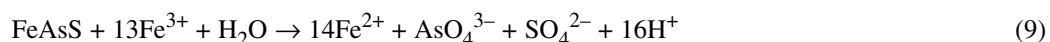




**Fig. 4** Photograph of biooxidation tanks in which gold-bearing arsenopyrite concentrate is vigorously aerated at the Tamboraque mine, 90 km east of Lima, Peru. Approximately 60 tons of concentrate is treated per day to partially decompose the concentrate before the gold is extracted using cyanide. (Photo kindly provided by Martha Ly.)

is shown in Fig. 4). Some new plants being planned in Uzbekistan are as much as twice as large as the Ashanti operation [35].

Gold is usually extracted from ores using cyanide. Recalcitrant ores are those in which gold is encased in a matrix of arsenopyrite/pyrite, so that even after fine milling, the gold cannot be efficiently recovered. Pretreatment of the ore is required to open up the molecular structure of the ore so that cyanide can penetrate the mineral and extract the gold. Since the quantities of ore to be treated are huge and most of the gold is present in a small pyrite/arsenopyrite fraction, the ore is crushed and a gold-bearing concentrate is prepared by flotation. Prior to 1986, concentrate pretreatment processes were physico-chemical. For example, the concentrate was roasted at 700 °C in the presence of oxygen or digested with acid under pressure in an oxygen-enriched atmosphere (autoclaved). In contrast, biomining bacteria decompose ores and concentrates at atmospheric pressure and at temperatures which are close to ambient.



Without pretreatment, only 30–50 % of the gold is recovered, depending on the concentrate, while after biooxidation, more than 95 % of the gold is recoverable. Since gold-bearing concentrates are valuable substrates relative to copper, it is economically viable to carry out the pretreatment biooxidation processes in efficient, aerated, temperature- and pH-controlled tank fermenters. A typical Biox plant operates at about an 18 % w/v solids concentration with a total solids retention time of about 4 days.

Acidity is controlled at pH 1.6 and the temperature at 40 °C. As the process is exothermic, a considerable amount of energy for cooling is required to maintain the process at this temperature [41].

An alternative to the Biox process is the Bacox process developed by BacTech (Australia) [42]. The BacTech and Biox processes use similar highly aerated stirred-tank reactors with the major difference being that the BacTech process is operated at close to 50 °C. As a result, biooxidation of the concentrate is carried out by moderately thermophilic bacteria, although the exact composition of bacterial population is unclear [43]. Like the Biox process, the Bacox process has been reported to be highly robust and has the advantage that less cooling is required. A disadvantage is that the solubility of oxygen and carbon dioxide is lower at the higher temperatures.

A process in which a gold-bearing concentrate is treated in a heap rather than a tank reactor has recently been reported. In this process (developed by Geobiotics, Hayward, CA, USA) the concentrate is agglomerated onto a support rock, which is then stacked on a pad, inoculated with microorganisms, and irrigated [44]. Air is blown through the stack, and after a period the partly oxidized material is removed for gold recovery.

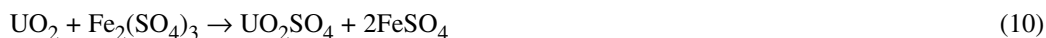
Unlike the bioleaching of copper ores, where the copper is solubilized in the biological process, the gold is not solubilized by microbial action, but a separate chemical process is required. Since gold is not leached from the ores, the term "biooxidation" is used to describe the treatment of gold ores as opposed to the term "bioleaching".

### Advantages and disadvantages of gold recovery using biooxidation

A major advantage of biooxidation is that relatively little of the ore need be decomposed to allow near-complete gold recovery. The gold particles create a weakness in the pyrite/arsenopyrite crystal lattice, and biooxidation takes place preferentially in these areas of weakness [45]. Capital costs for biooxidation have reported to be about two-fold lower than roasting or pressure oxidation, and operating costs are also lower [41]. Waste disposal following biooxidation is comparatively easy. The pH of the ferric arsenate effluents is raised to above pH 5 with lime. This precipitates arsenic as  $\text{FeAsO}_4$  which is almost insoluble (<0.2 mg/l arsenic) and may be disposed of to a tailings dam [41]. Biooxidation of gold-bearing ores has proved to be a remarkably reliable process. Early concerns about the possibility of phage infection and process instability were unfounded. A major drawback of the biooxidation compared with the physicochemical pretreatment processes is that in many cases the consumption of cyanide in the subsequent gold-recovery process is considerably higher following biooxidation.

### Uranium

During 1988, approximately 300 tons of uranium with a value of over US\$ 25 million was recovered from a single mine (Dennison mine, Lake Elliot district, Canada) [36]. Much like copper, uranium is recovered by the conversion of insoluble uranium oxides to soluble sulfates though the action of ferric iron and sulfuric acid produced by microbes.



As explained earlier, almost all uranium recovery was carried out in situ. However, with the reduction in demand for uranium in more recent years, this mine has stopped production, and no microbially assisted uranium recovery is currently taking place.

## Cobalt

A continuously aerated stirred-tank process is being used at Kasese (Uganda) to extract cobalt from a stockpile of 1.1 million tons of pyrite concentrate [46]. The concentrate contains 1.38 % cobalt and large, 1.35 million liter tanks are used to recover about 92 % of the cobalt. This process began operation in 1998 and about 240 tons of cobalt-containing pyrite is treated per day using an undefined mixture of acidithiobacilli and leptospirilli that grow optimally at 37 °C.

## Other metals

Metals that are present in an insoluble reduced sulfur form and which are rendered soluble when oxidized to a sulfate may be potentially recovered by bioleaching. This includes minerals containing NiS and ZnS, etc. Although bioleaching provides the possibility of recovering metals from many low-grade deposits that would otherwise be considered waste, its application greatly depends on the value of the metal to be recovered. A major challenge is to find a suitable match between an ore body and bioleaching technology. For example, the technology for nickel recovery using the BioNic<sup>®</sup> process [47] has been thoroughly tested, but as yet no ore body of a suitable concentration and size has been identified to allow economic recovery at current nickel prices.

## FUTURE OUTLOOK

The use of microbes to extract metals from ores is now well established. The technical feasibility and robustness of heap and tank bioleaching processes for the recovery of a variety of metals from ores that operate at temperatures from ambient to 50 °C has clearly been demonstrated. Biooxidation plants with tank sizes of 1300 m<sup>3</sup> (with 2000 m<sup>3</sup> tanks under design) and the Sansu plant (Ashanti) that earns half of Ghana's foreign exchange, is evidence of this. Heap-leach and stirred-tank processes which operate at ambient or temperatures of 40–50 °C or less will continue and will be applied to new types of minerals.

There is much potential for the recovery of metals from ores where reaction rates are too slow using currently proven processes. A prime example of this is the extraction of copper from ores such as chalcopyrite. The solubilization of copper from chalcopyrite is temperature-dependent, and the reaction rate increases to economically workable levels at temperatures of 65 °C and preferably higher. Therefore, one requires organisms that are capable of producing ferric iron and acid leaching reagents at these higher temperatures. Most microbes that grow at these temperatures are much like bacteria in appearance, but are in fact different single-celled microorganisms called archaea. At these high temperatures, difficulties occur that are not as much of a problem at 50 °C or less. For example, the solubility of air is reduced, and oxygen gas, rather than air, is used as the oxidant. Evaporation rates are high, and special grades of stainless steel or ceramics materials are required for reactor construction to be able to withstand the very corrosive, high-temperature, acidic environment. Nevertheless, high-temperature mineral oxidation has been successfully demonstrated by BHP Billiton at a semi-commercial scale in a 300-m<sup>3</sup> reactor on a pyrrhotite feedstock at the Pering mine in South Africa [35]. The construction of a 20 000 tonnes per annum prototype plant at Chuquicamata in Chile is being planned by a BHP Billiton and Codelco alliance. Attempts to apply high-temperature leaching to heaps are more complicated, but where sufficient sulfide is present in an ore to generate the required heat, this may be attempted.

Increased concern regarding the effect of mining on the environment is likely to improve the competitive advantage of microbially based metal recovery processes. The enforcement of more stringent legislation to limit environmental pollution (e.g. uncontrolled metal and acid leaching from dumps or arsenic emission from smelters) would make bioleaching more attractive.

The application of biohydrometallurgy to metal recovery is likely to grow because where a suitable mineral deposit is available, to quote Brierley and Brierley [38], it offers advantages of operational simplicity, low capital and operating cost, and shorter construction times that no other alternative process can provide. Add to that, minimum environmental impact, and the use of this technology in the mining industry is set to increase.

## ACKNOWLEDGMENTS

The author wishes to acknowledge funding support from the BHP Billiton, the National Research Foundation, and The Human Resource for Industry Programme (Pretoria, South Africa) as well as the University of Stellenbosch. He also wishes to thank Chris du Plessis and Martha Ly for the photos used in Figs. 3 and 4, respectively.

## REFERENCES

1. D. E. Rawlings (Ed). *Biomining: Theory, Microbes and Industrial Processes*, Springer-Verlag, Berlin (1997).
2. C. L. Brierley. *Sci. Am.* **247** (2), 42–51 (1982).
3. D. E. Rawlings. *Annu. Rev. Microbiol.* **56**, 65–91 (2002).
4. W. Sand, T. Gehrke, R. Hallmann, A. Schippers. *Appl. Microbiol. Biotechnol.* **43**, 961–966 (1995).
5. D. E. Rawlings and S. Silver. *Bio/Technology* **13**, 773–778 (1995).
6. P. R. Norris. In *Microbial Mineral Recovery*, H. L. Erlich and C. L. Brierley (Eds.), pp. 3–27, McGraw-Hill, New York (1990).
7. D. Avery. *Not on Queen Victoria's Birthday: The Story of the Rio Tinto Mines*, Collins, London (1994).
8. A. Schippers and W. Sand. *Appl. Environ. Microbiol.* **65**, 319–321 (1999).
9. T. Sugio, C. Domatsu, O. Munakata, T. Tano, K. Imai. *Appl. Environ. Microbiol.* **49**, 1401–1406 (1985).
10. L. G. Leduc and G. D. Ferroni. *FEMS Microbiol. Rev.* **14**, 103–120 (1994).
11. M. Vásquez and R. T. Espejo. *Appl. Environ. Microbiol.* **63**, 332–334 (1997).
12. B. M. Goebel and E. Stackebrandt. *Appl. Environ. Microbiol.* **60**, 1614–1621 (1994).
13. D. P. Kelly and A. P. Wood. *Int. J. Syst. Evol. Microbiol.* **50**, 511–516 (2000).
14. K. B. Hallberg and E. B. Lindström. *Microbiology* **140**, 3451–3456 (1994).
15. N. J. Coram and D. E. Rawlings. *Appl. Environ. Microbiol.* **68**, 838–845 (2002).
16. K. B. Hallberg and D. B. Johnson. *Adv. Appl. Microbiol.* **49**, 37–84 (2001).
17. D. E. Rawlings, H. Tributsch, G. S. Hansford. *Microbiology* **145**, 5–13 (1999).
18. D. A. Clark and P. R. Norris. *Microbiology* **142**, 785–790 (1996).
19. O. V. Golyshina, T. A. Pivovarova, G. Karavaiko, T. F. Kondrat'eva, E. R. B. Moore, W.-R. Abraham, H. Lünsdorf, K. N. Timmis, M. M. Yakimov, P. N. Golyshin. *Int. J. Sys. Evol. Microbiol.* **50**, 997–1006 (2000).
20. P. R. Norris, N. P. Burton, N. A. M. Foulis. *Extremophiles* **4**, 71–76 (2000).
21. D. T. Lacey and F. Lawson. *Biotech Bioeng.* **12**, 29–50 (1970).
22. D. G. Lundgren and M. Silver. *Ann. Rev. Microbiol.* **34**, 263–283 (1980).
23. R. C. Blake, K. Sasaki, N. Ohmura. *Hydrometallurgy* **59**, 357–372 (2001).
24. J. Rojas, M. Giersig, H. Tributsch. *Arch. Microbiol.* **163**, 352–356 (1995).
25. T. Gehrke, J. Telegdi, D. Thierry, W. Sand. *Appl. Environ. Microbiol.* **64**, 2743–2747 (1998).
26. R. Hallmann, A. Friedrich, H.-P. Koops, A. Pommerening-Röser, K. Rohde, C. Zenneck, W. Sand. *Geomicrobiol. J.* **10**, 193–206 (1992).
27. H. Tributsch. *Hydrometallurgy* **59**, 177–185 (2001).

28. F. K. Crundwell. In *Biohydrometallurgy: Fundamentals, Technology and Sustainable Development*, Part A, V. S. T. Ciminelli and O. Garcia Jr. (Eds.), pp. 149–158, Elsevier, Amsterdam (2001).
29. K. J. Edwards, B. Hu, R. J. Hamers, J. F. Banfield. *FEMS Microbiol. Ecol.* **34**, 197–206 (2001).
30. T. Gehrke, R. Hallmann, K. Kinzler, W. Sand. *Water Sci. Technol.* **43**, 159–167 (2001).
31. T. A. Fowler, P. R. Holmes, F. K. Crundwell. *Hydrometallurgy* **59**, 257–270 (2001).
32. J. Rojas, M. Giersig, H. Tributsch. *Arch. Microbiol.* **163**, 352–356 (1995).
33. J. A. Rojas-Chapana and H. Tributsch. *Hydrometallurgy* **59**, 291–300 (2001).
34. H. A. Schnell. In *Biomining: Theory, Microbes and Industrial Processes*, D. E. Rawlings (Ed.), pp. 21–43, Springer-Verlag, Berlin (1997).
35. D. E. Rawlings, D. Dew, C. du Plessis. *Trends Biotech.* **21**, 38–44 (2003).
36. R. G. L. McCready and W. D. Gould. In *Microbial Mineral Recovery*, H. L. Erlich and C. L. Brierley (Eds.), pp. 107–126, McGraw-Hill, New York (1990).
37. C. L. Brierley. In *Biomining: Theory, Microbes and Industrial Processes*, D. E. Rawlings (Ed.), pp. 3–17, Springer-Verlag, Berlin (1997).
38. J. A. Brierley and C. L. Brierley. *Hydrometallurgy* **59**, 233–239 (2001).
39. P. C. Van Aswegen, M. W. Godfrey, D. M. Miller, A. K. Haines. *Miner. Metallurg. Process.* **8**, 188–192 (1991).
40. E. Livesey-Goldblatt, P. Norman, D. R. Livesey-Goldblatt. In *Recent Progress in Biohydrometallurgy*, G. Rossi and A. E. Torma (Eds.), pp. 627–641, Associazione Mineraria Sarda, Iglesias, Sardinia (1983).
41. D. W. Dew, E. N. Lawson, J. L. Broadhurst. In *Biomining: Theory, Microbes and Industrial Processes*, D. E. Rawlings (Ed.), pp. 45–80, Springer-Verlag, Berlin (1997).
42. P. C. Miller. In *Biomining: Theory, Microbes and Industrial Processes*, D. E. Rawlings (Ed.), pp. 81–102, RG Landes and Springer-Verlag, Berlin (1997).
43. P. D. Franzmann and T. L. Williams. In *IBS Biomine '97*, pp. QP1.1–10, Australian Mineral Foundation, Glenside, Australia (1997).
44. J. L. Whitlock. In *Biomining: Theory, Microbes and Industrial Processes*. D. E. Rawlings (Ed.), pp. 117–127, Springer-Verlag, Berlin (1997).
45. R. Claasen, C. T. Logan, C. P. Snyman. In *Biohydrometallurgical Technologies*, Vol. I, A. E. Torma, J. E. Wey, V. I. Lakshmanan (Eds.), pp. 479–488, TMS Press, Warrendale, Pennsylvania (1993).
46. A. Briggs and M. Millard. In *IBS Biomine '97*, pp. M2.4.1–12, Australian Mineral Foundation, Glenside, Australia (1997).
47. D. W. Dew and D. M. Miller. In *IBS Biomine '97*, pp. M7.1.1–9, Australian Mineral Foundation, Glenside, Australia (1997).