



A Mintek perspective of the past 25 years in minerals bioleaching

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Synopsis

The microbial leaching of metal sulfides is now an established biotechnological technology. Over the past 25 years, refinements in the engineering design of bioleaching processes have paralleled advances in our understanding of the diversity and role of the micro-organisms driving the process and the mechanisms by which micro-organisms enhance metal sulfide oxidation. Commercial success started with the treatment of refractory gold concentrates using mesophilic micro-organisms, followed by the development of tank bioleaching processes for the treatment of base metal concentrates. This was, initially, a mesophilic process with limited potential for recovery of copper from chalcopyrite concentrates due to slow rates and low copper extractions. The exploitation of thermophiles represents a major breakthrough in the development of bioleaching technology for the treatment of chalcopyrite-containing ores and concentrates. This development also opened the route to heap bioleaching of chalcopyrite ores, which is now a major focus of research programmes and piloting campaigns. This paper reviews the historical development of minerals bioleaching processes and gives an update on the current status of commercial tank and heap bioleach operations around the world.

Introduction

The story of bioleaching begins a lot earlier than one might imagine. In China, records indicate that bacteria were used in the recovery of copper well over 2,000 years ago, in the third century BC^{1,2}. It is also known that pre-Romans recovered silver, and the Romans recovered copper, from a mineral deposit located in the Huelva province of southern Spain. This later became the site of the famous Rio Tinto mine. The Rio Tinto (the Red River) obtained its name from the red colour of the water caused by the presence of a high concentration of ferric iron (Figure 1). This dissolved ferric iron arises by natural microbial action on the sulfide minerals that occur in the hills that are the source of the Rio Tinto. From earliest records, the Rio Tinto has been known as a river that has undrinkable water and is devoid of fish³.

Commercial exploiters of copper-bearing orebodies have almost certainly made unwitting use of micro-organisms down the

centuries, but it was only in the middle of the previous century that their contribution was recognized. This began with the discovery and isolation (from acid drainage at a coal mine) in 1947 of the sulfur- and iron-oxidizing bacterium, *Acidithiobacillus ferrooxidans*, and continued into the following decade when that bacterium was found to be responsible for accelerated leaching of copper from waste rock dumps^{2,4}. Since then, deliberate use of these and other micro-organisms has expanded worldwide, particularly in copper dump- and heap-leaching applications in South America, and, globally in tank bioleaching of refractory gold concentrates.

Landmarks in bioleach process development

Most of the major technological advances in the field have occurred in the past 25 years. By the early 1980s, key hydrometallurgical technologies such as solvent extraction and electrowinning (SX-EW) for copper recovery, the acidic heap leaching of copper oxide ores, and the cyanide leaching of free-milling gold ores had been commercially well established. However, the application of micro-organisms for the heap, dump and *in situ* leaching of uranium and copper minerals was still somewhat incidental. The role of bacteria in oxidative leaching was recognized and studied, but the use of engineering features to enhance and control bacterial activity in the extractive processes was not common⁵.

Within the past 25 years, several major landmarks in bioleach process development can be identified. First among these was the development and commercialization of a process for agitated tank bioleaching of sulfide

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Figure 1 – The distinctive red colour of the Rio Tinto in Spain arises because of the action of naturally-occurring micro-organisms

concentrates, at the Fairview Gold Mine in South Africa in 1986⁶. This major breakthrough placed bioleaching firmly on the metallurgical map. The foundation for the commercialization of agitated tank bioleaching technology undoubtedly lay in the engineering of the process, since the reactors are not only large (Figure 2), but also require high intensities of agitation, aeration and heat exchange. It can be argued that some of the cutting edge developments that have taken place in three-phase (gas-liquid-solid) mixing technology in the past 25 years were driven by the need to service ever larger agitated tank-bioleach processes.

'Thin layer' leaching, where crushed and acid-cured ore is stacked 2 to 3 meters high and then rinsed, was first applied at the Lo Aguirre Copper Mine in Chile in 1980, and is regarded as the first instance of heap bioleaching⁷. A further significant milestone in heap bioleaching was the introduction of forced aeration for the heap bioleaching of secondary copper sulfide ores at the Girilambone Copper Mine in Australia in 1993⁷. Heap bioleaching of secondary copper sulfide minerals had been practised, mainly in Chile, since 1980, but the Girilambone operation was the first to incorporate forced aeration in the plant design. Many of the existing operations soon followed suit.

A milestone of a different sort in bioleach process development was the identification of higher temperature organisms, or thermophiles. This development has expanded the potential for the commercial application of bioleaching processes, significantly. The bioleaching of chalcopyrite ores and concentrates, and more efficient bioleaching of refractory gold concentrates, are two such applications. Agitated tank bioleaching of chalcopyrite- and enargite-containing concentrates using thermophiles has been practised at semi-commercial scale producing 20,000 t/a copper in the BioCOP[®] process, although operation of the plant has since been stopped for commercial reasons⁸.

In recent years, the application of modern microbiological techniques has enabled the identification and understanding of dozens of different bioleach micro-organisms, capable of functioning over a vast range of conditions, and this remains a subject of ongoing development in the field. As the understanding of the role and functions of bioleach microbes grows, so does the potential to harness the benefits of this microbiological diversity. This growing understanding of the

microbiology of bioleach micro-organisms is likely to be of major benefit in thermophilic heap bioleaching, where bacterial succession in a transient environment could be one of the keys to the successful development of the process.

Thermophilic heap bioleaching is the next landmark in the unfolding story of bioleach process development. This has long been considered the 'Holy Grail' of bioleaching technology, since it has the potential to unlock immense value from the large, low-grade chalcopyritic ore deposits in which the bulk of the world's unexploited copper reserves are contained, but which, currently cannot be processed economically. There are significant advances taking place in this field at the present time, and Mintek is playing a leading role in these developments. It has already been noted that the successful development of agitated tank bioleach technology was founded firmly on the engineering of the bioleach reactor. It is therefore significant, but hardly surprising, to note that the development of high-temperature heap bioleaching is following a similar path, with a deep understanding of the engineering and control of the heap being at the core of the process development.

Mintek's contribution to bioleach process development

Small beginnings

Mintek has played a significant role in the development of bioleaching technologies in the past 25 years, and has established a global reputation in the field. Mintek's involvement in bioleaching began modestly, with the establishment in the early 1980s of a small research group in what was then the Ore-Dressing Division. The first internal report in Mintek's archives that features bioleaching is a literature survey from 1982, and by the following year, a steady stream of test work reports began to appear. The early days of bioleach research at Mintek were focused on the heap leaching of base metal ores, with nickel sulfide being the main mineral of interest. The proceedings of the Mintek 50 Conference, which commemorated Mintek's 50th anniversary in 1984, included one paper on the heap bioleaching of low-grade nickel ores⁹. This was one of the first papers to be published by the fledgling research group, and included details of small-scale tests in Erlenmeyer flasks, as well as the results of column-leach tests in 0.3 m, 1 m and 2 m tall columns.



Figure 2 – Bioleach reactors rank amongst the largest high intensity process reaction vessels in the world, as evidenced by these approximately 900 m³ reactors at the Ashanti BIOX[®] plant in Obuasi, Ghana

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Gold bioleaching

By around 1986, the emphasis of Mintek's research work began to shift towards the agitated tank bioleaching of refractory gold concentrates. The late 1970s and early 1980s had seen a surge in the price of gold, and by the mid-1980s, the (then) mining house Gencor was actively developing the technology. By 1986, Gencor had commissioned the world's first refractory gold bioleach demonstration plant, treating a flotation concentrate at the Fairview mine, located near Barberton in South Africa⁶. Another major South African mining house, Anglo American Corporation (AAC), took a strategic decision to develop bioleach technology for its own use, in conjunction with Mintek. For close to ten years, AAC was a significant co-funder of Mintek's research effort, and this resulted in a rapid expansion of the bioleach research group at Mintek.

From the outset, AAC and Mintek viewed the design and scale-up of the bioleach reactors as the most critical aspect of the process development. With this in mind, the project advanced rapidly to the point where two demonstration-scale plants were built, one at Mintek and the other at the (then) Vaal Reefs Gold Mine, near Orkney in South Africa (Figure 3). Extensive design and scale up data were obtained from these plants, which formed the basis for developing an in-house software package for bioleach reactor design that is still in use today.

Despite all this exciting process development work, which was focused on refractory gold concentrates, AAC did not find an application for the technology in its own stable. In the early-to mid-1990s, Anglo American South America (AMSA) began funding development work at Mintek on the application of agitated tank bioleaching to copper sulfide concentrates. It was found that the technology was directly transferable for the leaching of secondary copper sulfide minerals, but the primary copper sulfide—chalcopyrite—was very difficult to leach. From the techno-economic studies performed then, it emerged that smelting remained the processing route of choice for those cases where clean, high-grade copper concentrate could be produced with a high recovery during flotation. These findings led to the subsequent bioleach processing developments at Mintek being focused on tailoring bioleaching conditions to suit the dissolution of chalcopyrite, particularly as contained in complex, low-grade sulfide concentrates, which are not well suited to smelting.

Towards the latter part of the 1990s, Mintek formed a technology partnership with BacTech, an Australian- and Canadian-based company that offered similar bioleach technologies. This partnership succeeded in commercializing their refractory gold bioleach technology, Bacox™, first at the Beaconsfield Gold Mine in Tasmania, Australia in 1999¹⁰ (Figure 4), and soon thereafter (in 2001) at the BioGold toll treatment facility located near the city of Laizhou, in the Shandong Province of PR China¹¹. Both of these plants remain in operation today.

Base metal concentrate bioleaching and the chalcopyrite challenge

The partnership with BacTech also concentrated on the development of base-metal bioleaching. The bioleaching of

chalcopyrite has challenged many researchers in the field, and the debate over the mechanisms involved in the passivation of chalcopyrite in a sulfate leaching medium continues to the present day¹². Mintek's approach to the problem was aimed at developing a practical solution, and this included the use of regrinding to the order of 10 to 35 µm, higher-temperature micro-organisms, and control of the redox potential in the process. It was found that a combination of some, or all, of these parameters provided a practical solution, and the bioleaching of chalcopyrite—in both tanks and heaps—has been achieved by Mintek in large-scale demonstration plants.

The use of bioleaching—or indeed any hydrometallurgical process—for the treatment of base-metal concentrates has not found widespread application⁸. There are sound reasons for this: smelting terms are competitive, and cannot be matched by producers seeking to establish onsite hydrometallurgical leaching and cathode production facilities (leaving aside strategic drivers toward local beneficiation and value addition). However, in the case where sulfide concentrates



Figure 3—A section of the Vaal Reefs bioleach pilot plant, which was designed to treat 20 t of high-grade pyrite concentrate per day



Figure 4—The Beaconsfield Bacox™ plant, located in the Tamar valley, near the city of Launceston in northern Tasmania, Australia

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contain significant quantities of impurities that incur penalties at a smelter, or are too low in grade for acceptance by a smelter, hydrometallurgical treatment may be a more cost-effective treatment option for the producer. With this in mind, Mintek's base-metal bioleaching development in the past ten years, has focused on these types of concentrates.

In 2001, Mintek and BacTech, together with the Mexican metal producer, Industrias Peñoles S.A. de C.V., successfully demonstrated the bioleaching of a polymetallic concentrate containing chalcopyrite, sphalerite, galena, silver and gold using moderate thermophiles at an operating temperature of 45°C, in an integrated demonstration plant that was commissioned and operated in Monterrey, Mexico (Figure 5). The plant, with a design capacity of 1 t/d of copper, produced more than 40 t of LME A-grade cathode copper.

More recently, Mintek has completed a programme of integrated pilot plant development work in which thermophiles were used to bioleach low-grade copper and nickel copper concentrates containing chalcopyrite⁸. This work was conducted on European concentrates, under the umbrella of the BioMinE project, which was partly funded by the European Commission's Sixth Framework Programme, and in which Mintek played a leading role. Within this four-year project, which ran from 2004 to 2008, Mintek has also developed and applied modern molecular techniques for the identification and quantification of bioleach micro-organisms.

Heap bioleaching

There is no doubt that the heap bioleaching of copper ores has been the most extensive and successful commercial application of bioleach technology. There are sound reasons for this: as the oxide caps of porphyry copper deposits were depleted, mine operators needed to develop technology to replace the acid heap leaching process, to make use of existing refinery infrastructure¹³. Heap bioleaching of secondary copper sulfides proved to be that technology. However, because the technology was developed 'on the fly' by metallurgical operations in need of a replacement technology, many teething problems were experienced, and it has taken time to optimize the engineering and operation of these heaps. Important advances in areas such as heap inoculation, agglomeration, the judicious application of acid and forced aeration have improved the process considerably^{13–15}.

Mintek's primary area of process development in the past ten years has been the application of heap bioleaching technology for primary copper ore deposits containing chalcopyrite. The approach taken has been to promote the preservation of heat within the heap, in order to attain a high internal heap temperature, thereby overcoming the passivation of chalcopyrite. This has required the development of an appropriate operational strategy and control system, with fairly sophisticated experimental techniques in columns are required to simulate industrial conditions^{16–18}. Mintek's high-temperature heap bioleach technology for chalcopyrite has been successfully demonstrated in partnership with the National Iranian Copper Industries Company (NICICO) in Iran, where (at the time of writing) fourteen 20,000 t pilot heaps have been operated^{19,20} (Figure 6). NICICO has recently made a decision to utilize this technology for the Darehzar project, located at

the Sarcheshmeh Copper Complex. This development, and the large heap leach trials on chalcopyritic ore at the Escondida mine in Chile, are breaking new ground in the heap bioleaching of primary chalcopyrite ore.

Microbiology and mechanisms

Microbial diversity and characterization

The modern era of bioleaching began with the discovery, in 1947, that bacteria are associated with acid rock drainage, and the characterization and naming of *Thiobacillus ferrooxidans* in 1951²¹. This microbe was for many years the most studied iron- and sulfur-oxidizing acidophile²² and was later renamed to *Acidithiobacillus ferrooxidans*²³. Findings based on the use of modern, molecular identification techniques are, however, now suggesting that this organism is of less importance in commercial bioleaching processes than was previously thought²⁴.

Today we know that there are many different genera and species of microbes capable of sulfur and iron oxidation present in bioleaching environments. These microbes are classified on the basis of their temperature ranges for growth as mesophiles, moderate thermophiles and thermophilic archaea. A number of excellent reviews describing the characteristics of the different cultures have recently been published^{25–28}.



Figure 5—The Mintek-BacTech-Peñoles polymetallic copper bioleach demonstration plant, located in Monterrey, Mexico



Figure 6—The Mintek-NICICO chalcopyrite copper heap bioleach demonstration plant at the Sarcheshmeh Copper Complex, located in the province of Kerman, Iran

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While careful considerations were made in the design and engineering of bioleaching operations, microbiological aspects have been subjected to far less scrutiny and control²⁷ and, somewhat surprisingly, there have been relatively few accounts of the compositions and dynamics of microbial populations in commercial bioleaching operations. One reason for this has been the lack of accurate and appropriate methods for analysing populations that are active in bioleaching environments.

The development of modern molecular identification and quantification techniques represents the turning point for unequivocally distinguishing between strains of bioleaching micro-organisms as well as between species and genera^{29,30}. Techniques such as gene libraries constructed from extracted DNA, restriction enzyme analysis, fluorescence *in situ* hybridization and PCR-based techniques have been used in recent years to identify and follow changes in microbial consortia in tank and heap leach operations^{29,31,32}.

These days, we know that the most important micro-organisms in tank bioleach processes that operate from ambient temperatures to about 40°C are considered to be a consortium of iron and sulfur oxidizing *Acidithiobacillus ferrooxidans*, the sulfur-oxidizing *Acidithiobacillus thiooxidans* and *Acidithiobacillus caldus* and the iron oxidizing *Leptospirillum ferrooxidans* and *Leptospirillum ferriphilum*^{25,27}.

Studies on microbial consortia dominating bioleach reactors operating in the 45–50°C range have been less well reported²⁵. In pilot scale, multi-stage stirred tank operations used to treat a polymetallic sulfide ore at 45°C, *At. caldus*, *L. ferriphilum*, *Sulfobacillus*-like bacteria and *Ferroplasma*-like archaea were found to dominate the reactors³¹. Species of *Acidimicrobium* may also occur in systems operating at temperatures around 50°C^{3,25}.

There are even fewer reports on the types of microbes that occur in bioleaching processes operating at temperatures above 70°C. However, it has become clear that under these conditions, archaea rather than bacteria dominate, with species of *Sulfolobus*, *Acidianus* and *Metallosphaera* being most prominent^{25,33}. *A. brierleyi* has recently been shown to be the dominant microbe in thermophilic bioreactors operated at Mintek during the treatment of chalcopyrite-containing concentrates³².

In general, the types of micro-organisms found in heap leaching processes are similar to those found in stirred tank processes, with *At. ferrooxidans*, *At. thiooxidans* and *L. ferrooxidans* being most frequently detected, although the proportions of the microbes may vary depending on the mineral and the conditions under which the heaps or tanks are operated^{25,34}.

Microbial adaptation

The acclimatization of micro-organisms to a particular mineral system by subjecting them to progressively higher amounts of the major elements present has become common practice. Many fundamental studies on the tolerance of cultures to metal ions have been carried out over the years^{35,36}, and in general bioleaching processes have proven to be remarkably robust.

Since the bioleach tanks form a major part of the capital cost, adaptation of the cultures to tolerate high concen-

trations of elements such as copper, iron, zinc, arsenic and silver, to minimize reactor volume forms a major part of the optimization process³⁷. It is well established that micro-organisms that are isolated after a period of growth in continuously-operated bioleaching reactors are much more efficient at mineral oxidation than the culture originally placed in the tanks. A gradual improvement in microbial consortium performance may be experienced over a period of several years before a steady state is reached²⁷.

This concept was recently illustrated with the successful adaptation of a moderately thermophilic culture during a test work programme performed at Mintek on a complex copper-polymetallic concentrate. The concentrate contained high levels of silver and base metals such as copper, iron and zinc, which had an inhibitory effect on the performance of the culture. Stable operation could only be maintained at low feed solids concentrations and pH levels above 1.8. Long-term adaptation of the culture performed in a continuously-operated reactor system over a period of three years, allowed further improvement of the process, and stable operation of the bioleaching process can now be achieved at a 15% feed solids concentration, without the need for pH control³⁷.

Similar observations were made during the operation of a commercially operated biooxidation plant, where the arsenic resistance of a mesophilic culture improved significantly after a few years' operation²⁵. This may be because the existing microbial consortium had adapted to grow faster by the mutation of inherent genes or by the acquisition of new metal resistance genes from the horizontal gene pool³⁸. This represents an important challenge for bioleaching technology to better understand, control and accelerate this adaptation process.

Genetic engineering

The original idea of generating a 'superbug' by genetically modifying micro-organisms was actively undertaken by several researchers around 20 years ago. Although it has been possible to change the metabolic or other properties in several heterotrophic micro-organisms by the introduction of appropriate genes, it has been very difficult or impossible to do so in bioleaching bacteria³⁹.

Currently, the genetic modification of mineral processing bacteria tends not to have a high priority among researchers. Reasons for this include: (i) reservations that engineered strains would be sufficiently robust to survive and compete effectively in the complex environment of a mineral processing operation, (ii) before strain improvement by genetic engineering can be contemplated, it will be necessary to establish those attributes that provide the organisms with their competitive edge and, from that, determine which genes to target, and (iii) there is the generally held view that indigenous bacteria growing in a particular environment are likely to be those best adapted to that environment¹⁴.

Considerable effort has, however, been spent over the past years to understand the biochemistry of iron and sulfur oxidation, bacteria-mineral interactions (chemotaxis, quorum sensing, adhesion, biofilm formation) and several adaptive responses and resistance mechanisms which allow the micro-organisms to survive in a bioleaching environment²⁵. All of these are considered key phenomena for understanding the bioleaching process.

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The use of genomics, metagenomics and high throughput proteomics to study the global regulatory responses, whereby microbes adapt to a changing environment, has begun to emerge in the last few years, and will in future years play a key role in the understanding of the molecular mechanisms underlying microbe-mineral interactions. This, taken together with the physicochemical, geological and mineralogical aspects of the process, will allow improvement of the efficiency of the technology^{25,40}.

Bioleaching mechanisms

The mechanism by which micro-organisms enhance metal sulfide oxidation and leaching have been surrounded by controversy and over the years there has been a considerable debate whether the bio-oxidation of minerals is by a so-called 'direct' or 'indirect' mechanism^{3,14,30,41,42}. In the direct mechanism, the bacteria are assumed to attach to the sulfide mineral surfaces, directly leaching the mineral by means of an enzymatic process. In the indirect mechanism, the primary attack of the sulfide mineral is assumed to be a chemical ferric leach with the role of the bacteria, whether attached or not, to oxidize ferrous iron to ferric iron and sulfur to sulfate⁴³. Consequently, the (bio)chemical fundamentals of the leaching reactions have been the subject of intensive research over the past two decades⁴⁴.

It is, now, generally recognized and accepted that bioleaching is mainly a chemical process where ferric iron and protons are responsible for the leaching reactions. The role of the micro-organisms is to produce the leaching reagents and to create the space in which the leaching reactions take place. Micro-organisms typically form an exopolysaccharide (EPS) layer when they adhere to the surface of a mineral. It is within this EPS layer, rather than in the bulk solution, that the oxidation reactions take place, and therefore, the EPS serves as the reaction space²⁵.

Consensus appears to have been reached on the current lack of evidence as to the existence of an enzyme that justifies the theory of the direct attack. The terms 'direct' and 'indirect' mechanisms are now redundant and have been replaced by 'contact' and 'non-contact' leaching to indicate that the mechanism is the same, though the proximity of the microbe to the mineral surface may differ¹⁴.

It is now also a well-known fact that the dissolution reaction is not identical for all metal sulfides and that the oxidation of different metal sulfides proceeds via different intermediates. Briefly, a thiosulfate mechanism has been proposed for the oxidation of acid insoluble metal sulfides such as pyrite and molybdenite, and a polysulfide mechanism for acid soluble metal sulfides such as sphalerite, chalcopyrite, arsenopyrite or galena^{25,44,45}.

Tank bioleaching of concentrates

Reactor design and scale-up

Design challenges

The design of bioleach reactors presents a significant set of challenges to the process engineer. These include the need to transfer a large quantity of oxygen (and some carbon dioxide) into the process fluid, to maintain a fast-settling mineral slurry in suspension, and to maintain a constant

temperature in the process (usually by removing heat that is generated by the exothermic oxidation reactions). This must all be achieved in the presence of a 'fourth phase'—the biomass, which may be sensitive to high shear rates—and in a vessel which can withstand the acidic, corrosive, abrasive environment that bioleach bacteria thrive in. With the advent of thermophiles, the selection of appropriate materials of construction for the bioleach reactor presents an even greater challenge. In metallurgical terms, bioleaching is a slow process, with typical residence times of the order of 4 to 6 days, compared to a flotation cell or even an autoclave, where retention times are measured in minutes or hours. A large process volume is therefore required, and bioleach reactors are amongst the largest high-intensity process vessels that have ever been engineered. The challenge for the design engineer is to create a nearly uniform environment in the bioleach reactor, so that the conditions for biomass growth and oxidative activity are optimal throughout the reaction space.

The physical and chemical demands of the bioleach process dictate that the bioleach reactor should be a mechanically-agitated, stirred tank⁴⁶. Air stirred reactors, without mechanical agitation, are unable to meet the oxygen transfer requirement of the process. Several other novel designs have been proposed⁴⁷, but the stirred-tank reactor remains the only type of reactor that has been used in practice. Process modelling using basic chemical reaction engineering principles⁴⁸ indicates that the process volume can be minimised by arranging the reactors in a series, from large to small. However, practical constraints (such as commonality of spares) make this ideal unattainable, and all commercial bioleach plants have been designed with a set of equal volume reactors, typically with two to three primary reactors in parallel, feeding into a series of two to three secondary reactors in series.

Impellers

At the heart of any stirred-tank reactor lies the impeller. In a primary bioleach reactor, where the highest intensity process usually takes place, the impeller is required to achieve an oxygen transfer rate of up to 30 kg/(m³.h), whilst maintaining solids with a density of 3,500 to 4,000 kg/m³ in suspension, and removing several megawatts of heat. Twenty-five years ago, at the advent of commercial bioleaching, the best-known impeller for gas liquid mixing was the so-called Rushton turbine, a six-blade flat-blade disk turbine (often designated as the 6-FDT). This radial-flow turbine was widely used in fermentation reactors, and was often recommended for three-phase (gas-liquid-solid) applications⁴⁹. A Rushton turbine was used in one of the first BIOX® plants at the São Bento Gold Mine in Brazil, which was commissioned in 1991⁵⁰. However, this turbine suffers from several drawbacks: it has a high power number, the power number decreases with increasing aeration rate, and its ability to suspend solids decreases with increasing aeration rate. Motors and gearboxes needed to be designed for the ungassed condition, to ensure that the impeller could continue to operate when the air supply failed – and with the sheer size of bioleach reactors, this resulted in a severe engineering constraint. This is illustrated by the São Bento design, where the 580 m³ reactor was fitted with a 336 kW

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motor, an installed power per unit volume of 579 W/m³. Something new was needed. Around this time, the first high-solidity-ratio axial-flow impellers were being developed, and they found almost immediate application in bioleach reactors. The most well-known of these impellers is the Lightnin A-315 impeller⁵¹, which is still in wide use today. Others included the Mixtec BX04 impeller⁵²⁻⁵⁴, which has also been used in commercial bioleach installations. The power number of this type of impeller remains stable over a wider range of gas flow rates than is the case for a 6-FDT. Being an axial-flow impeller, it has good solids-mixing characteristics, and retains this capability even at high gas flow rates. High-solidity-ratio-axial-flow impellers remain the industry standard in commercial bioleach reactors, although a multi-bladed radial-flow disk turbine known as the BROGIM®, and manufactured by the French company Milton Roy Mixing, is installed in the Kasese bioleach plant in Uganda⁵⁵.

Gas dispersion, mass transfer and solids suspension

Both Gencor and Mintek-AAC, the leading pioneers of tank bioleaching, devoted extensive research funding to developing an understanding of the design and scale-up of three-phase bioleach reactor systems. These research and development programmes included the evaluation of the hydrodynamics, gas-liquid mass transfer, solids suspension and heat transfer in vessels of varying sizes, using both 'sterile' model systems and 'live' bacterial-oxidation reaction vessels. In these studies, extensive comparisons of the performance of the various impeller types were made.

Gencor's approach to the problem of reactor design and scale-up was made easier by their ability to conduct their research in-house. For this, the Fairview and São Bento BIOX® plants provided the test beds. At Fairview, the BIOX® demonstration plant had reactors ranging from 60 to 90 m³ in size, and the São Bento BIOX® plant comprised a 580 m³ reactor⁵⁰. The Fairview plant was used to evaluate the Lightnin A-315 impeller in the early 1990s. Additional research work was performed at the Gencor research facility, which was equipped with a 1.4 m³ test vessel⁵⁶.

Mintek and AAC constructed two pilot plants, one at Mintek and the other at AAC's Vaal Reefs Gold Mine. The Mintek plant comprised a 12 m³ primary reactor, and two 6 m³ secondary reactors^{57,58}. The larger plant at Vaal Reefs had two primary reactors, each with a volume of 125 m³, and a single secondary reactor with a volume of 25 m³^{59,60}. These plants were operated simultaneously, and were utilized for extensive studies of bioleach kinetics, mass transfer, solids suspension and heat transfer. In addition, Mintek conducted research work in a smaller reactor with a volume of 0.27 m³⁶¹.

The approach taken by Mintek and AAC in these studies was to understand the process requirements and their interactions, how they change on scale-up, and to use this understanding to derive a model for the design of commercial-scale bioreactors. For example, mass transfer in a stirred tank can be modelled easily using the well-known equation of the form

$$k_L a = \alpha \left(P_g / V_p \right)^{\beta} \left(v_s \right)^{\gamma}$$

which relates the overall volumetric mass transfer coefficient ($k_L a$) to the gassed agitator power (P_g) per unit

pulp volume (V_p) and the superficial gas velocity (v_s). By measuring mass-transfer coefficients at various power inputs and aeration rates, the constants and exponents in this equation can be determined for various internal reactor configurations (such as the type, size, and position of the agitator and gas sparger, and the aspect ratio of the reactor). Small- to medium-scale test work showed that the fundamental design parameter is the 'critical' dissolved oxygen concentration: this is the oxygen concentration below which the rate of mineral oxidation is limited by the oxygen supply. This was found to be in the region of 1 mg/L⁶⁰.

However, the measurement of mass-transfer coefficients becomes more difficult as the reactor increases in size, since the gas and liquid phases are not perfectly uniform, and so more complex models that incorporate the measurement of gas- and liquid-phase oxygen concentration profiles are required^{62,63}.

The power required for uniform solids suspension in a large mechanically-agitated vessel is exorbitant, and over 50 years ago a method for determining a 'just-off-the-bottom' suspension condition was described⁶⁴. This is useful for defining a suitable solids suspension condition in a leach reactor. The general form of the equation for this condition is

$$N_{JS} = S v^{0.1} d_p^{0.2} \left[g(\rho_s - \rho_l) / \rho_l \right]^{0.45} C_s^{0.13} D^{-0.85}$$

and relates the impeller speed required achieve the just-suspended condition with the kinematic viscosity of the liquid phase (ν), the mass mean particle diameter (d_p), the density of the solids (ρ_s) and of the liquid (ρ_l), the solids concentration by mass (C_s), and the impeller diameter (D). In this equation, S is a dimensionless constant which depends on the type of impeller and the tank geometry.

This correlation has been refined by various investigators in the intervening years⁶¹, but the general form remains the same. The effect of aeration on the ability of an agitator to suspend solids has been incorporated into this approach⁴⁹, by correlating the increased impeller speed required to maintain the solids suspension criterion (N_{Jsg}) in a straight-line relation with the volumetric gas flow rate (Q_g), where a is an experimentally-determined constant, as

$$N_{Jsg} = N_{JS} + a Q_g$$

The superficial gas velocity is a function of the volumetric gas flow rate, according to

$$v_s = Q_g / A$$

where A is the surface area of the reactor. Finally, the gassed impeller power is related to the impeller speed (N) by the dimensionless power number (N_p) as

$$P_g = N_p \rho N^3 D^5$$

where ρ is the pulp density. Using these equations, and gathering sufficient experimental data in reactors ranging from 0.27 m³ to 125 m³ in volume, for a wide variety of impeller types and internal reactor configurations, Mintek was able to achieve the goal of developing an in-house approach for the design of agitation systems in bioleach reactors, incorporating both gas-liquid mass transfer and solids suspension. This approach allows the minimum agitator power input and aeration rate, that are determined based on the fundamental requirements of the process, to be

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specified. However, Mintek has found that, in practice, this approach has been of little value in the design of agitators for commercial-scale bioleach reactors, since agitator suppliers tend to take a quite different approach to the problem. Their approach is usually based on an intimate knowledge of the hydrodynamics of a particular impeller, and the quantity of gas that is required to be dispersed. The question is: how can the quantity of gas to be dispersed be known without understanding the fundamental mass transfer requirements of the process, so that the oxygen utilization and, therefore, the aeration rate can be specified? Agitator supply companies will usually specify an oxygen utilization based solely on the size of the reactor and the oxygen requirement, and use this to specify the impeller power requirement based on (fairly conservative) hydrodynamic considerations alone. Mintek's experience suggests that the mass-transfer and solids suspension requirements of commercial bioleach processes may be achieved at significantly lower overall energy inputs (considering both agitation and aeration) than is usually specified by the plant designers.

Heat transfer and materials of construction

A major component of the design of a bioleach reactor is the cooling system. The oxidation of sulfide minerals is exothermic, as indicated in Table 1^{65,66}.

There are other components to the overall energy balance, but the dominant factor is usually the exothermic heat arising from the oxidation of the sulfides. Other factors are the agitation power, the bacterial growth reaction (which is mildly endothermic), convective, conductive and radiant heat losses to the surroundings, and evaporation. In high-temperature bioleach reactors (utilizing thermophilic bacteria), evaporative heat losses will be more significant, and may dominate the energy balance in reactors where the oxidation reaction rate is low (near the end of the leach train). Both Mintek and Gencor reported on the validation of the energy balance across large bioleach reactors, which was achieved by measuring the heat removed from the reactor, and comparing this with the heat load from theoretical calculations^{50,56,58,60}.

For most bioleach operations, substantial quantities of low-grade heat must be removed from the process vessels. For example, the heat load in each 580 m³ São Bento BIOX® reactor is about 3 MW⁵⁰, and the heat of reaction in each primary reactor at the Ashanti BIOX® plant in Ghana is 2,97 MW⁶⁷. In mechanically agitated vessels, heat is usually removed by circulating cooling water through helical coils located on the inside of the vessel walls. However, in a bioleach reactor, the heat load is usually so large that it is not physically possible to achieve such a design. By way of example, the installed cooling coil tube length in each São Bento bioleach reactor is 1.77 km⁵⁰. A more space-efficient way of installing the required length of tubing is in a vertical configuration, in which the cooling pipes perform a dual function as the cooling surface and as the baffles. This design also facilitates easier removal of the coils for maintenance⁵⁹, and it has become the standard design configuration for bioleach reactors.

There have been significant advances in the materials used to construct bioleach reactors. There are three main factors which dictate the selection of materials of construction

for the various 'wet-end' components that make up a bioleach reactor, including the vessel itself, the impeller and its shaft, the cooling baffles, and the sparger. The first is the process fluid composition, which can generally be described as acidic (pH values of 1.0 to 1.4 are typical), oxidative (ferric iron concentrations of between 10 and 50 g/L are usual, at Eh levels of 500 to 700 mV vs Ag/AgCl), and abrasive (the slurry, usually, has a solids concentration between 5 to 20 per cent by mass, with particle sizes ranging from 1 to 100 µm). The second is process water quality and, in particular, the chloride content of the water, which can have a major impact on the selection of an appropriate material of construction. The operating temperature is the third major factor, and the advent of thermophilic bioleaching processes has been accompanied by major developments in materials selection.

Initially, some pilot plants and even a few commercial plants were constructed using rubber-lined mild steel: the Mintek and Vaal Reefs pilot plants had rubber-lined mild steel reaction vessels and agitators shafts and impellers^{57,60} and the BIOX® plant at Wiluna was lined with Linatex rubber⁶⁸. However, problems were experienced with the failure of the rubber linings, particularly those of the impellers and their shafts. After a few catastrophic failures, there was a rapid move towards the selection of stainless steel for all bioleach reactor components in contact with the process fluid. In Western Australia, where the local water supply often contains chlorides, corrosion problems were experienced at the various refractory gold bioleach plants (including the BIOX® plants at Harbour Lights and Wiluna, and the BacTech plant at Youanmi Deeps). For these applications, the use of a duplex stainless steel that is able to withstand the chloride attack, designated as SAF 2205, was indicated⁶⁸. At the Ashanti BIOX® plant in Ghana, most of the plant is constructed using 304 L stainless steel, although SAF 2205 is used for the cooling coils⁶⁷. In some cases, such as the Laizhou Bacox™ plant in PR China (Figure 7), SAF 2205 has been the material of choice for the entire plant, even when chloride is not present in the water supply¹¹.

In recent times, the development of the BioCOP™ thermophile bioleach technology by Billiton, working in cooperation with Codelco, culminating in the construction and

Table 1

Heats of reaction for the bacterial oxidation of some common sulfide minerals

Mineral	Chemical formula	Heat of reaction (kJ/kg mineral)
Pyrite	FeS ₂	12,481
Pyrrhotite	Fe _{1-x} S	-11,373
Arsenopyrite	FeAsS	-9,415
Chalcopyrite	CuFeS ₂	8,686
Covellite	CuS	8,190
Chalcocite	Cu ₂ S	6,218
Digenite	Cu ₉ S ₅	6,877 [†]
Bornite	Cu ₅ FeS ₄	7,292
Pentlandite	(Ni,Fe) ₉ S ₈	-10,174

[†]based on an estimated heat of formation of digenite

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Figure 7—The inside of one of the 700 m³ bioleach reactors at the Laizhou Bacox™ plant in Shandong, PR China: the octagonal sparger, A-315 impeller and two sets of cooling baffles are all clearly visible

operation of the Alliance Copper Limited commercial demonstration plant, has resulted in notable advances in the selection of materials for the design of the bioleach reactors^{69,70}. These reactors are designed to operate at temperatures in excess of 80°C, and under these conditions even 316 L stainless steel components were found to fail catastrophically within three months⁷⁰. Significantly, therefore, the reactors for the prototype BioCOP™ plant were constructed from ceramic-lined concrete, using proprietary technology supplied by Stebbins.

Size does count

At the outset of the development of tank bioleaching, around 1986 to 1990, the volumes of the bioleach reactors at both the Fairview BIOX® pilot plant and the Mintek-AAC pilot plant were similar, and ranged between 21 and 125 m³^{50,57,58}. By 1990, this had increased to 580 m³ with the Sao Bento BIOX® reactor⁵⁰ and since then there has been a steady increase in the volume of bioleach reactors specified for commercial plants. The Ashanti BIOX® plant in Ghana was commissioned in 1994, with 900 m³ reactors⁷¹. Five

years later, in 1999, the Kasese cobalt bioleach plant was commissioned using BRGM's bioleach technology, with 1,350 m³ reactors⁷². The largest reactors are now 1,500 m³, and these were installed at the Bogosu BIOX® plant, located in Ghana, in 2007⁷¹. It is certainly noteworthy that the BioCOP™ commercial demonstration plant for thermophile bioleaching, located at Chuquicamata in Chile, has reactors with volumes of 1,260 m³⁷⁰.

This progression has been made possible by a combination of factors, but probably the most significant is advances in the engineering of the motors, gearboxes, and agitator shafts that are required for these huge, intensive process reaction vessels. It is surely a matter of time before the 2,000 m³ threshold is achieved.

Bioleaching of refractory gold concentrates

Commercial installations: BIOX®, Bacox™ and BIONORD®

There is no doubt that the development of refractory gold concentrate bioleaching to the point of commercial implementation (and beyond) was accompanied by significant advances in the understanding of bioleaching on many levels, encompassing the mechanisms, microbiology, and engineering of the process. It is equally true that, today, bioleaching is the technology of choice for the treatment of refractory gold concentrates in most locales, with the exception of North America, where pressure oxidation technology is favoured. Refractory gold bioleaching is a mature, robust, efficient, environmentally acceptable and cost-effective technology that is suitable for use in remote locations. The process has been applied in Africa, South America, Australasia and Asia; Table II lists all the industrial-scale tank bioleach plants throughout the world for the treatment of refractory gold concentrates^{6,71,73}.

The development of the technologies used in almost all of these plants can be credited to two providers: the BacTech-Mintek joint venture, which developed the Bacox™ technology for the Youanmi, Beaconsfield and Laizhou plants, and Gencor, which developed the BIOX® technology for the other installations. (Gencor originally developed the

Table II

Commercial refractory gold tank bioleaching operations

Plant	Location	Current owner	Current capacity (t/d)	Years of operation
Fairview	Barberton, South Africa	Barberton Mines Limited	65–80	1986-present
São Bento	Brazil	Eldorado Gold Corporation	380	1991-present
Harbour Lights	Western Australia	-	40	1991-1994
Wiluna	Western Australia	Agincourt Resources Limited	158	1993-present
Ashanti	Obuasi, Ghana	AngloGold Ashanti Limited	960	1994-present
Youanmi Deeps	Western Australia	Goldcrest Resources	120	1994-1998
Tamboraque	San Mateo, Peru	Iamgold Corporation and Minera Lizandro Proano SA	60	1998-2003 (restarted 2006)
Beaconsfield	Tasmania, Australia	Beaconsfield Gold NL	70	2000-present
Laizhou	Shandong, PR China	Sino Gold Mining Limited	100	2001-present
Olympiada	Krasnoyarsk, Russia	Polyus Gold	1,000	2001-present
Suzdal	Kazakhstan	Celtic Resources Holdings Limited	196	2005-present
Fosterville	Victoria, Australia	Perseverance Corporation, Limited	211	2005-present
Bogoso	Ghana	Golden Star Resources	820	2006-present
Jinfeng	PR China	Sino Gold Mining Limited & Guizhou Lannigou Gold Mine Limited	790	2006-present
Kokpatas	Uzbekistan	Navoi Mining and Metallurgy	1,069	2008-present

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BIOX® technology and applied it to its Fairview and São Bento plants. They also licensed it to non-Gencor operations, and eventually sold the technology to Gold Fields Limited, which also licensed the technology to non-Gold Fields operations.)

Several of these operations have interesting features, which illustrate the adaptability of the process to a variety of feed materials and operational circumstances. The Fairview BIOX® plant has evolved from a pilot plant treating 10 t/d of concentrate to a full-scale production facility that now treats concentrates produced at several mines in the historic mining district of Barberton in South Africa. This evolution from pilot- to production-scale plant has resulted in a non-standard reactor configuration, and the plant currently has two 340 m³ primary reactors⁷¹.

The São Bento BIOX® plant in Brazil is unusual because it was incorporated into an existing pressure oxidation flowsheet, in order to facilitate an expansion in capacity. The original bioleach plant, commissioned in 1991, was designed to achieve a partial oxidation of 30% of the sulfides, with the bioleach residue being fed to the autoclave. Two additional expansions were achieved in 1994 and 1998, by adding two more bioleach reactors. The São Bento operation is currently under care and maintenance^{6,71}.

In the operation of the Youanmi Deeps Bacox™ project in Western Australia (which was shut down in 1998 when the mine became exhausted), it was deliberately aimed to utilize moderate thermophiles operating at between 45 and 47°C, which is above the generally accepted optimal operating range of 35 to 42°C of mesophilic bacteria⁷⁴. This operation was also characterized by requiring a partial oxidation of the sulfide minerals: the gold-rich arsenopyrite component was oxidized, whereas the gold-deficient pyrite was not. This operation demonstrated the ability of the bioleach process to target selective minerals for oxidation.

The Beaconsfield Bacox™ plant, which is located in an environmentally sensitive region of northern Tasmania, Australia, is also unique in that it incorporates a Merrill-Crowe gold recovery circuit, whereas the other operations utilize carbon absorption for gold extraction. At this plant, detoxification of all cyanide species prior to disposal was a requirement. The rationale for the choice of a Merrill-Crowe circuit was that the high soluble gold tenor, combined with the low solution volumes after filtration of the leached slurry, significantly reduced the volume of solution requiring cyanide detoxification. This meant that a small Caro's acid plant could be used for cyanide destruction, with capital and operating cost advantages¹⁰.

The Laizhou Bacox™ plant, located in the province of Shandong in the People's Republic of China, is also unique in that it is a toll treatment operation. This plant treats a wide variety of bought-in concentrates, mainly from the region, but even from as far afield as Greece¹¹. This operation has shown that the process is robust and flexible, with the ability to treat a wide variety of feed materials with differing chemical and mineralogical compositions.

The Suzdal BIOX® plant, located near the town of Semey in Kazakhstan, has shown that the bioleach process can tolerate extreme and varying climatic conditions. At this plant's location, temperatures can vary between 38°C in summer and minus 45°C in winter. Despite these extreme climatic conditions, this plant is located in the open⁶.

The expansions of the Fairview and São Bento BIOX® plants have already been discussed, but many of the commercial operations have been or are being expanded. The modular nature of bioleach reactors facilitates expansion of capacity at these operations. The following plant expansions have occurred:

- The Wiluna BIOX® plant was expanded (in 1996) from an original capacity (in 1993) of 115 t/d of concentrate to its current capacity of 158 t/d of concentrate, by the addition of three new reactors to the original six⁶
- The Ashanti BIOX® plant was expanded (in 1995) from the original design capacity (in 1994) of 720 t/d of concentrate to 960 t/d by the addition of a fourth module. Each module comprises six 900 m³ reactors⁶
- The Laizhou Bacox™ plant, which is owned by Sino Gold Mining Limited, has recently undergone a doubling of the original design capacity (in 2001) of 100 t/d of concentrate, by the addition of a second module⁷⁵
- The Suzdal BIOX® plant is currently being expanded from the design capacity (in 2005) of 196 t/d of concentrate to over 520 t/d of concentrate, by the addition of a new module and by increasing the feed solids concentration to the process⁷¹
- The Kokpatas BIOX® plant in Uzbekistan is currently planning a doubling of its capacity to over 2,000 t/d of concentrate, by duplicating the existing bioleach plant⁷¹.

One new BIOX® plant is currently in development, located at Amantaytau, near the town of Zarafshan in Uzbekistan⁷¹. A second project, located at Mayskoye in the Chukotka region of Russia, was planned⁷¹ but appears to have been shelved⁷⁶.

There is one other known commercial-scale application of refractory gold bioleaching, located at the Olympiada mine in the Yenisei area of the Krasnoyarsk Region in Siberia, Russia. The mine is owned by Polyus Gold, and the sulfide treatment plant comprises two separate plants, Mills 2 and 3, that incorporate milling, flotation and bioleaching, with a combined design capacity of 8 million t/a of ore. The bioleach plants treat around 1,000 t/d of a complex concentrate that contains pyrite, pyrrhotite, arsenopyrite and stibnite. This operation is situated in an extreme environment, where winter temperatures reach around minus 40°C, and so the plant (including the bioleach reactors) is situated within a building that insulates it from these harsh conditions. A locally developed bioleach technology known as BIONORD® is used at this operation⁷⁷.

Bioleaching of base metal concentrates

Development work on base metal concentrate bioleaching commenced in earnest during the 1990s, in part stimulated by the proven success of the commercial gold bioleach technology. The use of mesophilic bacteria to oxidize sulfide minerals such as cobaltiferous pyrite, pentlandite and millerite (nickel), sphalerite (zinc), galena (lead), chalcocite, covellite, cubanite and bornite (all copper) has been demonstrated, and in some cases the bioleaching process has successfully been integrated with downstream metals recovery processes^{66,78,79}.

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In the early 1990s, Billiton demonstrated the BioNIC™ process using mesophiles in a demonstration plant with a design capacity of 300 kg/d of concentrate. This plant produced more than 700 kg of Class 1 nickel in a six month-long campaign. Subsequently, an integrated pilot plant situated at the Yabula Nickel Refinery in Queensland, Australia, was successfully operated as part of a feasibility study⁶⁶.

In 1998, the world's first and only still operational commercial bioleaching plant that treats a base metal concentrate (that is excluding the commercial demonstration BioCOP™ copper bioleaching plant at Chuquicamata, which has been closed down), was established at the site of the Kilembe Copper Mine in Uganda (Figure 8). The plant, owned and operated by the Kasese Cobalt Company, was designed to produce about 1,000 t/a of cobalt cathode from a cobaltiferous pyrite concentrate, using mesophilic bacteria. The technology was supplied by the French company, BRGM^{78,80}.

During the early- to mid-1990s, Mintek's development programme focused on the application of bioleaching for the treatment of copper sulfide concentrates. These were mainly secondary copper minerals, with some chalcopyrite present. Successful treatment of the secondary copper sulfide concentrates using a mesophilic culture was demonstrated, but the chalcopyrite-containing concentrates were difficult to leach⁶⁵.

Bioleaching of chalcopyrite

Bioleaching of chalcopyrite-containing concentrates has proven to be challenging, since the surface of chalcopyrite tends to passivate at the temperatures and redox potentials found in typical mesophilic bioleach processes, effectively stopping the leaching of the mineral. Although the exact nature is still being debated¹², there is general consensus that the low recoveries of copper can be attributed to the formation of passivating layers on the chalcopyrite surface by substances such as elemental sulfur⁸¹, iron hydroxide precipitates (particularly jarosites^{82,83}) or intermediate polysulfides^{84,85}.

Over the past two decades, the optimization of bioleaching processes for the treatment of chalcopyrite ores and concentrates has been the subject of numerous research programmes. One of the most common solutions demonstrated to overcome the slow and incomplete extraction of copper from chalcopyrite is to operate the process at high temperatures using thermophiles. Test work performed at Mintek demonstrated that greater than 95% copper extraction from chalcopyrite-containing concentrates could be achieved in multi-stage continuously operated pilot plants, where the key parameters were delivery of sufficient oxygen and carbon dioxide for microbial growth and oxidation, and accommodation of an increased microbial sensitivity to solids concentration and particle size distribution^{86,87}.

Mintek has recently completed a programme of integrated pilot plant development work in which thermophiles were used to bioleach low-grade copper and nickel-copper concentrates containing chalcopyrite. The technical feasibility of the use of thermophilic micro-organisms to oxidize chalcopyrite has been demonstrated in an integrated pilot plant over an extended period of time. The study has confirmed that the thermophilic bioleach technology is ready for commercial

implementation⁸. A parameter that received careful consideration in the design of the thermophilic bioleach process was the economic trade off between the use of atmospheric air, oxygen, or oxygen-enriched air as electron acceptor.

A number of alternative approaches have been considered to increase the copper recovery from chalcopyrite-containing concentrates at moderate temperatures. The effect of redox potential on the leaching of chalcopyrite has been investigated extensively and it has been shown that chalcopyrite dissolution at low temperatures is highly dependent on redox potential, with better copper extraction rates observed at low than high redox potential levels^{88,89}. The use of redox control for the bioleaching of chalcopyrite concentrates is the subject of two Mintek patents^{90,91}.

In a recent study, it was demonstrated that the use of redox control has the potential to increase copper leaching rates from chalcopyrite-pyrite containing concentrates significantly, using moderate thermophiles at 45°C. Selective and high-rate leaching of the copper present as chalcopyrite was achieved, leaving a final bioleach residue composed almost entirely of pyrite. A key advantage of the process is that the bioleaching process costs are minimized, since the pyrite was not oxidized and the pyrite-rich bioleach residue can be sold for acid production or stored to avoid a negative environmental impact⁹².

Different authors have demonstrated the improvement of copper extraction from chalcopyrite through the use of chemical catalysts such as silver^{93,94}. It is, however, unlikely to be a cost effective option, unless the silver occurs naturally in the concentrate.

Another approach suggested to overcome the slow and incomplete extraction of copper from chalcopyrite at low operating temperatures is ultra-fine grinding of the concentrate, usually to particle sizes smaller than 20 µm. It was demonstrated in pilot-scale experiments that the fine grinding facilitated rapid copper extraction⁹⁷. This approach was successfully demonstrated by Mintek and its technology partner, BacTech, during pilot plant trials at the Mt Lyell mine site in Tasmania and at Mintek in mini-pilot plant facilities treating Mt Lyell chalcopyrite concentrate. The work showed that a hydrometallurgical circuit comprising regrinding,



Figure 8—The Kasese bioleach plant, which treats a cobaltiferous pyrite concentrate, comprises six bioreactors each with a volume of 1,400 m³. At the time of construction, these were the largest individual reactor volumes for a plant of this type

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bioleaching, solvent extraction and electrowinning could be successfully used to recover cathode copper from a chalcopyrite concentrate⁹⁵.

The use of bioleaching for the treatment of pure chalcopyrite concentrates has, however, not found widespread application, mainly due to competitive smelter prices. With this in mind, Mintek's base metal bioleaching development over the past ten years has focused on the treatment of complex copper-polymetallic concentrates as a niche application for tank bioleaching processes.

Copper polymetallic concentrates typically contain copper, occurring as chalcopyrite, pentlandite, galena, sphalerite, high silver grades and significant quantities of impurities such as arsenic, bismuth, lead, antimony and molybdenum. When treating these polymetallic concentrates, there are a number of key benefits which favour bioleaching as opposed to smelting. Some of these include:

- Bioleaching processes can easily tolerate the presence of the impurities contained in the concentrates, whereas these contaminants pose problems when processed via the smelting route and would incur high smelter penalties
- In some instances, smelting provides low or no credit for the precious metals present in the concentrates. Conventional extraction methods can in most cases be used to recover the precious metals from bioleaching residues
- The need to produce an economically acceptable concentrate grade for smelting often results in significant losses of metal values over flotation. Bioleaching processes can treat lower grade bulk flotation concentrates with the consequent advantage of achieving higher overall recoveries of metal values
- Biohydrometallurgical processes employing tank bioleaching of concentrates are more amenable to modular construction and consequently are less sensitive to the economies of scale applicable to smelting^{79,96}.

In 2001, the technology progressed to demonstration scale when Mintek and its partners, Industrias Peñoles S.A. de C.V. of Mexico and BacTech, successfully demonstrated the bioleaching of a complex copper-polymetallic concentrate containing chalcopyrite using moderate thermophiles at an operating temperature of 45°C, in an integrated demonstration plant (with a total capacity of 170 m³) that was commissioned and operated in Monterrey, Mexico⁷⁹. Because of the high levels of silver contained in this concentrate, the use of thermophiles was not possible due to their sensitivity to silver⁹⁷.

Recoveries of 95% copper (as cathode) and 95% zinc (as precipitate) could be obtained at a concentrate feed rate of 2.7 t/d, provided the concentrate was milled to 100% <30 µm, and gold and silver extractions of up to 96% could be achieved. Stable, closed-circuit operation was maintained and the plant (with a solvent extraction and electrowinning design capacity of 1 t/d of copper), produced more than 40 t of LME A-grade cathode copper (Figure 9). On completion of the demonstration trial, a feasibility study was conducted for a commercial bioleach plant envisaged as having an initial capacity of 25,000 t of copper, with an option to increase the capacity in the future⁷⁹.

The demonstration of thermophile technology by Billiton and Codelco is well described^{70,98,99}. Piloting of the process, termed BIOCOP™ (encompassing both mesophile and thermophile technologies), was carried out at Codelco's Chuquicamata mine site in 1997. Mesophile technology was initially used to treat the Chuquicamata concentrates, which consist mainly of a mixture of chalcocite and chalcopyrite and concentrates from Mansa Mina containing arsenic from enargite. During 2000, the pilot unit was converted to use thermophiles operating at 78°C⁹⁹.

During 2003 and 2004, Alliance Copper, a joint venture between BHP Billiton and Codelco, demonstrated the thermophilic bioleaching of chalcopyrite concentrate, in a semi-commercial plant situated at Chuquicamata in Chile, which was designed to produce 20,000 t/a of copper cathode. An interesting feature of this plant was that the air supply was supplemented with pure oxygen, which necessitated the use of an automated system to control the dissolved oxygen concentration in the process^{70,98}.

Indirect agitated bioleaching

An alternative option for the treatment of base metal concentrates which was extensively evaluated over the years is the use of 'indirect bioleaching'. In the 'indirect bioleaching' process, the bacterial oxidation of ferrous iron to ferric iron is performed in a vessel, usually referred to as a bacterial ferric iron generator (BFIG) that is physically separate from the leach reactor. The sulfide feed material in the leach reactor is contacted with ferric-iron solution originating from the BFIG. From the reactor product, the liquid and solid phases are separated, with the liquid phase proceeding to metal recovery by, for example, solvent extraction and electrowinning (SX-EW) and returning to the BFIG, which completes the liquor circulation loop between the leach reactor and the BFIG⁷⁹.

The separation of the processes has several important implications. If the processes are separated, the bacteria are not in direct contact with the elemental sulfur produced by the sulfide-mineral reactions, and so the oxidation product would be elemental sulfur and not sulfate. The chemical oxidation reactions do not require oxygen, and oxygen only needs to be supplied to the bacterial reactors. Separation of



Figure 9—Pure copper cathode (>99.99%) produced in the large-scale pilot plant in Mexico

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the processes would also allow optimization of each of the processes separately: the sulfide reactors could be operated at high temperatures, and the use of immobilized bacteria could be considered for the intensification of the bacterial reactions⁶⁵.

During test work programmes performed at Mintek, it was shown that the optimal application for the process would be the leaching of a concentrate of either secondary copper sulfides, or of chalcopyrite that leaches at low redox potential between 35 and 45°C, neither of which contains economic quantities of precious metals. For such an application, indirect agitated bioleaching can provide virtually perfect and self regulating acid and iron balances, provided a special BFIG is utilized in which iron hydrolysis (and hence at least some iron precipitation) can be accommodated. Mintek holds a patent on such a process¹⁰⁰.

In similar test work performed on sphalerite concentrates as part of the recent EC-funded BioMinE project, a key challenge that has successfully been addressed was the intensification of the ferrous iron bio-oxidation step. A preliminary, techno-economic assessment for indirect bioleaching of zinc and zinc polymetallic concentrates was produced, which indicated some scale-up challenges that needed to be addressed, but indicated the potential for favourable economics¹⁰¹.

Heap bioleaching of ores

Base metal heap bioleaching

The commercial-scale heap bioleaching of whole ores containing secondary copper sulfides, predominantly as chalcocite, has found wide-spread application during the past 25 years and is the major application of bioleaching today²⁴.

Heap bioleaching is conducted on whole ore after crushing, which allows a significant energy saving in avoiding the milling and concentration steps that form part of both smelting and agitated tank bioleaching processes.

Dump bioleaching of sub-economic copper sulfide minerals has been commercially practiced since the 1960s. Serious efforts to maximize biological activity in heaps commenced in the 1980s and stand-alone bioheap leaching has become relatively well established over the past few years, practised at Lo Aguirre, Cerro Colorado, Quebrada Blanca, Ivan-Zar and Zaldivar in Chile and Girilambone in Australia, amongst others^{14,42,73,102}. A list of both historical and current industrial copper heap bioleach operations is presented in Table III⁷³.

Initially, the technology development was driven by process operators, who converted their processes from the acid leaching of oxide ores to the bioleaching of secondary copper sulfide ores. However, in recent years, considerable research and development has focused on understanding the process requirements better. Important improvements in areas such as agglomeration, forced aeration and inoculation of the heaps improved the process considerably. An example is the positive effect of aeration on microbial activity and copper extractions demonstrated at Girilambone and Quebrada Blanca, after the installation of forced aeration systems^{14,74,103}.

Whereas chalcocite can be bioleached quite effectively at temperatures slightly above the average ambient temperature, higher temperatures are needed to maximize copper extraction from chalcopyrite ores. Heap bioleaching of chalcopyrite ores is currently receiving much attention and it has been the topic of research, both in the form of theoretical models and pilot plant trials. Particularly notable in this

Table III

Industrial heap bioleaching operations for secondary copper ores and mixed oxide/sulfide ores (copper dump bioleach operations are not included)⁷³

Industrial heap bioleach plant and location/owner	Cathode copper production (t/a)	Years of operation
Lo Aguirre, Chile/Sociedad Minera Pudahuel Ltda.	15 000	1980-1996 (mine closure due to ore deposit depletion)
Mount Gordon (formerly Gunpowder), Australia/Western Metals Ltd.	33000	1991-Present
Mt. Leyshon, Australia/(formerly Normandy Poseidon)	750	1992-1995 (stockpile depleted)
Cerro Colorado, Chile/BHP Billiton	115 000	1993-present
Girilambone, Australia/Straits Resources Ltd & Nord Pacific Ltd.	14 000	1993-2003 (ore depleted)
Ivan-Zar, Chile/Compañía Minera Milpro	10 000-12 000	1994-Present
Punta del Cobre, Chile/Sociedad Punta del Cobre, S.A.	7 000-8 000	1994-Present
Quebrada Blanca, Chile/Teck Cominco Ltd.	75 000	1994-present
Andacollo Cobre, Chile/Aur Resources, del Pacifico & ENAMI	21 000	1996-present
Dos Amigos, Chile/CEMIN	10 000	1996-present
Skouriotissa Copper Mine (Phoenix pit), Cyprus/Hellenic Copper Mines	8 000	1996-present
Zaldivar, Chile/Barrick Gold Corp.	150 000	1998-present
Lomas Bayas, Chile/XSTRATA plc	60 000	1998-present
Cerro Verde, Peru/FreeportMcMoran & Buenaventura	54 200	1997-present
Lince II, Chile	27 000	1991-present (sulfide leaching since 1996)
Monywa, Myanmar/Ivanhoe Mines Ltd,	40 000	1998-present
Myanmar No.1 Mining Enterprise		
Nifty Copper, Australia/Straits Resources Ltd.	16 000	1998-present
Equatorial Tonopah, Nevada/Equatorial Tonopah, Inc.	25 000 (projected)	2000-2001 Failed
Morenci, Arizona/FreeportMcMoran	380 000	2001-present
Lisbon Valley, Utah/Constellation Copper Corporation	Projected at 27 000	2006-present
Jinchuan Copper, China/Zijin Mining Group Ltd.	10 000	2006-present
Spence, Chile/BHPBilliton	200 000	Commissioned 2007
Whim Creek and Mons Cupri, Australia/Straits Resources	17 000	2006-present

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regard are the published mathematical theories of Dixon and Petersen¹⁰⁴, and the implementation at pilot-plant scale of the principles advocated by those theories by Mintek¹⁵ and BHP Billiton.

Major development efforts focused on chalcopyrite are currently underway, with the leaders in the field being Mintek/NICICO at Sarcheshmeh for the treatment of chalcopyrite-containing sulfide ore, and BHP Billiton at Escondida for the treatment of run-of-mine sulfide ore^{15,19,99}.

The experimental approach for column leach test work, to obtain heap leach process design information, has also become much more sophisticated in order to observe and quantify the phenomena that are at work in high temperature heap bioleaching. In order to obtain accurate design information for sulfidic copper heap leach pilot plants, special 6 m tall so-called 'Smart Columns' were devised by Mintek (Figure 10), in which the development of the vertical temperature profile in the bulk of a large heap can be simulated^{16,20}. 'Smart column' results have been validated on a number of 20,000 t pilot heaps, which provides confidence for future scale-up from column results, especially when treating chalcopyrite material where the control of heap temperature is important¹⁶. The good correlation observed between the temperature profiles in 'Smart Columns' and in 20,000 t pilot heaps is illustrated in Figure 11.

High temperature heap bioleaching also requires more elaborate process control than has been industrial practice during the heap leaching of oxide and secondary copper sulfide ores. Mintek has produced the first computerised administration and guidance system (HeapStar®) for heap leach operators, to keep track of the irrigation and drainage liquor allocations, and varying irrigation and aeration requirements over a number of heaps at different stages of their life cycles^{16,20}.

Mintek's high-temperature heap bioleach technology for chalcopyrite has been successfully demonstrated in partnership with the National Iranian Copper Industries Company (NICICO) in Iran, treating low-grade chalcopyrite ore from the Darehzar deposit. The pilot plant has been in operation since 2005 and by 2009 fourteen 20,000 t heaps have been put into operation^{19,20,100}. The test heap material contained 0.6% copper, of which about 50% is in the form of chalcopyrite, and the balance occurs essentially as chalcocite. Temperatures of around 40°C were maintained in the heaps, with maxima of around 45°C being observed. An acceptable rate of copper extraction could be maintained, while the formation of jarosite remained under control. NICICO has recently made a decision to utilize this technology for the Darehzar project, located at the Sarcheshmeh Copper Complex. This will represent the first commercial scale implementation of heap bioleach technology for a primary chalcopyrite ore.

Another plant which is currently being commissioned is the copper bioleaching operations at Escondida mine, operated by BHP Billiton in northern Chile. In early 1999, test work commenced at Escondida for the bioheap leach treatment of run-of-mine (ROM) sulfide ore containing 0.3–0.7% copper. Ores tested included low grade sulfide ore with copper sulfide minerals including chalcocite, covellite and chalcopyrite as well as oxide and mixed oxide/sulphide ores. A 300,000 t trial heap at Escondida indicated that the

ore could be successfully treated, and paved the way for the full commercial plant which will produce 180,000 t/a of copper cathode. The commercial heap will be constructed on a prepared, lined pad with piped solution collection and forced air distribution. When completed in 2010, the heap base will be 4.9 × 2.0 km, constructed in seven lifts of 18 m each up to a height of 126 m^{99,105}.

Nickel sulfide heap bioleaching has been piloted at several operations, and has been successfully demonstrated at large scale at the Talvivaara Mine, located in Sotkamo, Finland. In 2005, a 50,000 t demonstration plant was constructed at the Talvivaara mine site, and was inoculated with indigenous bacteria collected from the site. Temperatures higher than 50°C were measured in the pregnant leach solution and these elevated temperatures (which were facilitated by the presence of rapidly oxidizing pyrrhotite in the ore) were maintained over the boreal winter conditions. At the end of 2006, 94% nickel, 83% zinc, 3% copper and 14% cobalt were reported as having been recovered. The study has proven that the Talvivaara black schist ore is well suited for bioheap leaching¹⁰⁶. The Talvivaara Mining Company, which operates the site, has recently launched the commissioning of an industrial operation that is anticipated to be in full-scale production in 2011¹⁰⁷.

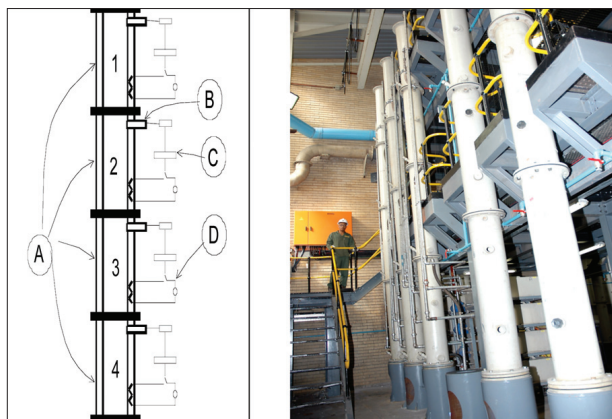


Figure 10—The Mintek 'Smart Columns' (A) four 1.5 m sections; (B) O₂ analysis; (C) reaction kinetics and heat generation calculation; (D) heating mantle response

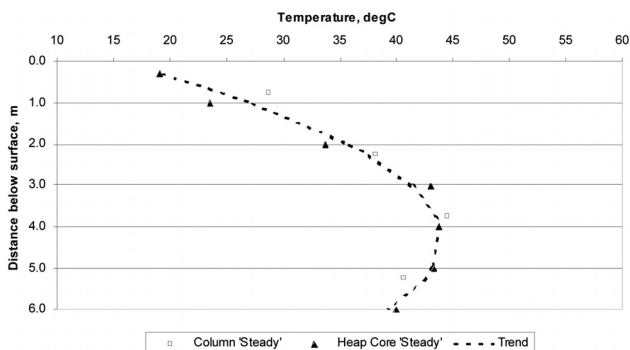


Figure 11—'Smart Column' and heap vertical temperature profiles

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Furthermore, the HydroZinc™ process of Teck Cominco and the BioHeap™ process developed by Pacific Ore Technology for the heap bioleaching of zinc and nickel-copper ores, respectively, are reported to be in an advanced state of development¹⁰⁰. Large-scale trials have demonstrated that high recoveries of nickel, copper and cobalt can be achieved using the BioHeap™ proprietary bacteria and patented processes. The process is also applicable to other sulfide ores such as zinc, polymetallic and refractory gold ores¹⁰⁸.

Gold heap bioleaching

Heap bioleaching of low-grade, refractory gold ores as a pre-treatment process has experienced only limited application at commercial scale. Newmont Mining Company operated six pilot heaps at their Gold Quarry Mine, Nevada, USA in 1990. All pilot plants were inoculated with an iron oxidizing microbial consortium grown on site. In 1994, a demonstration heap containing 708,000 t of inoculated ore was constructed, and in 1999 Newmont commissioned a commercial biooxidation heap process using the BIOPRO™ technology for pre-treatment of refractory gold. Biooxidation was carried out on crushed ore-stacked pads with an air ventilation system at the base to supply oxygen to the microbial population with which the rock had been inoculated⁴², and temperatures up to 81°C were measured¹⁰⁹. A total of 12 t of gold was produced over the lifetime of the commercial-scale plant^{73,74}.

Another innovative process for biooxidation of refractory gold ores is the GEOCOAT® technology developed by Geobiotics¹¹⁰. The process involves the coating of concentrates onto a suitable substrate, either barren rock or low-grade ore, followed by stacking the coated material in a conventional heap fashion. The heap is irrigated with acidic solutions, containing iron and nutrients, while low pressure ambient air is supplied at the heap base¹¹¹. The first commercial plant using the technology was used for the treatment of refractory gold ores at the Agnes Gold Mine in Barberton, South Africa. Although the technology was initially developed for the treatment of refractory gold concentrates, it is also claimed to be suitable for treatment of nickel, copper and cobalt concentrates and was applied to sphalerite concentrates at the Rosh Pinah mine of Kumba Resources in Namibia³⁴.

Microbiology and inoculation of heap leach operations

The microbiology of heap bioleach processes is still poorly understood. It is accepted that differences in parameters such as temperature, pH and aeration in different parts of the heap and at different times of the heap lifetime could have an effect on the populations present¹⁸.

Until a few years ago, direct microbial counts and indirect measurements such as oxygen uptake rates, redox potential, pH, ferrous iron concentration and temperature have been used as an indication of the bulk activity of micro-organisms in the heap. In addition, microbial enrichments from solutions and ores have provided an initial view of micro-organisms associated with the process. It was, however, not known whether these cultured strains were the key players in the process^{72,112}. The development of new rapid culture-independent molecular techniques to detect and quantify

populations was a significant advancement, and is a valuable tool in accurately describing biodiversity and following changes in microbial consortia present in heap leach systems^{14,112–114}.

As in the case of tank bioleaching, there have been relatively few studies on the microbiology of heap leach systems, and most of these have analysed the liquid phases i.e. pregnant leach solutions and raffinate¹¹⁵. Since the micro-organisms are not only present in the liquid fraction, but also attached to the ores surfaces, it is important to include the attached population when assessing the microbial composition within the heap. Current studies are focused on addressing this issue, and it is envisaged that the ability to correlate microbial types and numbers to changes in the chemical and physical profile with time in the heap, would assist in solving process issues such as how a heap should be inoculated, which microbial cultures to add and when to inoculate. It could potentially be a step towards optimizing rates, achieving faster heap start-up, and achieving better metal extractions.

Various mechanisms for the inoculation of heap leach operations can be considered. The most suitable procedure for inoculation needs to be identified according to the requirements and constraints of each case, and ought to be verified by experimental test work prior to commercial implementation¹⁶.

Looking to the future—the next 25 years

Tank bioleaching of concentrates

Rawlings²⁵ stated that ‘much of the future of biomining is likely to be hot’, and that ‘many of these will be stirred tank-type processes’. However, tank bioleaching of copper concentrates using moderate thermophiles and thermophiles has not progressed beyond semi-commercial scale⁸. The only application of tank bioleaching of refractory gold concentrate that has been reported to deliberately utilize moderate thermophiles remains the Bacox™ moderate thermophile process, which was implemented at the Youanmi Deeps project in Western Australia.

The Brierleys predicted in 2001 that ‘in the near future, stirred-tank bioleaching of chalcopyrite concentrates will be a commercial reality’⁷². The near future of 2001 is the recent past in 2009, and the Brierleys’ prediction has not been realized, despite several successful demonstrations of the technology. The principal reason for this is that hydro-metallurgical (and not only biohydrometallurgical) processing of high-grade copper concentrates struggles to compete economically with established smelting technology.

The two main demonstrations of tank bioleaching using thermophiles have targeted complex or ‘dirty’ chalcopyrite-containing concentrates, which are less readily acceptable by smelters. Therefore, although neither demonstration resulted in sustained commercial application, the treatment of a complex polymetallic sulfide concentrate which may contain elements such as arsenic or bismuth (which incur penalties at the smelter) remains the most likely niche for the application of agitated tank bioleaching for base metal concentrates. If the concentrate contains chalcopyrite, then thermophiles are likely to be required.

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There is another possible application of tank bioleaching using thermophiles, which has been proposed on a few occasions, and in two different guises. One of the persistent shortcomings of the low-temperature bioleaching of refractory gold concentrates containing sulfide minerals such as arsenopyrite and pyrrhotite is that the bioleach residue often contains a small but significant quantity of elemental sulfur. This elemental sulfur reacts readily with cyanide in the subsequent cyanide leach process, which creates two problems. In the first instance, the cyanide consumption is increased, and in the second instance, the thiocyanate formed by the reaction between sulfur and cyanide usually needs to be destroyed. Both the formation and destruction of thiocyanate result in increased costs. Several researchers^{6,101,116-118} have proposed the use of thermophilic micro-organisms as a means to minimize the formation of elemental sulfur, and so to alleviate these two problems. Lindström and co-workers^{116,117} proposed and patented a sequential two-stage process comprising moderate thermophile and thermophile bioleaching, which demonstrated a significant reduction in cyanide consumption and thiocyanate formation. Van Niekerk and Van Aswegen⁶ described a similar two-stage process using mesophiles and thermophiles and Morin *et al.*¹⁰¹ referred to continuous bench-scale piloting tests on two arsenopyrite-bearing concentrates, in which a ten-fold decrease in cyanide consumption is reported for the thermophile process over the mesophile process.

Van Niekerk and Van Aswegen⁶ list several perceived obstacles to the implementation of thermophile tank bioleaching, including the need for exotic materials of construction (such as duplex stainless steels or ceramic lined concrete), the need for oxygen enrichment of the air supply to overcome mass transfer limitations caused by a lower oxygen solubility at a higher operating temperature, a higher rate of evaporation at the higher operating temperature, and the lower feed solids concentration that the thermophile culture can tolerate. However, there are convincing counter-arguments to each of these obstacles. As already described, a duplex stainless steel such as SAF 2205 has been selected for the construction of low-temperature tank bioleaching plants; Neale *et al.*⁸ have described extensive bench-scale pilot-plant test work using thermophiles to oxidize copper concentrates using a standard air supply without experiencing a mass transfer limitation; the same authors have shown that, at large scale, the evaporation rates are manageable, and that the increased rate of sulfide oxidation at the higher operating temperature compensates for the lower feed-solids concentration.

Therefore, cost and environmental factors may yet result in the next commercial implementation of thermophile tank bioleaching (or at least a sequential process such as one of those described) being a refractory gold application.

Heap bioleaching of ores

Heap bioleaching technology for the treatment of chalcopyrite ores is still in its infancy, and it is envisaged that challenges such as engineering of heaps to achieve and maintain high temperatures when the mineral sulfide content is low, and the ability to maintain and control different microbial populations within the heaps to ensure effective leaching of pyrite to

generate heat and to leach chalcopyrite, will be a priority in the years to come. One of the main challenges is to provide sufficient microbial diversity throughout the life of the heap to ensure optimum heap performance. To achieve this, more studies on the microbial composition at different stages in the life of heaps will have to be performed.

A need also exists for a laboratory procedure and mathematical model, whereby the gangue-acid reactions during heap leaching can be predicted from the results of small-scale laboratory tests¹⁵. During the early prospecting stages of a project, only small quantities of samples are available for test work, while the acid consumption, a major economic driver of the heap leaching process, needs to be determined as early as possible. Particularly, as higher temperature operations may become more commonly engineered into heap leaching designs, the need for reliable models of the acid-gangue reaction equilibria will grow, and such models will need to incorporate the effect of temperature, since the extent of gangue-acid reactions are very sensitive to temperature. Such an approach requires a mineralogical study of the ore, knowledge of the intended process and flowsheet, the results of dilute leach tests (to exclude the effect of precipitation reactions from the observations), and a simultaneous mathematical solution for the chemical equilibria and the temperature profile.

Uranium ores and concentrates

The uranium market has been in the doldrums for most of the past 25 years, but in the past few years the uranium price has risen dramatically. A number of new uranium exploration projects are being undertaken, and a few have recently been brought into production. This renewed activity in the uranium market has sparked fresh interest in uranium extraction technologies. Some of the older wisdom, developed during the previous uranium boom, is being revived. Wadden and Gallant¹¹⁹ described experiments on *in situ* uranium heap leaching using intermittent flooding and forced aeration. For uranium ores bearing uraninite together with either naturally-occurring or admixed pyrite, bioleaching of the material would generate acid, ferric iron and heat in the leach from the oxidation of the sulfide, rather than having to add fresh reagents. This could be considered in a heap bioleaching process⁵, or a tank bioleaching process¹²⁰. The advances that have occurred in bioleaching during the period of the suppressed uranium market have made new technologies available that have not been applied to large scale uranium extraction before, and which can now be considered for new uranium ventures.

Trade Marks

Bacox™ is a trade mark of BacTech and Mintek.
BioCOP™ is a trade mark of BHP Billiton.
BioHeap™ is a trade mark of Pacific Ore Technology.
BioNIC™ is a trade mark of BHP Billiton.
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References

- CONCHA, A., OYARZUN, R., LUNAR, R., and SIERRA, J. Over a century of bioleaching copper sulphides at Andacollo. *Min. Mag.* (Lond.), Nov. 1991. pp. 324–327.
- LAWRENCE, R.W. and POULIN, R. Biooxidation of copper sulphides. *EPD Congress 1996*. Warren, G.W. (ed.). Warrendale, The Minerals, Metals & Materials Society, 1996. pp. 893–906.
- RAWLINGS, D.E. Microbially assisted dissolution of minerals and its use in the mining industry. *Pure Appl. Chem.*, vol. 76, no. 4. 2004. pp. 847–859.
- COTO, O., BALLESTER, A., BLÁZQUEZ, M.L., and GONZÁLEZ, F. Bioleaching of a Cuban copper concentrate in the presence of silver. *Biorecovery*, vol. 2. 1993. pp. 121–140.
- MUÑOZ, J.A., GONZÁLEZ, F., BLÁZQUEZ, M.L., and BALLESTER, A. A study of the bioleaching of a Spanish uranium ore. Part I: A review of the bacterial leaching in the treatment of uranium ores. *Hydrometallurgy*, vol. 38, 1995. pp. 39–57.
- VAN NIEKERK, J., and VAN ASWEGEN, P.C. The BioX® process: current status of operating plants and future developments. [Http://www.bioxgf.co.za/content/publications/pdfs/Current%20Status%20of%20Operating%20BIOX%20Plants%20and%20Future%20Developments.pdf]. Undated. 11 pp.
- READETT, D.J. Straits Resources Limited and the industrial practice of copper bioleaching in heaps. *Australasian Biotechnol.*, vol. 11, no. 6. 2001. pp. 30–31.
- NEALE, J.W., ROBERTSON, S.W., MULLER, H.H., and GERICKE, M. Integrated Piloting of a thermophilic bioleaching process for the treatment of a low-grade nickel-copper sulphide concentrate. *Proceedings of the SAIMM Southern African Hydrometallurgy Conference 2009*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 2009. pp. 119–154.
- MILLER, P.C., CORRANS, I.J., and SOUTHWOOD, A.J. Bacterial heap leaching of low-grade nickel material. *Mintek 50, Proceedings of the International Conference on Mineral Science and Technology*. Haughton, L.F. (ed.). vol. 1. Randburg, Mintek, 1985. pp. 341–352.
- NEALE, J.W., PINCHES, A., AND DEEPLAUL, V. Mintek-Bactech's bacterial-oxidation technology for refractory gold concentrates: Beaconsfield and beyond. *J. S.Afr. Inst. Min. Metall.*, vol. 100, no. 7. 2000. pp. 415–421.
- MILLER, P., JIAO, F., and WANG, J. The bacterial oxidation (BACOX) plant at Laizhou, Shandong Province, China – the first three years of operation. *Proceedings of the Bac-Min 2004 Conference*. Carlton, The Australian Institute of Mining and Metallurgy, 2004.
- KLAUBER, C. A critical review of the surface chemistry of acidic ferric sulphate dissolution of chalcopyrite with regards to hindered dissolution. *Int. J. Miner. Process.*, vol. 86, 2008. pp. 1–17.
- GERICKE, M., MULLER, H.H., NEALE, J.W., NORTON, A.E., and CRUNDWELL, F.K. Inoculation of heap-leaching operations. *Proceedings of the 16th International Biohydrometallurgy Symposium*. Harrison, S.T.L., Rawlings, D.E. and Petersen, J. (eds.). Cape Town, Compress, 2005. pp. 255–264.
- WATLING, H.R. The bioleaching of sulphide minerals with emphasis on copper sulphides—A review. *Hydrometallurgy*, vol. 84, 2006. pp. 81–108.
- VAN STADEN, P.J. Base metals heap leaching applications and process parameters. *Base Metals 2007: The Fourth Southern African Conference on Base Metals*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 2007. pp. 321–327.
- VAN STADEN, P.J. Heap leach research at Mintek. *ALTA 2008 Copper*. Melbourne, ALTA Hydrometallurgical Services, 2008. 13 pp.
- ROBERTSON, S.W., AND VAN STADEN, P.J. The progression of metallurgical testwork during heap leach design. *The SAIMM Southern African Hydrometallurgy Conference 2009*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 2007. pp. 31–42.
- VAN STADEN, P.J., ROBERTSON, S.W., GERICKE, M., NEALE, J.W., and SEYEDBAGHERI, A. Maximizing The value derived from laboratory test work towards heap leaching design. *The Fifth Southern African Base Metals Conference 2009*, Johannesburg, The Southern African Institute of Mining and Metallurgy, 2009. 7 pp.
- VAN STADEN, P.J., SHADAEE, B., and YAZDANI, M. A collaborative plan towards the heap bioleaching of low grade chalcopyritic ore from a new Iranian mine. *Proceedings of the 16th International Biohydrometallurgy Symposium*. Harrison, S.T.L., Rawlings, D.E. and Petersen, J. (eds.). Cape Town, Compress, 2005. pp. 115–123.
- ROBERTSON, S.W., VAN STADEN, P.J., VERCUIL, A., GLOVER, G., AND SHADAEE, B. Heap bioleaching of low-grade chalcopyrite ore from the Darehzare deposit. *ALTA 2007 Copper*. Melbourne, ALTA Hydrometallurgical Services, 2006. 13 pp.
- BRIERLEY, C.L. Mining Biotechnology: Research to commercial development and beyond. Rawlings, D.E. (ed.), *Biomining: Theory, Microbes and Industrial Processes*. Springer, Berlin, 1997. pp. 3–16.
- NORRIS, P.R. Acidophilic diversity in mineral sulphide oxidation. Rawlings, D.E. and Johnson, D.B. (eds.), *Biomining*. Springer, Berlin, 2007. pp. 199–212.
- KELLY, D.P., and WOOD, A.P. Reclassification of some species of *Thiobacillus* to the newly designated genera *Acidithiobacillus* gen. nov., *Halothiobacillus* gen. nov., and *Thermithiobacillus* gen. nov. *Int. J. Syst. Evol. Microbiol.*, vol. 50, 2000. pp. 511–516.
- RAWLINGS, D.E., TRIBUTSCH, H., and HANSFORD, G.S. Reasons why 'Leptospirillum'-like species rather than *Thiobacillus ferrooxidans* are the dominant iron-oxidising bacteria in many commercial processes for the bio-oxidation of pyrite and related ores. *Microbiology*, vol. 145, 1999. pp. 5–13.
- RAWLINGS, D.E. Characteristics and adaptability of iron- and sulfur-oxidizing microorganisms used for the recovery of metals from minerals and their concentrates, *Microbial Cell Factories*, vol. 5, 2005. pp. 4–13.
- SCHIPPERS, A. Microorganisms involved in bioleaching and nucleic acid-based molecular methods for their identification and quantification. Donati, E.R., Sand, W. (eds.), *Microbial Processing of Metal Sulfides*. Springer Dordrecht, The Netherlands, 2007. pp. 3–33.
- RAWLINGS, D.E. and JOHNSON, D.B. The microbiology of biomining: Development and optimization of mineral-oxidizing microbial consortia. *Microbiology*, vol. 153, 2007. pp. 315–324.
- JOHNSON, D.B., and HALLBERG, K.B. Carbon, Iron and Sulfur Metabolism in Acidophilic Micro-organisms. *Adv. Microb. Phys.*, vol. 54, 2009. pp. 201–255.
- JOHNSON, D.B., and HALLBERG, K.B. Techniques for detecting and identifying acidophilic mineral-oxidizing microorganisms. Rawlings, D.E. and Johnson, D.B. (eds.), *Biomining*. Springer, Berlin, 2007. pp. 237–257.
- ROSSI, G. Biohydrometallurgy: A sustainable technology in evolution. *Proceedings of the 15th International Biohydrometallurgical Symposium*. Tsezos, M., Remoudaki, E., and Hatzikioseyan, A. (eds.) Athens, Greece. 2003. pp. 1–21.
- OKIBE, N., GERICKE, M., HALLBERG, K.B., and JOHNSON, D.B. Enumeration and characterization of acidophilic microorganisms isolated from a pilot plant stirred tank bioleaching operation. *Appl. Env. Microbiol.*, vol. 69, 2003. pp. 1936–1943.
- DINKLA, I.J.T., GERICKE, M., GEURKINK, B.K. and HALLBERG, K.B. *Acidianus briarley* is the dominant thermoacidophile in a bioleaching community processing chalcopyrite containing concentrates At 70°C. *Adv. Mat. Res.*, vol. 71–73, 2009. pp. 67–70.
- MIKKELSEN, D., KAPPLER, U., MCEWAN, A.G., and SLY, L. Archaeal diversity in two thermophilic chalcopyrite bioleaching reactors. *Env. Microbiol.*, vol. 8, 2006. pp. 2050–2055.

A Mintek perspective of the past 25 years in minerals bioleaching

34. RAWLINGS, D.E., DEW, D., and DU PLESSIS, C. Biomineralization of metal-containing ores and concentrates. *Trends In Biotechnology*, vol. 21, 2003. pp. 38–44.
35. DAS, A., MODAK, J.M., and NATARAJAN, K.A. Studies on multi-metal ion tolerance of *Thiobacillus ferrooxidans*. *Min. Eng.*, vol.10, 1997. pp. 743–749.
36. DOPSON, M., BAKER-AUSTIN, C., KOPPINEEDI, P.R., AND BOND, P.L. Growth in sulphidic mineral environments: metal resistance mechanisms in acidophilic micro-organisms. *Microbiology*, vol.149, 2003. pp. 1959–1970.
37. GERICKE, M., MULLER, H.H., VAN STADEN, P.H., AND PINCHES, A. Development of a tank bioleaching process for the treatment of complex Cu-polymetallic concentrates. *Hydrometallurgy*, vol. 94, 2008. pp. 23–28.
38. RAWLINGS, D.E. Adaptability of Biomining Microorganisms to industrial processes. Rawlings, D.E. and Johnson, D.B. (eds.), *Biomining*. Springer, Berlin, 2007. pp. 177–198.
39. JEREZ, C.A. The use of genomics, proteomics and other OMICS technologies for the global understanding of biomining microorganisms. *Hydrometallurgy*, vol. 94, 2008. pp. 162–169.
40. VALENZUELA, L., CHIB, A. BEARD, S., ORELLA, A., GUILIANA, N., SHABANOWITZ, J., HUNT, D.F., and JEREZ, C.A. Genomics, metagenomics and proteomics in biomining microorganisms. *Biotechnology Advances*, vol. 24, 2006. pp. 197–211.
41. HANSFORD, G.S. Travels through bioleaching. *Proceedings of the 16th International Biohydrometallurgy Symposium*. Harrison, S.T.L., Rawlings, D.E. and Petersen, J. (eds.). Cape Town, Compress, 2005. pp. xxvii–xxxii.
42. MISHRA, D., KIM, D.-J., AHN, J.-G., and RHEE, Y.-H. Bioleaching: A Microbial Process of Metal Recovery. A Review. *Metals and Materials International*, vol. 11, 2005. pp. 249–256.
43. HANSFORD, G.S. Recent developments in modelling the kinetics of bioleaching. Rawlings, D.E. (ed.), *Biomining: Theory, Microbes and Industrial Processes*. Springer, Berlin, 1997. pp. 153–175.
44. ROHWERDER, T., GEHRKE, T., KINZLER, K., and SAND, W. Bioleaching review part A: progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation. *Appl. Microbiol. Biotechnol.*, vol. 63, 2003. pp. 239–248.
45. SCHIPPERS, A., and SAND, W. Bacterial leaching of metal sulfides proceeds by two indirect mechanisms via thiosulfate or via polysulfides and sulphur. *Appl. Environ. Microbiol.*, vol. 65, 1999. pp. 319–321.
46. ACEVEDO, F. The use of bioreactors in biomining processes. *EJB Electronic J. Biotechnol.*, vol. 3, no. 3, 2000. pp. 1–11.
47. ROSSI, G. The design of bioreactors. *Hydrometallurgy*, vol. 59, 2001. pp. 217–231.
48. PINCHES, A., CHAPMAN, J.T., TE RIELE, W.A.M., and VAN STADEN, M. The performance of bacterial leach reactors for the pre-oxidation of refractory gold-bearing sulphide concentrates. *Biohydrometallurgy: Proceedings of the International Biohydrometallurgy Symposium*. Norris, P. and Kelly, D.P. (eds.). Kew, Antony Rowe Limited, 1987. pp. 329–344.
49. CHAPMAN, C.M., NIENOW, A.W., COOKE, M., and MIDDLETON, J.C. Particle-gas-liquid mixing in stirred vessels. Part III: three phase mixing. *Chem. Eng. Res. Des.*, vol. 61, 1983. pp. 167–181.
50. DEW, D.W. and GODFREY, M.W. Sao Bento Biox reactor. *Colloquium: Bacterial Oxidation*. Johannesburg, The Southern African Institute Of Mining And Metallurgy, 1991. 20 pp.
51. OLDSHUE, J.Y. Fluid mixing In 1989. *Chem. Eng. Prog.*, vol. 85, no. 5, 1989. pp. 33–42.
52. GREENHALGH, P., RILEY, R.P., and BAGULEY, W. Development of the VELMIX bio-reactor. *Proceedings of the Randol Gold Forum '90*. Golden, Randol International Limited, 1990. pp. 115–121.
53. RILEY, R.P., BAGULEY, W., and GREENHALGH, L.P.H. Development of the VELMIX bio-oxidation reactor. *International Deep Mining Conference: Innovations in Metallurgical Plant*. Johannesburg, The Southern African Institute Of Mining and Metallurgy, 1990. pp. 131–140.
54. RILEY, R.P., BAGULEY, W., and GREENHALGH, L.P.H. Development of the BX04 impeller system for bio-oxidation reactors. *Proceedings of the Randol Gold Forum '92*. Golden, Randol International Limited, 1992. pp. 181–190.
55. BOUQUET, F., and MORIN, D. BROGIM: A new three-phase mixing system –testwork and scale-up. *Proceedings Of the 16th International Biohydrometallurgy Symposium*. Harrison, S.T.L., Rawlings, D.E. and Petersen, J. (eds.). Cape Town, Compress, 2005. pp. 173–182.
56. MILLER, D.M. Effect of temperature on BIOX operations. *Colloquium: Bacterial Oxidation*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 1991. 18 pp.
57. PINCHES, T., NEALE, J., HUBERTS, R., and DEMPSEY, P. Development of the Mintek bacterial oxidation process (MINBAC). *Proceedings of the Randol Gold Forum '93*. Golden, Randol International Limited, 1993. pp. 221–228a.
58. PINCHES, A., HUBERTS, R., NEALE, J.W., and DEMPSEY, P. The MINBAC™ bacterial-oxidation process. *Xvth CMMI Congress*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 1994. pp. 377–392.
59. DEMPSEY, P., HUMAN, P., PINCHES, A., and NEALE, J.W. Bacterial oxidation at Vaal Reefs. *International Deep Mining Conference: Innovations In Metallurgical Plant*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 1990. pp. 111–123.
60. NEALE, J.W., PINCHES, A., MULLER, H.H., HANNWEG, N.H., and DEMPSEY, P. Long-term bacterial oxidation pilot plant operation at Mintek and Vaal Reefs. *Colloquium: Bacterial Oxidation*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 1991. 25 pp.
61. NEALE, J.W., and PINCHES, A. Determination of gas liquid mass-transfer and solids-suspension parameters in mechanically-agitated three-phase slurry reactors. *Miner. Eng.*, vol. 7, no's. 2/3, 1994. pp. 389–403.
62. OOSTERHUIS, N.M.G., and KOSSEN, N.W.F. Oxygen transfer in a production scale bioreactor. *Chem. Eng. Res. Des.*, vol. 61, 1983. pp. 308–312.
63. OOSTERHUIS, N.M.G., and KOSSEN, N.W.F. Dissolved oxygen concentration profiles in a production-scale bioreactor. *Biotech. Bioeng.*, vol. 26, 1984. pp. 546–550.
64. ZWIETERING, T.N. Suspending of solid particles in liquid by agitators. *Chem. Eng. Sci.*, vol. 8, 1958. pp. 244–253.
65. NEALE, J.W., PINCHES, A., KRUGER, P.P., and VAN STADEN, P.J. Copper bioleaching. *ALTA 1996 Copper Hydrometallurgy Forum*. Melbourne, ALTA Hydrometallurgical Services, 1996. 27 pp.
66. WATLING, H.R. The bioleaching of nickel-copper sulfides. *Hydrometallurgy*, vol. 91, 2008. pp. 70–88.
67. NICHOLSON, H.M., LUNT, D.J., RITCHIE, I.C., and MARAIS, H.J. The design of the Sansu concentrator and BIOX® facility. *Xvth CMMI Congress*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 1994. pp. 393–402.
68. BRIERLEY, C.L., and BRIGGS, A.P. Selection and sizing of biooxidation equipment and circuits. *Mineral Processing Plant Design, Practice, and Control: Proceedings*. Mular, A.L., Halbe, D.N., and Barratt, D.J. (eds.). vol. 2. The Society For Mining, Metallurgy, and Exploration, 2002. pp. 1540–1568.
69. BATTY, J.D., and POST, T.A. Bioleach reactor development and design. *ALTA 1999 Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum*. Melbourne, ALTA Hydrometallurgical Services, 1999. 16 pp.
70. BATTY, J.D., and RORKE, G.V. Development and commercial demonstration of the BioCOP™ Thermophile Process. *Hydrometallurgy*, vol. 83, 2006. pp. 83–89.
71. VAN NIEKERK, J. Recent advances in BIOX® Technology. *Hydrometallurgy Conference 2009*. Johannesburg, The Southern African Institute of Mining and Metallurgy, 2009. pp. 167–176.
72. BRIERLEY, J.A., and BRIERLEY, C.L. Present and future commercial applications of biohydrometallurgy. *Hydrometallurgy*, vol. 59, 2001. pp. 233–239.
73. BRIERLEY, C.L. How will biomining be applied in future? *Trans. Nonferrous Met. Soc. China*, vol. 18, 2008. pp. 1302–1310.
74. BRIERLEY, J.A. A Perspective on developments in biohydrometallurgy. *Hydrometallurgy*, vol. 94, 2008. pp. 2–7.
75. BACTECH. Technology overview. [<http://www.bactech.com/green/overview.asp>]. Undated.
76. POLYMETAL. Polymetal announces acquisition of Mayskoye gold deposit in consortium with a group of Russian investors for total consideration of US\$105 million. Press release. [<http://www.polymetal.ru/en/242/4175>]. 29 April 2009.
77. SOVMEN, V.K., BELYI, A.V., DANNEKER, M.Y., GISH, A.A., and TELEUTOV, A.N. Biooxidation of refractory gold sulfide concentrate of Olympiada deposit. *Adv. Mater. Res.*, vol. 71–73, 2009. pp. 477–480.
78. PAVLIDES, A.G. and FISHER, K.G. The Kasese cobalt project. *Extraction Metallurgy Africa '98*. Johannesburg, The South African Institute of Mining and Metallurgy, 1998. 20 pp.

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79. VAN STADEN, P.J. The Mintek/Bactech copper bioleach process. *ALTA Copper Hydrometallurgy Forum*. Brisbane, 19–21 Oct., 1998.
80. MORIN, D.H.R., and D'HUGUES, P. Bioleaching of a cobalt-containing pyrite in stirred reactors: a case study from laboratory scale to industrial application. Rawlings, D.E. and Johnson, D.B. (eds.), *Biomining*. Springer-Verlag, Berlin, 2007. pp. 35–54
81. MUÑOZ, P.B., MILLER, J.D., and WADSWORTH, M.E. Reaction mechanism for the acid ferric sulphate leaching of chalcopyrite. *Metallurgical Transactions B*, (June), 1979. pp. 55–65.
82. STOTT, M.B., WATLING, H.R., FRANZMANN, P.D., and SUTTON, D. The role of iron-hydroxy precipitates in the passivation of chalcopyrite during bioleaching. *Min. Eng.*, vol. 13, 2000. pp. 1117–1127.
83. SANDSTROM, Å., SHCHUKAREV, A., and PAUL, J. XPS characterisation of chalcopyrite chemically and bio-leached at high and low redox potential. *Min. Eng.*, vol.18, 2005. pp. 505–515.
84. HACKL, R.P., DREISINGER, D.B., PETERS, E., and KING, J.A. Passivation of chalcopyrite during oxidative leaching in sulfate media. *Hydrometallurgy*, vol. 39, 1995. pp. 25–48.
85. PARKER, A., KLAUBER, C., KOUGANIS, A., WATLING, H.R., and VAN BRONSWIJK, W. An X-ray photoelectron spectroscopy study of the mechanism of oxidative dissolution of chalcopyrite. *Hydrometallurgy*, vol. 71, 2003. pp. 265–276.
86. GERICKE, M., and PINCHES, A. Bioleaching of copper sulphide concentrate using extreme thermophilic bacteria. *Min. Eng.*, vol. 12, 1999. pp. 893–904.
87. GERICKE, M., PINCHES, A., and VAN ROOYEN, J.V. Bioleaching of a chalcopyrite concentrate using an extremely thermophilic culture. *Int. J. Min. Process.*, vol. 62, 2001. pp. 243–255.
88. HIROYOSHI, N., MIKI, H., HIRAJIMA, T., and TSUNEKAWA, M., Enhancement of chalcopyrite leaching by ferrous ions in acidic ferric sulfate solutions. *Hydrometallurgy*, vol. 60, 2001. pp. 185–197.
89. THIRD, K.A., CORD-RUWISCH, R., and WATLING, H.R. Control of the redox potential by oxygen limitation improves bacterial leaching of chalcopyrite. *Biotechnol. Bioeng.*, vol. 78, 2002. pp. 433–441.
90. PINCHES, A., MYBURGH, P.J., and VAN DER MERWE, C. Process for the rapid leaching of chalcopyrite in the absence of catalysts. US Patent 6,277,341: Appl.: 3 March 1997: Acc. 21 August 2001.
91. PINCHES, A., GERICKE, M., and VAN ROOYEN, J.V. A method of operating a bioleach process with control of redox potential. Patent WO 01/31072 A1: Appl.: 28 October 1999: Acc. 3 May 2001.
92. GERICKE, M., GOVENDER, Y., and PINCHES, A. Advances in tank bioleaching of low-grade chalcopyrite concentrates. *Adv. Mat. Res.*, vol. 71–73, 2009. pp. 361–364.
93. AHONEN, L., and TUOVINEN, O.H. Catalytic effects of silver in the microbiological leaching of finely ground chalcopyrite-containing ore materials in shake flasks. *Hydrometallurgy*, vol. 24, 1990. pp. 219–236
94. GÓMEZ, E., BALLESTER, A., BLÁZQUEZ, M.L., and GONZÁLEZ, F. Silver-catalysed bioleaching of a chalcopyrite concentrate with mixed cultures of moderately thermophilic microorganisms. *Hydrometallurgy*, vol. 51, 1999. pp. 37–46.
95. RHODES, M., DEEPLAUL, V., and VAN STADEN, P.J. Bacterial oxidation of Mt Lyell concentrates, ALTA Copper 1998: (Brisbane, Qld.), ALTA Metallurgical Services, Melbourne, 1999. 24 pp.
96. GERICKE, M., MULLER, HH., VAN STADEN, P.J., and PINCHES, A. Development of a tank bioleaching process for the treatment of complex Cu-polymetallic concentrates. *Hydrometallurgy*, vol. 94, 2008. pp. 23–28.
97. MIER, J.L., GOMEZ, C., BALLESTER, A., BLÁZQUEZ, M.L. and GONZALEZ, F. Effect of silver and bismuth on bioleaching of copper sulphide concentrates with thermophilic microorganisms. *Hydrometallurgy 94, International Symposium, Institution Of Mining And Metallurgy, Society Of Chemical Industry*, Cambridge, July 11–15, 1994. p. 369.
98. DOMIC, E.M. A review of the development and current status of copper bioleaching operations in Chile: 25 Years of successful commercial implementation. Rawlings, D.E. and Johnson, D.B. (eds.), *Biomining*. Springer-Verlag, Berlin, 2007. pp. 81–95
99. CLARK, M.E., BATTY, J.D., VAN BUUREN, C.B., DEW, D.W., and EAMON, M.E. Biotechnology in minerals processing: Technological breakthroughs creating value. *Hydrometallurgy*, vol. 83, 2006. pp. 3–9.
100. VAN STADEN, P.J., GERICKE, M., and CRAVEN, P.M. Minerals biotechnology: Trends, opportunities and challenges. *Hydrometallurgy 2008*, Phoenix, Arizona, 17–20 Aug. 2008.
101. MORIN, D., PINCHES, T., HUISMAN, J., FRIAS, C., NORBERG, A., and FORSSBERG, E. Progress after three years of BioMinE—research and technological development project for a global assessment of biohydrometallurgical processes applied to European non-ferrous metal resources. *Hydrometallurgy*, vol. 94, 2008. pp. 58–68.
102. SCHNELL, H.A. Bioleaching of copper. Rawlings, D.E. (ed.), *Biomining: Theory, Microbes and Industrial Processes*. Springer, Berlin, 1997. pp. 21–43.
103. GALLEGUILLAS, P., REMONSELLEZ, F., GALLEGUILLAS, F., GUILIANI, N., CASTILLO, D., and DEMERGASSO, C. Identification of differentially expressed genes in an industrial bioleaching heap processing low-grade copper sulphide ore elucidated by RNA arbitrarily primed polymerase chain reaction. *Hydrometallurgy*, vol. 94, 2008. pp. 148–154.
104. DIXON, D.G and PETERSEN, J. Modelling the Dynamics of Heap Bioleaching for Process Improvement and Innovation. *Hydro-Sulfides 2004: Intl. Colloquium on Hydrometallurgical Processing of Copper Sulfides (Santiago)*. University Of Chile, Santiago, pp. 13–45.
105. HOLMES, D.S. Review of International Biohydrometallurgy Symposium, Frankfurt, 2007. *Hydrometallurgy*, vol. 92, pp. 69–72.
106. RIEKKOLA-VANHANEN, M. Talvivaara black schist bioheap leaching demonstration plant. *Adv. Mat. Res.*, vols. 20–21, 2007. pp. 30–33.
107. WAKEMAN, K., AUVINEN, H., and JOHNSON, D.B. Microbiological and geochemical dynamics in simulated-heap leaching of a polymetallic sulphide ore. *Biotechnol. Bioeng.*, vol. 101, 2008. pp. 739–750.
108. CHADWICK, J. Bio/hydro—Different metallurgical options. *Int. Mining*, May, 2007. pp. 41–44.
109. PRADHAN N., NATHSARMA K.C., SRINIVASA RAO K., SUKLA L.B., and MISHRA B.K. Heap Bioleaching of Chalcopyrite: A Review. *Min. Eng.*, vol. 21, pp. 355–365.
110. HARVEY T.J., and BATH M. The Geobiotics GEOCOAT™ Technology—progress and challenges. Rawlings, D.E. and Johnson, D.B. (eds.), *Biomining*. Springer-Verlag, Berlin, 2007. pp. 97–112.
111. PEACY, J., GUO, X.J., and ROBLES, E. Copper Hydrometallurgy—Current Status, Preliminary Economics, Future Direction and Positioning versus Smelting. *Proceedings: International Symposium Copper 2003—Cobre 2003*, Hydrometallurgy Of Copper, vol. vi.
112. DEMERGASSO, C., GALLEGUILLAS, P., ESCUDERO, L., ZEPEDA, V., CASTILLO, D., and CASAMAYOR, E. Molecular characterization of microbial populations in a low-grade copper ore bioleaching test heap. *Hydrometallurgy*, vol. 80, 2005. pp. 241–253.
113. CORAM-ULIANA, N.J., VAN HILLE, R.P., KOHR, W.J., and HARRISON, S.T.L. Development of a method to assay the microbial population in heap bioleaching operations. *Hydrometallurgy*, vol. 83, pp. 237–244.
114. REMONSELLEZ, F., GALLEGUILLAS, F., JANSE VAN RENSBURG, S., RAUTENBACH, G.F., GALLEGUILLAS, P., CASTILLO, D., and DEMERGASSO, C. Monitoring the microbial community inhabiting a low-grade copper sulphide ore by Quantitative Real-Time PCR analysis of 16s rRNA genes. *Adv. Mat. Res.* vols. 20–21, 2007. pp. 539–542.
115. JOHNSON, D.B. Biodiversity and interactions of acidophiles: Key to understanding and optimizing microbial processing of ores and concentrates. *Trans. Nonferrous Met. Soc. China*, vol.18, 2008. pp. 1367–1373
116. LINDSTRÖM, B., SANDSTRÖM, A., and SUNDKVIST, J.-E. Two-stage bioleaching of sulphidic material containing arsenic. *U.S. Pat.* 6,461,577 B1. 8 Oct. 2002.
117. LINDSTRÖM, E.B., SANDSTRÖM, A., and SUNDKVIST, J.-E. A sequential two-step process using moderately and extremely thermophilic cultures for biooxidation of refractory gold concentrates. *Hydrometallurgy*, vol. 71, 2003. pp. 21–30.
118. MORIN, D.H.R. BioMinE: An integrated project for developing biohydrometallurgy in Europe—executive summary of its activities and outputs after three years. *Trans. Nonferrous Met. Soc. China*, vol. 18, 2008. pp. 1328–1335.
119. WADDEN, D. and GALLANT, A. The in-place leaching of uranium at Denison Mines. *Can. Metall. Q.*, vol. 24, no. 2. 1985. pp. 127–134.
120. KOTZE, M.H., GREEN, B.R., NEALE, J.W. and SWANEPOEL, L. Mintek's re-entry into uranium research and development. *ALTA 2006 Uranium*. Melbourne, ALTA Hydrometallurgical Services, 2006. 15 pp. ♦