6 Biological Processing: Biological Processing of Sulfidic Ores and Concentrates—Integrating Innovations

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6.1 Introduction

Biological processing of sulfidic ores and concentrates is a commercially proven hydrometallurgical process employing naturally occurring microorganisms to catalyze the oxidation of sulfide minerals to extract base metals, such as copper, nickel, and zinc, and to enhance the recovery of precious metals occluded (locked) within sulfide minerals, such as pyrite and arsenopyrite. Biological processing is also referred to as bioleaching, biomining, biohydrometallurgy, and minerals biooxidation, the latter when applied to precious metal ores or concentrates to enhance recovery of precious metals.

Biological processing has likely been unknowingly used for the recovery of copper from ores for over 2000 years (Rossi 1990), although the role of microorganisms in the leaching of sulfide minerals was unknown until the late 1940s and early 1950s (Colmer and Hinkle 1947; Colmer et al. 1950; Temple and Colmer 1951). Early records dating from 166 AD indicate the widespread practice of copper leaching in Cyprus and it is well known that the Romans recovered copper by leaching from a deposit located at what later became the Rio Tinto mine in southern Spain (Rossi 1990). This area of Spain is rich in metal sulfide minerals, so bioleaching of these sulfides most likely occurred during Roman times. Even in very early times copper, resulting from the biologically facilitated dissolution of copper sulfide minerals, was recovered from solution by displacement with iron. The Chinese king Liu-An (177–122 BC) described this electrochemical conversion process of cementation, or reduction of copper sulfate, using iron. Paracelsus (1493–1541), a Swiss physician and alchemist, also described copper cementation on iron, referring to it as a transmutation of elements (Rossi 1990).

Today biological processing is widely practiced at commercial scale for the extraction of copper and gold. Some 18–20 % of the world's mined copper production is now the result of biological processing. This estimate is obtained by examining world copper mine production, copper produced by solvent extraction/electrowinning (SX/EW) (about 22 %), and approximating percentages of oxide ores versus sulfide ores (ICSG 2013). Chile and the United States account for 93 % of the world's electrowon copper (Edelstein 2013). Identifying the major copper sulfide leach operations in these two countries and totaling these operation's annual production provide additional information to estimate production by biological processing.

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About 3 % of the global mined gold production is now the result of biological processing based on annual gold production from plants using biological processing (Biomin 2014) and comparing that with total annual mine production of gold (USGS 2014).

This chapter begins with a description of the chemistry and microbiology of biological processing of sulfide ores and concentrates. This is followed by an explanation of how the process is engineered and the innovations that have been introduced in commercial practices. The chapter concludes with a view of how biological processing technologies for ores may be applied in the future with new advances and the motivating factors for using biological processing.

6.2 The Microbiology and Chemistry of Biological Processing

It is important to understand the microbiological and chemical underpinnings of biological processing to appreciate the innovations that have revolutionized biological processing in the last several decades and continue to impact the technology.

6.2.1 Microbiology

The natural habitats of all microorganisms used in bioleaching and minerals biooxidation are natural outcroppings of sulfide minerals, mined areas where sulfide minerals have been exposed to air, acidic hot springs (e.g., Yellowstone National Park, Iceland and New Zealand), and volcanic areas.

All microorganisms used in biomining have several things in common. They:

- Are single-celled organisms that multiply by simple cell division.
- Derive energy for growth and cell functioning by oxidizing[1] ferrous iron (Fe^{2+}).

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (6.1)$$

- and certain reduced sulfur compounds such as elemental sulfur (S°).

$$S^\circ + H_2O + 1.5O_2 \rightarrow 2H^+ + SO_4^{2-} \quad (6.2)$$

- Obtain carbon for their cellular bodies from carbon dioxide (CO_2) in the atmosphere.
- Require oxygen (O_2) taken from the atmosphere; O_2 serves as the electron acceptor. Certain oxidized metals can also function as electron acceptors and this is discussed later.
- Need ammonium (NH_4^+) and phosphate (PO_4^{3-}) ions and certain trace elements as building blocks for amino acids, DNA, and other constituents. The trace elements required (Mg^{2+}, K^+, etc.) are often abundant in the ore or concentrate feedstock.
- Require a sulfuric acid environment to metabolize and multiply. The acidity should be less than pH 2.5 to ensure the metals of value that are being leached remain soluble in the leach solution and Fe^{2+} remains soluble and available as an energy source for the organisms.

Biomining microorganisms do not cause diseases in humans, animals, or plants. They can't survive in or on plants and animals, because their energy (food) source is inorganic and because they require a sulfuric acid environment.

Since the discovery in 1947 of *Thiobacillus ferrooxidans* (now *Acidithiobacillus ferrooxidans*), many more microorganisms have been discovered that are also involved in metals extraction (Norris 2007; Olson and Clark 2004; Schippers 2007; Brierley and Brierley 2013). The microorganisms used in biological processing are

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[1] Oxidation involves the removal of electrons from a substance. In biological processing, the microbes remove electrons from dissolved ferrous iron (Fe^{2+}) converting it to ferric iron (Fe^{3+}) and from elemental sulfur (S°) and other chemically reduced sulfur compounds converting them to sulfuric acid (H_2SO_4).

often grouped within temperature ranges at which they grow and where they are found in the natural environment.

Ambient temperature microorganisms (*Mesophiles*): These cylindrical-shaped bacteria are about 1 μm long by 1/2 μm in diameter. They only metabolize and multiply from about 10 to 40 °C. If the temperature is too low, these bacteria become dormant. If the temperature exceeds 45 °C the organisms, with some exceptions, die when their proteins coagulate. There is great diversity among the mesophilic bacteria that are active in industrial biomining applications. Some members of this group are *Acidithiobacillus ferrooxidans*, various species of *Leptospirillum, Acidithiobacillus thiooxidans*, and various *Ferroplasma* species, the latter being archaea[2] not bacteria. Some of the mesophilic organisms only oxidize ferrous iron, some oxidize only reduced sulfur, while some oxidize both.

Moderately thermophilic (*heat-loving*) *microorganisms*: There is not a precise temperature that divides the mesophilic microorganisms from the moderately thermophilic microbes, because some mesophilic microorganisms are thermotolerant and some moderate thermophiles are active at 25 °C. However, biomining organisms, whose optimum temperature is at or above 45 °C and actively function in the temperature range of 40 °C to about 60 °C, are considered moderate thermophiles. Most moderate thermophiles die when the temperature exceeds about 65 °C. These microorganisms are similar to the "mesophilic" biomining bacteria, except they are somewhat larger in length—about 2–5 μm long. Some bacteria included in this grouping are *Sulfobacillus thermosulfidooxidans* and *Acidimicrobium ferrooxidans*. Like the mesophilic organisms, some moderate thermophiles oxidize iron and some oxidize sulfur.

Extremely thermophilic archaea[2]: While similar in size (one μm in diameter) to bacteria, archaea have a different molecular organization. In the tree of life, archaea occupy the lowest branch and are extant members of an offshoot of primitive microbes. They have a spherical shape and characteristically lack a rigid cell wall; rather the contents of the single cell are enclosed by a membrane. These microbes, nevertheless, are extremely robust and grow and perform only at temperatures between 60 and 85 °C. Several archaea important in commercial biological processing of sulfide minerals are *Acidianus brierleyi, Sulfolobus metallicus*, and *Metallosphaera sedula*.

In addition to the mesophilic, moderately thermophilic, and extremely thermophilic microbes, there are a variety of other acid-loving microorganisms present in biomining operations that use organic matter as their energy source. The exact role of these organisms in biological processing is unknown; however, it has been suggested that these organisms benefit biological processing by scavenging organic matter that may be toxic to the organisms using inorganics as energy sources (Johnson and Roberto 1997). Small amounts of organic matter are present in commercial operations from the death of microbes, from entrainment of organic reagents used in mineral processing operations that precede the bioleaching/minerals biooxidation step, and from ores that naturally contain organic matter.

Microorganisms in biological processing operations can be analyzed with varying success using several techniques. Counting cells under a microscope, even using stains, is unreliable because of difficulties in distinguishing microorganisms attached to mineral particles and because dead cells can't be differentiated from living cells. Cultivation techniques are not only labor intensive but also select for only a subset of the whole microbial community that is present. In recent years, nucleic-acid based molecular techniques have been increasingly applied to identify and quantify microorganisms present in commercial biological processing operations (Johnson and Hallberg 2007; Schippers 2007; Chávex et al. 2011). While these molecular techniques

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[2] Archaea, also called archaebacteria, are single-celled microorganisms that are genetically distinct from bacteria. Archaebacteria evolved separately and are regarded as "living" fossils of an ancient group of organisms bridging the evolutionary gap between bacteria and eukaryotes, the latter being multicelled organisms (Biology Online 2014).

have provided much new information about microbial diversity in biological processing operations, they are most applicable to determining the microbes present in the leach solutions and to those microorganisms that can be effectively "washed" from the mineral particles. Organisms firmly bound to mineral particles are not as successfully identified or quantified as those in the leach liquor.

There are a number of factors that affect the performance of biological processing microorganisms (Brierley and Briggs 2002).

Temperature: Temperature impacts biological processing by selecting for the group of microorganisms that will predominate at a specific temperature range.

pH: All microorganisms currently used in commercial biological processing are acid-loving and perform best when the pH is between 1.2 and 2.3. Above pH 2.5 soluble ferric iron hydrolyzes (reacts with water) and precipitates from solution as various compounds. What this means in an operating plant is that the key microbial energy source (Fe^{2+}) and the ferric iron product (Fe^{3+}) of the microbial oxidation, which is the oxidant of sulfide minerals, becomes limited. The higher pH is also not favorable for the dissolution of metal cations, which may be the products of value, such as copper and zinc. The ultimate consequences of a pH that is too high in a commercial biological processing plant are a decline in PLS (pregnant leach solution) tenor for base metals and lower than anticipated extraction of precious metals.

Microorganisms are remarkably adaptable and slow changes in acidity and other operating parameters allow time for microbial populations to adapt to a range of adverse conditions without the loss of important members of the microbial population. Abrupt changes in pH and other conditions will often result in the loss of microorganisms in the biological process.

Oxidation-reduction potential: In biological processing, oxidation-reduction potential (redox) is controlled by the ratio of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) in the leach solution. The Fe^{2+}:Fe^{3+} ratio selects certain microorganisms in an operating biological processing plant (Rawlings et al. 1999). For example, if the redox potential is low, because of increasing Fe^{2+} in solution relative to Fe^{3+}, the bacterium, *Acidithiobacillus ferrooxidans* will predominate, because this organism has a faster growth rate than other iron-oxidizing microorganisms when an abundance of its ferrous iron energy source is available. However, as the redox potential increases due to a lower Fe^{2+}:Fe^{3+} ratio, *Leptospirillum ferrooxidans* will predominate, because these organisms have a higher affinity for Fe^{2+} than does *A. ferrooxidans*; in other words, *L. ferrooxidans* will oxidize available Fe^{2+} before *A. ferrooxidans. A. ferrooxidans* is also more sensitive to inhibition from high concentrations of Fe^{3+} in solution. Therefore, in a stirred-tank reactor, in which the redox potential remains relatively constant and is high, *L. ferrooxidans* is likely to be the predominating iron-oxidizing microorganism in the reactor.

Oxygen: Bioleaching microorganisms in commercial plants require O_2. O_2 accepts the electrons in the redox reactions catalyzed by the microorganisms. The surest way to cause a production problem in a biological processing operation is to limit O_2. Getting air into the circuits and distributing it efficiently are significant engineering challenges in the design of biological processing plants.

Nutrients: The leaching microorganisms have few nutritional requirements: PO_4^{3-}, NH_4^+, and a few trace elements. Trace elements, such as Mg^{2+} and K^+, are generally present in sufficient quantities from the degradation of rock in the acid leach. PO_4^{3-}, NH_4^+, and K^+ are added to stirred-tank biological processing operations (Brierley and Briggs 2002).

Carbon dioxide: Microorganisms require carbon for synthesis of cellular components. The microbes used in biological processing of sulfide ores and concentrates obtain carbon from atmospheric CO_2 and convert this to cellular constituents, such as enzymes, by chemical reduction of the CO_2 in a complex metabolic pathway. Microorganisms expend considerable energy in assimilation of this carbon, called "carbon fixation". CO_2 is generally available from the air or from the acid neutralization of limestone added for pH control in stirred tank bioreactors. CO_2 limitation in heaps can occur, if the ore has little or no carbonate mineralization or CO_2 consumption by the microbial population is high.

Energy (*food*) *source*: Microorganisms used in biological processing of sulfide ores and concentrates require an energy source and that energy source is ferrous iron (Fe^{2+}) for the iron-oxidizing microbes and chemically reduced sulfur compounds, such as S°, for the sulfur-oxidizing microorganisms.

Microorganisms obey the laws of thermodynamics; they do not perform any oxidation reactions that are not thermodynamically possible. Microbes are also referred to as "catalysts" because they speed up certain reactions. For example, the oxidation of Fe^{2+} to Fe^{3+} in an acid solution is extremely slow chemically; microorganisms increase the rate of this oxidation by some 500,000 times (Lacy and Lawson 1970). The reason the organisms are so good at iron oxidation is because they must oxidize a lot of it to obtain enough energy to fix CO_2 and synthesize complex proteins, carbohydrates, DNA, etc.

Salinity: The microorganisms involved in bioleaching are relatively intolerant to the chloride ion (Cl^-). The diversity of the population as well as rates of ferrous iron oxidation are negatively affected at Cl^- concentrations greater than about 3–4 g/L (Gahan et al. 2009). Attempts to adapt the biological processing microorganisms to higher Cl^- concentrations have been unsuccessful (Lawson et al. 1995).

Soluble cation and anion metal/metalloid concentrations: Leaching microorganisms are tolerant to high concentrations of most heavy metal cations and can readily be adapted to even higher concentrations. In stirred-tank bioleach plants, heavy metal cation concentrations can exceed 20 or 30 g/L; adaptation of the microbial culture to anticipated metal concentrations is an important design step. There are some cationic metals/metalloids, which can be toxic to the organisms. For these substances to be toxic, they must be soluble. Mercury and silver, though toxic, are usually not serious problems, because silver has a low solubility in acidic leach solutions and mercury adsorbs to rock, mitigating its toxic effect. Arsenate (As^{5+}) is not toxic, but arsenite (As^{3+}) is. It is important, particularly in heap leach operations, that the redox potential is sufficiently high to ensure that, when arsenic-bearing minerals such as realgar (AsS), orpiment (As_2S_3) and arsenopyrite (FeAsS) are solubilized either through acid addition or oxidation, that As^{3+} is oxidized to As^{5+}. Ferric iron effectively oxidizes As^{3+}, but particular attention may be necessary in commercial plant start-up to ensure adequate ferric iron is available to oxidize any As^{3+} in solution.

$$2Fe^{3+} + H_3As^{III}O_3 + H_2O \rightarrow 2Fe^{2+} + H_3As^{V}O_4 + 2H^+ \quad (6.3)$$

Nitrate anion (NO_3^-) presents toxicity issues; NO_3^- concentrations in excess of 200 mg/L slow the rate of Fe^{2+} oxidation by the microorganisms. Like other anions, such as Cl^-, the mechanism of toxicity is likely to be disruption of the cell membrane and uncontrolled transport of NO_3^- into the cell, which suggests that adaptation of the microbes to NO_3^- may not be effective.

Fluoride (F^-) can be problematic in bioleaching, but not because the anion is toxic. Acidophilic microbes maintain an intracellular pH near neutral, thus a huge proton gradient exists across their cell membranes when they grow in acidic environments of pH 2 or less. This gradient accounts for the organism's sensitivity to F^-. Below pH 3.45 fluoride (F^-) occurs predominately as HF. HF crosses the cell membrane as an uncharged molecule; once inside the cell HF disassociates, releasing protons that acidify and kill the cell (Brierley and Kuhn 2010). It is important to note that F^- toxicity levels are directly related to the presence of other ions in solution; fluoride complexes with aluminum and this complexation significantly reduces the toxicity of F^- to the biomining microorganisms, because the molecule is too large to cross the cell membrane of the microorganism.

Process reagents and materials: Process reagents, for example, flotation reagents, used in biological processing plants, must be tested to ensure they are not toxic to the microorganisms. Materials, such as rubber linings in tanks, leach pad liners, and all materials that microbes come in contact with in the process, should be evaluated in lab tests to ensure that there are no inhibitory effects.

Tailings waters, containing traces of cyanide (CN^-), thiocyanate (SCN^-), or cyanate (CNO^-), must not be used as process water or make-up water to bioleach circuits. These agents are respiratory inhibitors that deactivate microbial enzymes, and if they enter the circuit, the result is significant loss in plant performance at best (Bell and Quan 1997) and a total loss of microbial activity at worst. Obviously, the toxicity of cyanide has implications in the treatment of concentrates that have been previously cyanide leached.

Oils, greases, hydraulic fluids, water treatment chemicals, dust suppressors, and anti-scalant chemicals are common substances in metallurgical plants and are potential inhibitors to the leaching microorganisms. Some of these agents are surfactants, which damage the organism's cell membrane causing the membrane to break open. Little quantitative data are available on the exact concentrations that induce problems. Good housekeeping in metallurgical plants is necessary to avoid contaminating anything in which the microorganisms come in contact with (Brierley and Briggs 2002).

Biocides are used in stirred-tank reactor cooling circuits to eliminate microbial contamination. For obvious reasons, biocides must never be allowed in any part of the circuit in which the biological processing takes place.

6.2.2 Chemistry of Biological Processing

6.2.2.1 Oxidation of Sulfide Minerals by Microbially Produced Ferric Iron

Ferric iron (Fe^{3+}) is the reagent that oxidizes the sulfide minerals. The primary function of the microorganisms is to produce the strong oxidant ($Fe^{3+)}$ for the dissolution of the sulfide minerals (see reaction 6.1); the other role of the organisms is to oxidize the elemental sulfur (S°) (see reaction 6.2) that is usually a by-product of the ferric iron oxidation of the sulfide minerals. Metal ions go into solution as metal cations (e.g., Cu^{2+}, Zn^{2+}, Ni^{2+}); iron is solubilized as Fe^{2+}, which is the energy source for the microorganisms; the corresponding anion is SO_4^{2-}. Reactions 6.4 and 6.5 illustrate the two-stage oxidation of chalcocite (Cu_2S), a common copper sulfide mineral found in supergene deposits.

$$\underset{\text{chalcocite}}{Cu_2S} + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + \underset{\text{blaubleibender covellite}}{CuS} \quad (6.4)$$

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S^{\circ} \quad (6.5)$$

The oxidation of chalcocite, as shown in reaction 6.4, occurs at a relatively low redox potential (370 mV Ag/AgCl electrode; ~600 mV SHE[3]) and is kinetically fast. Because of this, many operators of copper sulfide leach operations consider the first mole of copper produced from Cu_2S as an acid dissolution reaction. However, it is an oxidation-reduction reaction, which consumes ferric iron and must be considered in the air requirement calculations in plant design, because the re-oxidation of the resulting Fe^{2+} by the microbes requires oxygen (see reaction 6.1). The oxidation of Cu_2S also produces CuS (reaction 6.4), often referred to as blaubleibender covellite, but is a member of a series of nonstoichiometric copper sulfides (e.g., dijurleite, $Cu_{1.97}S$; digenite $Cu_{1.8}S$; yarrowite, $Cu_{1.12}S$, etc.) The oxidation of this "CuS" product (reaction 6.5) requires a much higher redox potential (650 mV Ag/AgCl electrode; ~870 mV SHE) than reaction 6.4 and "CuS" is kinetically slow to leach. In heap bioleaching of secondary copper sulfide ores, the slow rate of leaching of the "CuS" product is an important consideration in the design of the leach circuit. In both reaction 6.4 and reaction 6.5, one of the reaction products of the oxidation is ferrous iron, which is then re-oxidized to ferric iron by the iron-oxidizing microorganisms (reaction 6.1). Another reaction product

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[3] Standard Hydrogen Electrode.

of the oxidation of "CuS" is elemental sulfur (S°), which is oxidized to sulfuric acid by sulfur-oxidizing microorganisms present in the leach circuit according to reaction 6.2.

As noted for chalcocite and its oxidation product "CuS", sulfide minerals oxidize at different redox potentials and at different rates. For example, sphalerite (ZnS) oxidizes rapidly at a relatively low redox potential

$$\underset{\text{Sphalerite}}{ZnS} + 2Fe^{3+} \rightarrow Zn^{2+} + S^{\circ} + 2Fe^{2+} \quad (6.6)$$

Chalcopyrite oxidation (reaction 6.7) is thermodynamically favorable in an acidic ferric sulfate system with an oxidation-reduction potential of 427 mV (SHE) (Basson 2010); however, the dissolution of the mineral is severely limited. This has been widely attributed to passivation of the chalcopyrite surface (Warren et al. 1982). The passivation is only overcome at solution redox potentials of greater than 1000 mV (SHE) at low temperatures—redox potentials that are well above those achieved in hydrometallurgy and bioleaching operations—or by operating at temperatures above 60 °C (Crundwell 2014). Crundwell (2014) describes the mechanisms of chalcopyrite dissolution in terms of the semiconductor properties of chalcopyrite and demonstrates how these mechanisms explain the observed passivation. Crundwell's (2013, 2014) theory differs radically from other proposed models of chalcopyrite passivation (Munoz et al. 1979; Dutrizac 1989; Hackl et al. 1995; Stott et al. 2001; Tshilombo et al. 2002; Parker et al. 2003; Majuste et al. 2012, 2013) and provides reasons for slow rates of dissolution irrespective of reaction products formed on the chalcopyrite surface.

$$\underset{\text{Chalcopyrite}}{CuFeS_2} + 4Fe^{3+} \rightarrow 5Fe^{2+} + Cu^{2+} + 2S^{\circ} \quad (6.7)$$

To achieve the oxidation-reduction potential necessary to oxidize the targeted sulfide minerals, there must be sufficient iron in solution; 1 g/L or less of total iron in solution is enough to achieve a redox potential sufficiently high to oxidize most sulfide minerals, assuming most of the iron is efficiently maintained in the ferric form by the microorganisms (Wadsworth 1975). To avoid a decrease in the redox potential, plant conditions must be favorable for sustained oxidation of Fe^{2+} by the microorganisms. The only way to maintain the high redox potential is to ensure that everything the organisms require (O_2, CO_2, acidic conditions, nutrients, optimum temperature conditions, etc.) is optimized. This is normally achievable in stirred-tank reactors, but realizing optimum conditions for the organisms in dump (stockpile) and heap leach operations is much more difficult and usually not consistently attainable.

Precious metals (primarily gold and silver) are often associated with sulfide minerals, principally pyrite (FeS_2) and arsenopyrite (FeAsS). If the precious metals are occluded (embedded) within pyrite, arsenopyrite, or some other sulfide minerals, the ore or concentrate is referred to as being "sulfidic-refractory". In such sulfidic-refractory gold ores and concentrates the gold grains can be submicron in size. To effectively recover the precious metals, the sulfides must be oxidized. In biological processing, this oxidation is accomplished by microbially produced Fe^{3+} that oxidizes the pyrite and arsenopyrite accordingly,

$$\underset{\text{Pyrite}}{FeS_2} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^{+} \quad (6.8)$$

$$\underset{\text{Arsenopyrite}}{FeAsS} + 5Fe^{3+} \rightarrow As^{3+} + 6Fe^{2+} + S^{\circ} \quad (6.9)$$

As^{3+} is oxidized by Fe^{3+} to As^{5+} (see reaction 6.3).

The oxidation of sulfide ores and concentrates by the microbially produced ferric iron is a heat-generating reaction. Different sulfide minerals have differing heats of reaction; pyrite, when oxidized, releases the most heat among the common sulfide minerals (−12,884 kJ/kg of FeS_2). In commercial stirred-tank reactor plants employing biological processing heat generation must be considered in the engineering design.

For example, when biologically processing sulfidic-refractory gold concentrates in which the gold is locked in pyrite, a large amount of heat is generated and the reactors must be cooled. A critical consideration is the design of the cooling circuit.

6.2.2.2 Microbial Attachment of Mineral and Biofilm Formation

Most microorganisms present in biological processing systems are firmly attached to the mineral surfaces while other microorganisms are suspended in the aqueous phase. Microbes initially attach via electrostatic interaction and the attachment is preferentially to sulfur-rich zones and dislocation sites such as cracks, crystal defects, and mineral grain boundaries (Fig. 6.1) (Sand et al. 1999; Noël et al. 2010). Once attached the microorganisms begin producing a biofilm, which is an extracellular polymer principally composed of sugars and lipids. The biofilm eventually consists of a community of different microbes involved in the biological processing of sulfidic ores and concentrates. The polymer constituents in the biofilm complex and concentrate large amounts of ferric iron creating a reaction zone between the biofilm and the mineral sulfide, which significantly enhances the dissolution of the metals beneath the biofilm (Sand and Gehrke 2006; Zhang et al. 2014). The biofilm also serves to protect the microbial community from inhibitory conditions that may exist in the bulk solution.

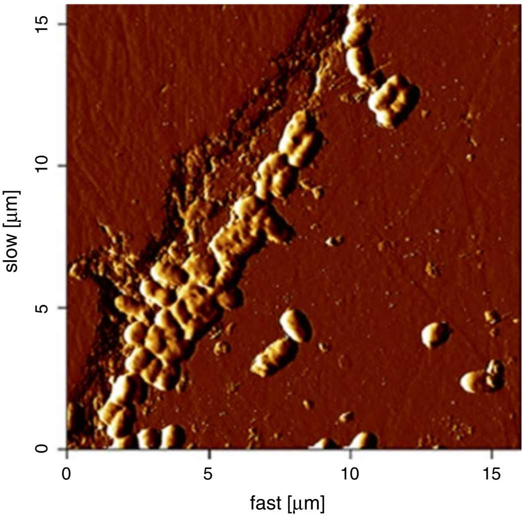

Fig. 6.1 Atomic force microscopy image of *Acidithiobacillus ferrooxidans* attached along a pyrite grain boundary (Noël et al. 2010)

6.3 Evolutionary and Revolutionary Developments in Commercial-Scale Biological Processing of Sulfide Ores and Concentrates

The stage was set in the mid- to late-1950s for the first commercial application of biological processing of sulfide ores, when technical papers were published about the newly discovered bacterium (Colmer and Hinkle 1947) *Thiobacillus ferrooxidans* (now *Acidithiobacillus ferrooxidans*) and its ability to facilitate oxidation of pyrite (Colmer et al. 1950; Temple and Colmer 1951) and other metal sulfides such as chalcocite (Cu_2S), covellite (CuS), chalcopyrite ($CuFeS_2$), and molybdenite (MoS_2) (Bryner et al. 1954; Bryner and Anderson 1957). The first commercial applications were dump (stockpile) bioleaching of submarginal grade, ROM (run-of-mine) copper sulfide ores. These applications led to further developments, which ushered in the contemporary era of biological processing. This section traces technical developments from the early years of commercial-scale biological processing through today's engineered heaps for treating sulfide ores and continuous stirred-tank reactors (CSTRs) for biological processing of concentrates.

6.3.1 Early Practices and Developments in Dump (Stockpile) Bioleaching of ROM Copper Ores

The first patent for commercial use of what became known as bioleaching issued in 1958 and was assigned to Kennecott Utah Copper (Zimmerley et al. 1958). Kennecott's Bingham

Mine near Salt Lake City, Utah (USA) employed the bioleach process at its ROM, copper dump leach operation. This biological process entailed stacking the ROM material in piles to depths of 100 m or more, applying dilute sulfuric acid over the ore piles, allowing the naturally occurring microorganisms to develop, and recovering the dissolved copper from the acidic solution that emerged from the bottom of the pile. The dissolved copper was recovered by cementation on iron, as described centuries earlier by King Liu-An and Paracelsus (Rossi 1990).

The dump leach operations at Bingham Canyon demonstrated to the copper industry that money was to be made by leaching submarginal grade ores. By the mid-1960s many copper operations were leaching submarginal grade, ROM ores in dump leach operations (Sheffer and Evans 1968). However, little was done initially with these ROM dump leach operations to enhance microbial activity. Most operations impounded acidic, ferrous iron-rich solutions from the cementation plant on the top surface of the dump where bacteria oxidized the ferrous iron to ferric iron. The ferric iron solutions in these impoundments flooded the dump material. This flood/leach method severely limited the amount of oxygen reaching the bacteria in the ore, because the solution filled the voids in the ore pile preventing air ventilation of the dump material. As a consequence, the oxygen-starved microbial populations were limited to the first few feet near the top of the dump (Bhappu et al. 1969) where some air was available.

Ironically, deliberate aeration of copper sulfide leach operations had been employed possibly as early at the eighteenth century at Rio Tinto in Spain (Jones 1905; Schlitt 2006). Ore was piled on top of horizontal stone flues that were connected to vertical chimneys surrounded by ore; this system ventilated the ore and increased copper leaching. In 1922, the Ohio Copper Company, which then operated Bingham Canyon, Utah, conducted underground (in-place) leaching of remnant block-caved, low-grade, copper sulfide ore. Rather than flooding the ore pile, solution was applied sparingly so only a thin film of solution flowed over the ore fragments, which prevented the voids in the ore pile to fill with solution. Large fans were placed in the galleries below the ore to ventilate the material, filling the void space in the ore pile with air (Anderson and Cameron 1926; Schlitt 2006). These measures increased the temperature in the ore pile as the microbial population produced ferric iron, which oxidized the sulfide minerals generating heat. Copper recovery also improved. However, the benefits of sparingly irrigating the ore and using aeration seemed to have been forgotten or ignored by dump leach operators and metallurgists when the ROM leaching process was reintroduced in the late 1950s and early 1960s.

By the 1970s, with increasing publication of research on the role of bacteria in dump leaching and the oxygen requirements of these microorganisms (Beck 1967), dump leach operators and metallurgists realized the importance of getting air into the dumps. The Anaconda Company experimented with “finger dumps” at Butte, Montana to increase exposure of the sides of the ore piles to the atmosphere (Robinson 1972). While effective in improving dump ventilation, finger dumps were somewhat impractical, because of the increased area needed for the ore piles. Pre-wetting of ROM dumps with acidified water, as the dumps were being built, was also initiated at Butte, Montana by the Anaconda Company (Schlitt 2006) and much later implemented during construction of the leach dumps at Toquepala in southern Peru (Gonzales and Nees 1996). At Butte, the acid-conditioned dumps were also aerated using horizontal and angled holes drilled into the face of the dump and cased with pipe through which air was blown. During the first leach cycle following pre-wetting and aeration, the copper tenor at Butte was twice that normally noted for similar dumps. The ultimate copper recovery was about 15 % greater than was typically obtained (Schlitt 2006). Other dump leach operations followed this practice of forced aeration with some variations including drilling and casing of vertical holes in assorted patterns. These efforts, which did improve copper recovery, have been summarized by Schlitt (2006). However, paradoxically none of these aeration tests performed in the 1970s led to widespread commercial use of forced aeration in dump leach operations over the ensuing 40 years.

The value of leach/rest cycles was also recognized early as a technique to promote improved copper extraction from ROM dumps. Rest cycles allow hold-up solutions in dumps to drain letting air fill the voids with subsequent oxidation of sulfide minerals by the microbially generated ferric iron; the sulfide oxidation heats the gases in the interior of the dump. The increased buoyancy of the heated gases induces convective air flow from dump faces. Leach cycles wash out dissolved copper and other soluble ions and add moisture to the ore bed to enhance microbial activity (Brimhall and Wadsworth 1973).

The development of solvent extraction technology for the recovery of copper from acidic leach solutions (pregnant leach solution, or PLS) coupled with electrowinning to produce cathode copper revolutionized the copper industry in the mid-1960s (Kordosky 2002). ROM dump leach plants converted from cementation to solvent extraction/electrowinning (SX/EW), which improved leaching practices by significantly reducing the amount of iron that was being added to the ore pile. Cementation had added large amounts of soluble iron to the leach solution

$$\mathrm{Cu}^{2+}(\mathrm{aq}) + \mathrm{Fe}(\mathrm{s}) \rightarrow \mathrm{Cu}(\mathrm{s}) + \mathrm{Fe}^{2+}(\mathrm{aq}) \quad (6.10)$$

and when this iron was oxidized by the bacteria, jarosite, a basic hydrous ferric sulfate compound, often precipitated in the impoundments on the top surfaces of the dumps that were initially used for the flooded leach process

$$3\mathrm{Fe}_2(\mathrm{SO}_4)_3 + 12\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{HFe}_3(\mathrm{SO}_4)_2(\mathrm{OH})_6 \downarrow + 5\mathrm{H}_2\mathrm{SO}_4 \quad (6.11)$$

When new ore was placed, often by truck dumping, where the impoundments had been, the surface became compacted eventually resulting in impermeable layers within the dump where leach solutions would collect. This caused saturation of portions of the dump restricting aeration and also resulting in poor contact of the ore with the leach solution below the compacted zones. Dump leach operations, now generally referred to as "stockpile" leaching, usually remain active for many decades. Submarginal grade materials are continually being added to stockpiles as mining of huge open-pit operations continues creating massive volumes of material under leach. Consequently, some stockpiles under leach today still experience compaction and saturation problems resulting from poor practices carried out decades earlier.

6.3.2 Innovations in Heap Bioleaching/Biooxidation of Coarsely Crushed Sulfide Ores

6.3.2.1 Copper Sulfide Heap Bioleaching

The revolutionary innovation of solvent extraction/electrowinning (Kordosky 2002) in the mid-1960s allowed copper companies to leach copper oxide ores in ROM and coarsely crushed ore heaps and produce a high quality cathode copper product. The leaching of oxide ores is accomplished by irrigating with dilute sulfuric acid. Oxide ore minerals do not require an oxidation step and copper recovery is typically excellent. However, heap leaching of copper sulfide ores is another story, because an oxidation step is required.

The "thin layer" (TL) acid cure process, originally developed for copper oxide ores, was adapted for bacterial ferric iron leaching (termed "BTL") of mixed oxide/sulfide ores by Sociedad Minera Pudahuel (SMP), which applied the process at the company's Lo Aguirre mine in Chile (Bustos et al. 1991). The BTL process resulted in good copper recovery from both oxide and sulfide ores. The BTL process was soon implemented by Compañia Minera Quebrada Blanca and Cerro Colorado, both in Chile, to leach secondary copper sulfide ores, containing chalcocite and blaubleibender covellite, in the mid-1990s (Bustos et al. 1993). At Quebrada Blanca, ore is crushed in three stages to 100 % minus 9 mm, heated to increase the ore temperature, agglomerated with sulfuric acid and 85 °C water, and conveyed to the stacking area. The ore is stacked to form 6–6.5 m high lifts. After field trials at Quebrada Blanca in the mid-1990s demonstrated enhanced copper recovery with forced ventilation, aeration lines were placed under each lift to provide oxygen for the bacteria. Low-pressure fans were used to ventilate the heap. Shade cloth was placed on the top of the heap to reduce evaporative cooling. After the lift was effectively leached, the top surface was compacted, drain lines were placed on the compacted surface, and air lines were strategically placed above the drain lines in the ore to avoid solution from entering the air lines as a result of phreatic head. Another lift was stacked and leached (Schnell 1997). Similar practices were employed by Girilambone Copper Company at the company's copper heap leach operation in New South Wales, Australia (Schlitt 2006).

Heap bioleaching of crushed secondary copper (supergene) ores is regarded today as a conventional process given the number and size of these facilities and the overall contribution to global copper production (Brierley and Brierley 1999, 2013). Copper recovery for these coarse ore, secondary heap leaching plants is typically in the 80–90 % range of "recoverable copper", which is defined as the copper associated with the oxide and the supergene mineral assemblages (Scheffel 2006); "recoverable copper" does not include copper associated with the hypogene mineral assemblages. Secondary copper heap bioleaching is often described as a flexible and simple technology; however, this descriptor is misleading, because notwithstanding the general success of these plants, operating issues arise. Identifying and resolving these issues involve a multidisciplinary approach, because the problems are almost never the result of a singular factor (Brierley 2014).

Many problems encountered in secondary copper ore heap bioleaching are attributable to insufficient knowledge of the resource over life-of-mine (Ausburn and Baum 2014; Milczarek et al. 2014). The ore body may not have been adequately characterized from geological, mineralogical, chemical, metallurgical, and biological perspectives. Examples of insufficient characterization that result in later processing problems are

- Inadequate evaluation of the matrix rock for its acid consumption properties
- Lack of detailed mineralogical examination (Ausburn and Baum 2014) to identify ore minerals and expose potential locking of ore minerals within unreactive matrix rocks
- Insufficient chemical, metallurgical, and biological testing of representative samples to correlate ore mineralogy data with ore reactivity, quantify reagent consumption, assess leach kinetics of each copper sulfide mineral, estimate heat balance, confirm oxygen requirements, and assure microbial viability and activity in the ore and leach solution over time (du Plessis 2014)
- Failure to sufficiently evaluate the ore over life-of-mine and the water source for potentially toxic constituents (e.g., chloride, fluoride and nitrate) using appropriate column tests to assess dissolution of these constituents over time and their effect on the microorganisms (Brierley and Kuhn 2010)
- Failure to adequately test hydrologic characteristics and physical integrity of the ore that affect solution and air permeability and establish heap height, method of heap leaching (multi-lift, single lift with between lift liner, on-off pad), and aeration and irrigation strategies (Milczarek et al. 2014)

Once the heap bioleach is in operation, solving problems that may have been averted or at least diminished somewhat by rigorous upfront characterization is challenging and necessitates consideration of the chemical, microbiological, metallurgical, and hydrological factors. Some of the most frequently encountered problems in secondary copper heap leaching are inadequate permeability (Milczarek et al. 2014) of the ore bed to air and solution caused by excessive fine particles and/or clays in the ore when stacked, poor agglomeration of the ore, compaction by truck-stacking (when used), decrepitation of the ore by the leach solutions, and over-irrigation once the heap is stacked. These factors lead to poor wetting of the ore, preferential flow paths within the heap, impermeable layers, and solution saturation of the void spaces in the heap that displaces air. The result is inadequate distribution of microorganisms in the heap, poor microbial population development, and slow rates of microbial iron, and sulfur oxidation. The manifestation is declining redox potentials as ferric iron consumption outpaces the rate of microbial iron oxidation, decreasing copper tenor in the PLS, inability to leach the covellite reaction product of chalcocite leaching as the redox potential declines, and ultimately poor overall copper recovery (Brierley 2014).

Suboptimal temperatures in secondary copper sulfide heaps—particularly those located at high altitudes, such as the Andes Mountains, and the high deserts in temperate climates—are also a common problem. Heap temperatures can range from 10 °C or less in the winter to 20 °C or slightly higher in the summer. The microbial oxidation rate of iron slows as the temperature declines resulting in decreased dissolution of copper sulfide minerals with the consequence of less copper production. Sulfide oxidation is an exothermic reaction with the amount of heat generated dependent on which sulfide mineral is being oxidized, the amount of sulfide oxidized, and the rate at which it is oxidized. Although pyrite oxidation generates the greatest amount of heat of the sulfide minerals common to secondary copper sulfide deposits, pyrite content is frequently low in secondary copper sulfide ores, particularly in supergene ores, and the pyrite that is present often doesn't oxidize to any great extent. A probable reason for its non-reactivity is electrochemical; pyrite, unless it is amorphous or has substitutions in the crystal lattice that destabilize the structure, typically has a higher rest potential[4] than chalcocite and covellite and will not oxidize until the minerals with the lower rest potentials have oxidized. By the time the redox potential of the leach solution in the heap is sufficiently high to oxidize pyrite, the recoverable copper has been extracted. Some operations use thermal covers (Petersen and Dixon 2007) to minimize heat loss from the top surface of the heap due to evaporation and night-time radiation, to take advantage of solar heating, and to capture the heat that is generated from the oxidation of the copper sulfide minerals. This technique assists in raising the heap temperature a few degrees Celsius. Other operators have used waste heat from onsite power generation to warm agglomerated ore being placed on the heap (Schnell 1997) and submerged combustion units to heat raffinate. Benefits of ore and raffinate heating are difficult to quantify, however. Excessive irrigation is a contributing factor to heat loss in a heap (Dixon 2000). Over-irrigation causes heat loss to the PLS and can diminish the rate of oxidation of sulfide minerals, because of potential heap saturation that results in exclusion of air from void spaces within the ore bed. Excessive irrigation is particularly a problem in operations that have been acid leaching oxide ores and are transitioning to secondary copper sulfide ores. The dissolution of copper from oxides is dependent on delivering acid to the ore mineral, so the irrigation and solution application rates are important components of the process. Whereas, the leaching of copper sulfide minerals is little affected by the rate of irrigation or solution application rate and over application and irrigation will eventually decrease solution copper grades (Bartlett 1998). Slower application rates and implementing extended rest cycles, which allow heat to build in the heap, with controls to ensure that the heap does not dry out, aid in mitigating the issues associated with cool heap temperatures.

Aeration of secondary copper heaps was first evaluated in the mid-1990s (Schnell 1997; Walsh et al. 1997; James and Lancaster 1998). Today, many but not all, secondary copper heap leach operations employ forced aeration of the heaps (Scheffel 2006). The purpose of forced aeration is to provide oxygen and CO_2 for the microorganisms to maximize the population and enhance oxidation rates. The need to aerate is based on multiple variables across the multidisciplinary areas pertinent to heap bioleaching. Heap construction is a significant factor; for example, if the heap is a valley fill with only one sloping

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[4] The rest potential of a mineral is that electro-potential at which the mineral will undergo corrosion. Minerals can be arranged in a galvanic (electro-potential) series for a specific electrolyte, such as acidic ferric sulfate. The more noble (resistant to corrosion/oxidation) the mineral, the higher it is in the galvanic series.

face open to the atmosphere, forced aeration may be a necessity. However, forced aeration may not be necessary, if the heap faces are well exposed to the atmosphere, the ore is quite permeable and the sulfide content of the ore is low, because convective air flow into the heap may be sufficient to sustain good microbial activity. The amount of time to oxidize the copper sulfide minerals may be longer than if forced aeration is used, but this may not be an important consideration, depending on pad space, heap design, and other factors (Scheffel 2006). Column testing with and without forced aeration may or may not predict whether forced aeration is required. Often sufficient air enters a typical metallurgical column test so the leach results from aerated column tests may be similar to those of non-aerated columns. Onsite pilot tests, which are not always completed for secondary copper sulfide ores, may also show forced aeration is unnecessary, because pilot tests are often of small tonnage and the heap may be exposed on the four sides to the atmosphere.

Despite some continuing challenges with commercial-scale leaching of secondary copper ores, the technology is the springboard to the more difficult undertaking of low-grade primary copper ore[5] bioleaching. It is imperative that technology is developed to economically and effectively leach low-grade primary copper ores, because 80 % of the world's copper resources is low-grade chalcopyrite; the grade of this resource is typically too low to concentrate and can't be economically processed other than by ROM stockpile or coarsely crushed heap leaching (Robertson et al. 2005). Meanwhile, stockpiles of ROM, chalcopyrite-bearing material mount at some mining operations as companies seek ways to retrofit existing stockpiles with technologies to enhance copper extraction and large deposits of low-grade primary copper sulfide ores have been discovered (du Plessis 2014).

6.3.2.2 ROM and Crushed Ore Heap Bioleaching of Low-Grade Primary Copper Ores—An Imperative Emerging Technology

It was readily apparent in the early 1960s that copper extraction from chalcopyrite-bearing ores was very poor, which led to active research programs on low-grade chalcopyrite leaching in the 1960s and 1970s (Dutrizac et al. 1969; Wadsworth 1972; Dutrizac and MacDonald 1974). Unfortunately research efforts precipitously declined in the late 1970s and early 1980s with the drop in world copper consumption and ensuing recession of the early 1980s (OTA 1988). With revival of the copper industry in the late 1980s, research efforts directed toward hydrometallurgical processing of copper sulfide minerals and chalcopyrite, in particular, gained momentum. However, much of the research was directed toward concentrates (Watling 2006). Research on bioleaching low-grade primary copper ores was seemingly a low priority. More than two decades have elapsed since the resurgence of the copper mining sector that stimulated research, but there is meager information in the published literature on bioleaching primary copper ores. As pointed out by Watling (2013), published studies on primary copper ores too often suffer from inadequate data on the mineralogy and chemistry of the samples used and the test work methodology to be of significant value.

What is known is that chalcopyrite ores tend to leach slowly and incompletely in an acidic ferric sulfate leaching solution at ambient temperature; about 10–20 % of the copper may be extracted before leaching ceases (Watling 2013). The sluggish nature of chalcopyrite bioleaching has been attributed to the mineral's crystalline structure and the changes it undergoes during acidic ferric sulfate leaching and/or passivation of the mineral in the potential range of approximately 640–840 mV (SHE) (Watling 2013). Three hypotheses have been proposed for the nature of the passivating layer: formation of a sulfur layer (Dutrizac 1989; Munoz et al. 1979); formation of copper polysulfide (Hackl et al. 1995; Tshilombo et al. 2002; Majuste et al. 2012); and precipitation of

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[5] Chalcopyrite and enargite are "primary" copper minerals and are found in ore deposits of various geological origins. These primary minerals have not undergone alteration by weathering and are characterized as being refractory (difficult to leach).

iron compounds (Parker et al. 2003). There is little question whether these products form during chalcopyrite bioleaching; the debate centers on whether the slowing and ceasing of chalcopyrite leaching are, in fact, the result of the formation of any of these over-layers (Crundwell 2013, 2014; Holmes and Crundwell 2013). Copper leaching is enhanced when pyrite is in direct contact with chalcopyrite due to the galvanic interaction between the two minerals (Nazari 2012) as chalcopyrite corrodes more rapidly than the pyrite. However, pyrite from different sources affects the rate of chalcopyrite leaching differently; some exert no influence while others, particularly pyrite containing silver, significantly enhance the rate of chalcopyrite leaching (Nazari 2012).

Research in the 1970s showed the thermophilic microorganisms, especially the extremely thermophilic archaea, improved the leaching of chalcopyrite ore (Brierley 1977) and the presence of these microorganisms accelerated galvanic leaching of the ore in the presence of pyrite (Berry et al. 1978). This research led to a large (6.4 t) long-term (2165 days) column leach test to evaluate bioleaching of a minus 15 cm, chalcopyrite-bearing ore (0.77 % Cu) starting at ambient temperature followed by 50 °C and finally 60 °C (Madsen and Groves 1983). Copper extraction rate increased substantially when the archaea were established in the column at 60 °C, however, the rate was not sustained past about 120 days. The decline in copper leach rate was attributed to the depletion of exposed chalcopyrite minerals in the ore, since the ore had been under leach for over 2000 days (Madsen and Groves 1983). Since 1983, research on ores and concentrates has confirmed chalcopyrite leaching is significantly enhanced using archaea at 60–82 °C (Watling 2013).

Many of the ROM stockpile bioleaching operations that have been operational for decades do contain chalcopyrite (Sheffer and Evans 1968; Gonzales and Nees 1996; Neira and Pearson 2012) and have in the past and continue to demonstrate profitable copper recovery. The percentage of copper leached from chalcopyrite in ROM stockpile operations has not been well documented over the decades often because the composition of the material placed on the early dumps was not carefully analyzed. Nevertheless, documented leaching of chalcopyrite occurs in some ROM stockpile operations, such as Toquepala in southern Peru, where about 80 % of the copper is present as chalcopyrite (Gonzales and Nees 1996) and Pinto Valley operations in Arizona (Neira and Pearson 2012). What characterizes ROM heap (dump) operations reporting chalcopyrite leaching? As early as the mid-1960s temperatures of 60–80 °C were documented in some low-grade dump leach operations with chalcopyrite ore and an increasingly rapid rate of copper solubilization at about 45 °C was noted in these operations (Beck 1967). Beck attributed this to chemical reactions rather than to bioleaching, because thermophilic bacteria and archaea were not known at the time and bacterial oxidation with the known mesophilic bacteria had been shown to be minimal at 40–50 °C. Increasing temperature in stockpiles is attributable to heat generation from pyrite oxidation, which will occur after leaching of sulfide minerals with lower rest potentials, have oxidized.

A pilot test at Kennecott's Bingham Canyon, Utah (now Rio Tinto Kennecott), initiated in 1995 and concluded in 1999, was a ROM heap with two lifts totaling 1.4 million t of ore grading 0.26 % Cu of which 0.17 % Cu (or about two-thirds of the copper) was associated with chalcopyrite. Details of the heap operation and performance have been published (Ream and Schlitt 1997; Schlitt and Ream 1997; Esdaile et al. 1999). Pyrite oxidation occurred, which maintained the temperature some 30 °C above ambient. Forced aeration was evaluated to see how it would affect oxygen levels in the heap; aeration was used on approximate 3 weeks cycles followed by a 2.5 week interlude. Overall, forced aeration didn't appear to significantly affect the copper leach rate. The elevated temperatures in the heap resulting from pyrite oxidation appeared to enhance natural convective airflow. While temperatures were independent of forced aeration, irrigation did influence the temperature. Modeling suggested that flushing water through an area of the heap would cool it down. It was also reported (Esdaile et al. 1999) that airflow rates increased during rest periods (no irrigation) and decreased when the area was under irrigation, suggesting that even a low irrigation rate causes some air-filled void spaces to flood. Copper recovery in the second lift approached 25 % in 13 months of leaching, although this recovery did include a contribution from the original lift.

At the Pinto Valley operation in Arizona (USA), low-grade (0.15 % Cu) chalcopyrite ore with a pyrite content of 0.7–1 % is bioleached in ROM stockpiles varying in depth from 15 to 182 m. Some 300 million tonnes of ore are under leach with an effective leach area of 144 ha. Copper recovery is 28.3 %. Three-dimensional modeling and a geophysical survey of the stockpiles have been used to identify areas of low permeability and solution saturated areas. Temperature and oxygen monitoring and a geotechnical site investigation have been conducted to better understand conditions within the stockpile that promote chalcopyrite leaching. Based on data from the characterization, improvements in irrigation have been made by skimming about 1 m off the top of the stockpiles to increase permeability and by acid injection to selected stockpiles where new ore has been added. Pyrite oxidation was found to be most effective near dump faces exposed to the atmosphere and this coincides with areas where the highest dump temperatures are recorded, as would be expected. Long rest periods and short leach cycles have also allowed temperatures in the dump to increase and the corresponding increase in oxygen with this regime has increased chalcopyrite leaching. The results of the characterization at Pinto Valley have the company looking to employ forced aeration of new dumps to improve performance (Neira and Pearson 2012).

Engineered heap technology was implemented in early 2006 at the Morenci, Arizona operations of Freeport McMoran Copper and Gold, Inc., with the objective of shortening the time scale required for chalcopyrite leaching by increasing the temperature in ROM stockpiles (Ekenes and Caro 2012). The engineered stockpiles, comprising an area of 0.5 million square meters, were equipped with aeration lines and monitoring wells and the stockpiles were drilled periodically to obtain solid samples for mineralogical and chemical analyses. The engineered stockpiles were initially inoculated with native bacteria via bio-augmented raffinate; bio-augmentation ceased after a period of time. The first measurable change observed was an increase in iron concentration in the PLS. The temperature of the engineered stockpiles increased over time and with placement of additional lifts the stockpile temperature was no longer adversely affected by seasonal temperature changes. The highest observed temperature in the stockpiles after about 2 years of operation and three lifts was in the 50–55 °C range. Pyrite oxidation was evident not only by increasing stockpile temperature and increasing PLS iron concentration but also by the amount of acid generated within the stockpiles. Copper recovery was not published, but it was noted that copper recovery outperformed the company's life-of-mine model by 25 % (approximately one million kg per month) (Ekenes and Caro 2012).

What has been learned from research, pilot plant operations, and ROM stockpiles containing chalcopyrite? Temperature is a critical factor in leaching low-grade primary copper ores. Getting temperatures in the heap into the thermophilic range of 60 °C and above is necessary to overcome the factors that cause leaching to slow and cease (Dew et al. 2011; Lee et al. 2011; Crundwell 2014). As pointed out earlier in this chapter, a high redox potential (>1000 mV SHE) is required to oxidize chalcopyrite at temperatures below 60 °C because of mineral passivation or the inherent mechanism of dissolution due to the semiconductor properties of chalcopyrite (see reaction 6.7). Such a high redox potential is very unlikely to be achieved in heap leaching. The most important consideration in heap leaching low-grade chalcopyrite is to increase the temperature in the heap to 60 °C and above through the oxidation of pyrite (Dew et al. 2011); pyrite oxidation requires a high solution redox potential (about 800–900 mV SHE) depending on the mineralogical nature of the pyrite.

Heap leaching primary copper minerals requires approaches that allow heat to build and be maintained in the heap. The amount of pyrite present in the ore and the rate at which it is leached are important considerations. Judicious control of solution application to avoid loss of heat in the PLS and to enhance convective air flow are critical; long rest/short leach cycles are an important component to this. Forced aeration must be considered on a case-by-case basis and its benefits are dependent on heap construction, permeability of the ore bed, the amount of pyrite present, the rate of oxidation of pyrite, heap temperature and other geotechnical, chemical, mineralogical, hydrological, and biological factors. Heap inoculation with the extremely thermophilic archaea will be necessary to operate the heap at temperatures above 55–60 °C (Logan et al. 2007), as there is little evidence the extremely thermophilic archaea will develop naturally in the heap or stockpile. In order to be successful, substantially more control of heap operating parameters is necessary for primary ore heap leaching than for secondary copper heap leaching.

6.3.2.3 Heap Bioleaching of Other Metal Sulfides

Heap and ROM stockpile bioleaching of other sulfide minerals, such as sphalerite, nickel sulfide minerals, and cobalt sulfide, is carried out similarly to that of heap bioleaching of copper sulfide ores. The same operational principles apply, however, the metals solubilized in the PLS are often recovered by methods other than solvent extraction. To date, only one major heap bioleach of a complex base metal sulfide ore has operated.

Bioleaching of a black schist deposit in Finland was initiated in 2008. The Talvivaara mine is one of the largest nickel deposits in the world. The sulfide content of the ore varies from 15 to 20 % and the sulfide minerals are pyrrhotite, pyrite, pentlandite, sphalerite, violarite, and chalcopyrite. The average grade of the ore is 0.23 % Ni, 0.50 % Zn, 0.13 % Cu, and 0.02 % Co (Saari and Riekkola-Vanhanen 2011). The complex mineralogy of Talvivaara and the project's location near the Arctic Circle make heap bioleaching challenging. Pyrrhotite oxidizes quickly and rapidly, consuming acid, requiring oxygen (2.25 kg O_2/kg S^{2-} as pyrrhotite), and generating heat. Initial temperatures in the heap are sufficiently high to support the extremely thermophilic archaea. However, as leaching progresses, temperature declines. The high acid consumption of pyrrhotite requires considerable initial acid addition, but acid is produced later in the leach cycle when pyrite oxidizes. Considerable attention to acid balance over the entire leach cycle is therefore required to operate such a complex circuit.

The Talvivaara heap leach has been managed as an on-off pad. After oxidation of the pyrrhotite and most of the sphalerite and pentlandite, the ore has been removed from the pad and placed in another pad area for secondary leaching. In the secondary bioleach pyrite and chalcopyrite leached along with cobalt, which is locked in the chalcopyrite matrix. Copper, nickel, cobalt, and zinc recoveries from PLS have been accomplished using gaseous hydrogen sulfide and pH control (Riekkola-Vanjanen and Palmu 2013).

6.3.2.4 Heap Biooxidation Pretreatment of Sulfide-Refractory Gold Ores

Heap biooxidation pretreatment entails the biooxidation of sulfide minerals, usually pyrite (FeS_2), arsenopyrite (FeAsS), or both, to expose micrometer-sized gold particles locked (embedded) within the sulfide matrix. The refractory-sulfidic ore is agglomerated with an acidic solution containing microorganisms. Because the ore heats during the biooxidation process as a result of pyrite and arsenopyrite oxidation, the ore is typically inoculated with mesophilic, moderately thermophilic, and extremely thermophilic microorganisms. When the heap biooxidation process is initiated, the microorganisms are cultured in a bioreactor. However, once the process is underway, fresh ore is conditioned and inoculated with effluent solution from the heap. The acid-conditioned, inoculated, and agglomerated ore is stacked on a HDPE lined pad on which is placed a layer of crushed rocks. Within the crushed rock layer is an array of perforated pipes for forced aeration of the ore pile. Low-pressure fans provide air for the ore heap (Logan et al. 2007). The heap is subjected to leach/rest cycles to conserve heat within the heap and to ensure drainage of the heap to allow void spaces to fill with air. Oxygen requirements can be high, depending on the amount of sulfide to be oxidized and the rate of oxidation.

Initially the stacked ore will be at ambient temperature, but as the sulfide minerals—particularly pyrite–oxidize, the ore bed heats. Initially the mesophilic microorganisms will be active, but as the temperature increases in the ore bed those organisms that are active at higher temperatures will be dominant. Eventually the extremely thermophilic archaea will dominate in those areas of the heap reaching temperature of more than 55–60 °C (Brierley 2003).

Once sufficient sulfide is oxidized to expose the gold, the heap is irrigated with fresh water to remove acid and soluble iron. This is an important step to avoid hydrogen cyanide production and to reduce cyanide consumption, because iron reacts with cyanide and can increase consumption to the point of making the process uneconomic. The oxidized and rinsed ore is then neutralized with lime. The neutralized ore can then be re-stacked and leached with a dilute cyanide solution to leach the gold. Alternatively the washed and oxidized ore can be lime-treated and milled in a CIL (carbon-in-leach) circuit to leach the gold with cyanide (Logan et al. 2007). Cyanide leaching requires a large pH change in the oxidized ore. Thiocyanate has been studied as an alternative to cyanide for extraction of gold from biooxidized residues, because thiocyanate can be used under acidic conditions (Li et al. 2012a, b, c, d, e). However, thiocyanate chemistry is complicated and consumption of the reagent can be unacceptably high, if conditions are not carefully controlled.

To date, only one industrial-scale plant for the biooxidation pretreatment of sulfidic-refractory gold ores has operated. Newmont Mining Company developed and employed the process to biooxidize a low-grade gold ore (about 2.64 g Au/t ore) at Gold Quarry, Nevada (USA), from 1999 to 2006 with more than 8.8 million t of ore biooxidized and about 12.2 t of gold recovered (Logan et al. 2007; Brierley and Brierley 2013).

Some gold ores are termed “double-refractory” because not only is the gold encapsulated in a sulfide mineral, but the ores contain carbonaceous matter, which adsorbs the gold-cyanide complex resulting in gold losses. This latter phenomenon is called “preg robbing”. Mitigating preg robbing with microorganisms has been researched (Brierley and Kulpa 1992, 1993; Kulpa and Brierley 1993; Ofori-Sarpong et al. 2013), but a process has not been engineered or economically assessed.

6.3.3 Biological Processing of Sulfidic Ores in Vats

Although vats have been used extensively for leaching oxide ores and for cyanide leaching, vats have not been developed for biological processing of sulfidic ores. Nevertheless, some of the hydraulic and gas diffusion inefficiencies, inherent in many low-grade ore heap leaching operations, might be overcome using a saturated, continuous leaching reactor, designed for coarse ore particles in the 3–6 mm range (du Plessis et al. 2013; du Plessis 2014). Vat leaching could be considered a hybrid technology between conventional coarse heap leach technology and CSTR technology for sulfidic concentrates. The goal of vat biological processing is to have high-rate leaching kinetics by overcoming the diffusion-related limitations encountered in heap leaching. Vat leaching may be particularly useful for leaching chalcopyrite ores, because redox conditions could be controlled more effectively and diffusion limitations often inherent in leaching chalcopyrite might be overcome in a saturated reactor. The technology may also be useful in oxidizing ores that have lengthy leach times with high acid consumption; the shortened leach cycle of a vat with smaller particle sizes than a heap leach may be more efficient and cost effective by reducing acid consumption (du Plessis 2014). Vat technology for biological processing has not yet been developed for commercial use.

6.3.4 Stirred-Tank Biological Processing of Sulfide Concentrates

CSTR biological processing of sulfide concentrates was pioneered by Gencor Process Research, Johannesburg, with the first commercial plant for sulfidic-refractory gold concentrate processing commissioned in 1986 at the Fairview mine in South Africa. Commissioning of three BIOX® plants soon followed: Harbour Lights in 1992 and Wiluna in 1993, both in Australia; and Sansu, Ghana in 1994. In 1990, the São Bento mine in Brazil installed a single BIOX® reactor in series with two pressure oxidation autoclaves. In total, 13 BIOX® plants have been commissioned. Six plants have subsequently been decommissioned (van Aswegen et al 2007; Biomin 2014; van Niekerk 2015). The largest BIOX® plant in operation is Kokpatas, Uzbekistan, commissioned in 2008, which processes 2138 t/day of sulfidic-refractory gold flotation concentrate. In 2013, Biomin South Africa (Pty) Limited acquired the BIOX® technology patents and Biomin continues development of the technology and is responsible for implementing the process at mining operations around the world.

Other CSTR biological processing technologies have been developed and implemented at commercial scale. BacTech commissioned three plants for biological processing of refractory-sulfidic gold concentrates: Youanmi, Western Australia, 1994; Beaconsfield, Tasmania, 1998; and Shandong, China, 2000. BIONORD®, a technology developed and owned by Polyus Gold, is used at the company's Olimpiada mine in Russia for sulfidic-refractory gold concentrate. BRGM, France, developed the BROGIM CSTR bioleach process for a polymetallic concentrate in Uganda (Morin and D'Hugues 2007). The Kasese Cobalt plant, commissioned in 1997, is the only currently operating stirred-tank biological process for base metals. The plant recovers cobalt, nickel, and copper.

All CSTR biological processing plants for pretreating sulfidic-refractory gold concentrates operate on basically the same principles and with the same process flow sheet (Fig. 6.2). The concentrate, which may be re-ground depending on gold recoveries in the mini-pilot plant run, is fed from the flotation circuit to a surge tank where

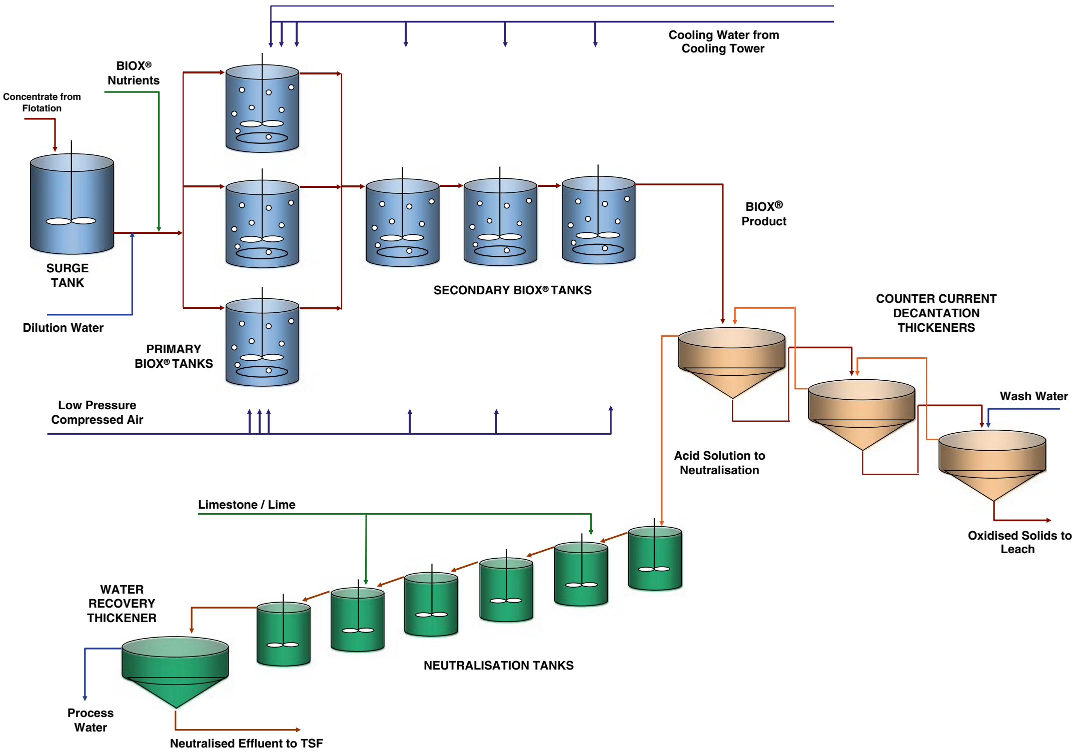

Fig. 6.2 Typical flow sheet for continuous stirred-tank biological processing of sulfidic-refractory gold concentrates (Courtesy of Biomin South Africa (Pty) Ltd.)

water is added. The biooxidation circuit is ordinarily configured with three primary reactors in parallel; this allows for a longer retention time of the solids to establish the microbial population and allows attachment of the microbes to the sulfide minerals. This prevents "wash-out" of the microorganisms from the circuit. The primary stage is followed by three (or more) secondary reactors in series.

Concentrate from the surge tank is typically diluted to 20 % solids before being fed along with nutrients (nitrogen, phosphorus and potassium salts) from a make-up tank by a feed splitter to the three primary reactors. The reactors are constructed of stainless steel to withstand the low pH and highly oxidizing conditions. Low pressure, compressed air is injected into the reactors through a diffuser ring at the bottom of the biooxidation reactor. Each reactor is equipped with a stainless steel impeller, which circulates slurry and breaks-up air bubbles from the sparge ring located directly below the impeller. The biooxidation reactors are equipped with internal cooling coils through which water is circulated from a cooling tower, because of the large amounts of heat generated from the oxidation of the sulfide minerals in the concentrate (Fig. 6.2).

The BIOX® technology underwent further development in 2013 and 2014 with the introduction of dual axial flow turbines for efficient dispersion of air in the biological reactors. This impeller design was installed at the Runruno plant in the Philippines. Development is underway for use of high-temperature microorganisms in at least one of the reactors to improve oxidation of reduced sulfur compounds produced from the ferric iron oxidation of sulfide minerals. Reduced sulfur compounds are cyanicides that increase cyanide consumption, which adds operating costs to the process. The thermophilic microorganisms, particularly the archaea, are more efficient at oxidizing these sulfur products, which should assist in reducing cyanide consumption.

Before plant commissioning, a microbial culture of mesophilic and thermo-tolerant microorganisms, adapted to the concentrate and used during laboratory piloting, is brought to the mine site and scaled-up in an onsite bioreactor. The industrial-scale reactors are started in batch using the microbial culture from the onsite bioreactor. The biooxidation circuit is then converted to continuous operation during commissioning (Fig. 6.3). CSTRs typically operate in the 40–45 °C range at a pH range of 1.1–1.5. pH is controlled in the reactors by adding limestone. The residence time of the mineral solids across a typical two-stage biooxidation circuit is 5 days. The percent of the sulfide to be oxidized for optimal gold recovery is determined in the lab in batch tests and during the mini-pilot plant phase. The plant is then designed for that percent sulfide oxidation, because the capital and operating costs of the plant are based largely on the amount of sulfide requiring oxidation. After the final stage of biooxidation, the contents of the reactor are subjected to solid/liquid separation. The solution is neutralized with limestone followed by lime before discharge to tailings. Any arsenic that leached during biooxidation is precipitated as stable ferric arsenate that meets environmental standards for disposal. The solids containing the gold are water washed in counter-current decantation thickeners before being directed to the neutralization tanks for treatment with limestone and lime. The neutralized slurry is then thickened; the water is recovered for reuse and the thickened oxidized residue is cyanide leached to extract the gold (Fig. 6.2). Gold recoveries in CSTR plants (Fig. 6.3) are typically in the range of 95–98 % (Brierley and Briggs 2002; van Aswegen et al. 2007).

When base metal sulfide concentrates are bioleached in CSTRs the metal of value is in the solution from the last stage reactor. The base metals can be recovered from solution by standard technologies including solvent extraction/electrowinning for copper, sulfide precipitation, or other methods.

The BioCOP™ process, developed by Billiton in the late 1990s and early 2000s, was specific for treatment of refractory copper sulfide concentrates not suitable for commercial smelting due to the content of deleterious elements, such as arsenic. The process utilized extremely thermophilic archaea operating at temperatures up to 85 °C. The solubilized copper was subsequently recovered by conventional solvent extraction and

Fig. 6.3 CSTR biooxidation circuit at the Kokpatas, Uzbekistan BIOX® plant (photo courtesy of Biomin South Africa (Pty) Ltd.)

electrowinning, producing a high value copper metal product. After considerable pilot testing in South Africa a 20 ktpa (cathode copper) prototype unit to prove the extremely thermophilic BioCOP™ technology was constructed and began operation in 2003 at CODELCO's Chuquicamata mine in Chile. The prototype unit consisted of six 1260 cubic meter reactors of Stebbins construction—a ceramic design—capable of withstanding the highly corrosive conditions at 85 °C. The primary and secondary reactors had the world's largest Lightnin® A315 agitators with each having a diameter close to 5 m (Batty and Rorke 2006). The prototype unit operated until mid-2005. While the plant operated with minimal problems, the decision was made not to proceed with a commercial-scale unit. No public explanation has been made available; however, questions have been raised about the technology's economic competitiveness with other processes.

6.4 Reductive Mineral Dissolution by Biological Processing—An Emerging Process?

As discussed earlier in this chapter, biological processing involving oxidation of sulfide minerals is a conventional industrial practice. However, many metals of value occur in ores that are already oxidized, for example, nickel laterites, which are estimated to account for about 70 % of the world's nickel resources (Dalvi et al. 2004). In these lateritic ores, the nickel is largely associated with goethite, α-$Fe^{III}O(OH)$, or limonite ore consisting of a mixture of hydrated iron(III) oxide-hydroxide minerals of varying composition.

The "Ferredox" processing concept, which was introduced in 2011 (du Plessis et al. 2011; Hallberg et al. 2011), uses the bacterium, *Acidithiobacillus ferrooxidans*, to couple the oxidation of elemental sulfur (S°) with the reduction of ferric iron contained in the mineral goethite (or limonite ore). The process is carried out under acidic and ambient temperature conditions in the absence of oxygen to facilitate the dissolution of metals. It has long been known that in the absence of oxygen, *Acidithiobacillus ferrooxidans* will oxidize elemental sulfur and use soluble ferric iron (Fe^{3+}) as an electron acceptor. The Ferredox concept is novel in that the ferric iron is associated with a solid mineral and, when the biologically catalyzed reduction occurs, the mineral undergoes dissolution releasing those metals associated with the mineral. The key reaction, when goethite is the ferric iron-containing mineral, is

$$S^{\circ} + 6FeO(OH) + 10H^{+} \rightarrow SO_4^{2-} + 6Fe^{2+} + 8H_2O \quad (6.12)$$

and this is carried out in the absence of oxygen. This bacterially catalyzed reductive dissolution reaction can also take place with the asbolane-lithiophorite group of minerals, (Mn, Co) (O, OH $_2$, Ni(OH)$_2$, releasing cobalt and manganese. In the case of this mineral group (du Plessis et al. 2011), the reaction may directly involve the oxidation of S° by *Acidithiobacillus ferrooxidans* in the absence of oxygen with electrons being accepted by manganese(IV)

$$Mn_3O_3(OH)_6 + S^{\circ} + 4H^{+} \rightarrow 3Mn^{2+} + 5H_2O + SO_4^{2-} \quad (6.13)$$

or by ferrous iron (Fe^{2+}) derived from the reductive dissolution of goethite

$$\begin{aligned} Mn_3O_3(OH)_6 + 6Fe^{2+} + 12H^{+} &\rightarrow 3Mn^{2+} \\ &+ 6Fe^{3+} + 9H_2O \quad (6.14) \end{aligned}$$

There are currently no commercial plants that use Ferredox; however, a proposed flow sheet for the conceptual Ferredox process is shown in Fig. 6.4 (du Plessis et al. 2011). The key elements of the flow sheet are

- An acid consuming reductive leach of the limonite according to reaction 6.12
- Recovery of the metals of value (Ni, Cu, etc.) from the PLS
- Ferrous iron oxidation (reaction 6.1) to convert the iron to either soluble ferric iron or precipitated as jarosite or schwertmannite, an iron-oxyhydroxysulfate mineral. If precipitated as a ferric-oxysulfate, this can be used as a sulfuric acid generating step (reaction 6.11)
- Soluble ferric iron can be used as an oxidant for elemental sulfur oxidation and the resulting ferrous iron can be used in reductive leaching (reaction 6.14)

6.5 Motivations for Commercial Use of Biological Processes and Closing Considerations

Biological processing of sulfidic ores has been applied commercially for over half a century, when the discovery was made that microorganisms catalyze the oxidation of sulfide minerals. Little was done initially to enhance the microbial processes in what was called dump bioleaching of submarginal grade, ROM ores (now referred to more generally as “stockpile” leaching). However, when it became apparent through research that microorganisms required oxygen to catalyze sulfide oxidation, different approaches were taken to improve the ventilation of the stockpiles. By the mid-1980s and early 1990s CSTRs were in commercial use to biooxidize flotation concentrates in which gold was encapsulated in a sulfide mineral matrix. This biological pretreatment process greatly improves gold recovery from these refractory concentrates. During the same time period, crushed ore heaps were engineered for effective bioleaching of base metals and for biological pretreatment processing of low-grade, sulfidic-refractory gold ores. Today some 20 % of the world’s mined copper and 3 % of the world’s mined gold are now produced by biological processing. New microorganisms are being discovered, new engineered schemes for using microorganisms are being perfected and new approaches to engineering biological processes are being invented. These innovations are expected to increase the range of ores that can be processed by microbial methods to include highly refractory primary copper ores, such as chalcopyrite and enargite, and oxidized minerals, such as nickel laterites that are not amenable to conventional biological oxidation approach.

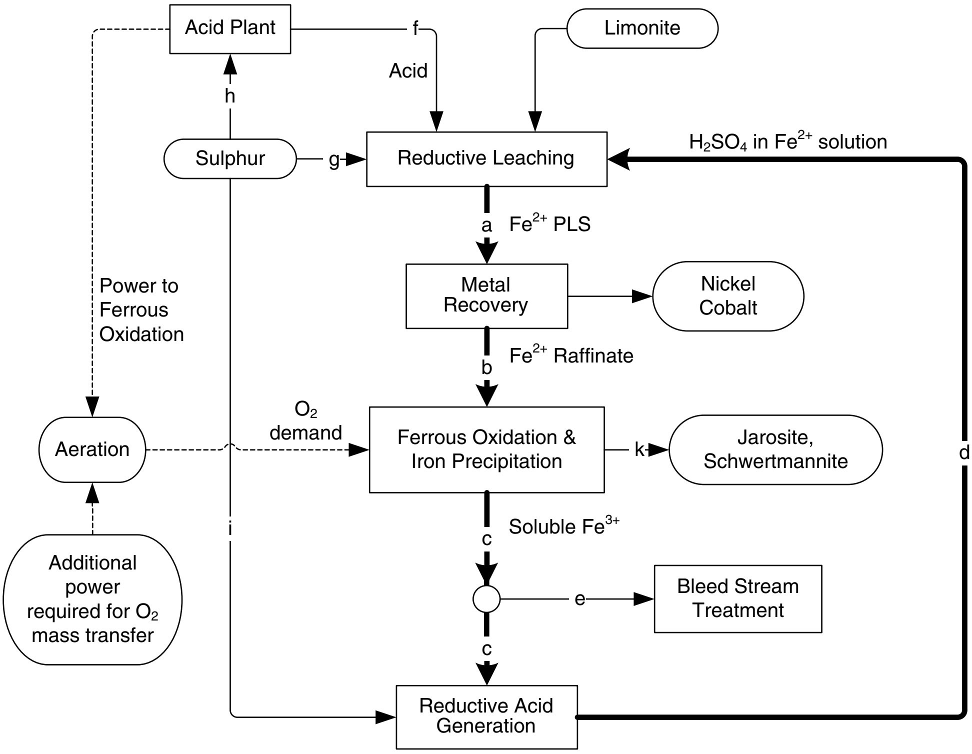

Fig. 6.4 Simplified Ferredox process flow sheet block diagram (du Plessis et al. 2011)

There are multiple reasons (Deloitte 2014) why biological processing of ores and concentrates is expected to grow in application and likely play an increasing role in future mineral processing:

Declining ore grades: Deposits of high-grade ores have largely been discovered and mined. Head grades have been steadily declining for many metals, including copper, nickel, and zinc. In some cases, copper grades are too low to support the cost of crushing, grinding, and flotation for processing by smelting. This leaves heap bioleaching of these low-grade ores as the viable option.

Easy-to-process-ore deposits are depleted: As existing mines become deeper and oxide and secondary copper ores are depleted, mining is taking place in the primary zone and newly discovered deposits have more complex ores. Hypogene ores, such as chalcopyrite and enargite, are typically low-grade and difficult to leach. Few cost-effective processing options exist, which is why a priority is being placed on developing and optimizing heap bioleaching of these ores. Complex ores are not only difficult to process by many conventional processing routes but also contain deleterious constituents making them unsuitable for some alterative processing. In biological processing of these materials, the deleterious constituents, such as arsenic, are first solubilized and then precipitated as a stable sludge that meets stringent environmental regulations and can be safely disposed in a tailings impoundment.

Increasing energy costs: As ore head grades decline, production costs increase. More energy is expended to recover the metal of value. In some countries where mining takes place (e.g., Chile and South Africa), energy costs are also increasing, because of greater demand for power by the public and private sectors and other bottlenecks in electrical supply. Biological processing, particularly heap leaching, requires less energy than some other alternative processes. Nevertheless, electrowinning of copper produced by heap bioleaching remains a significant consumer of electrical power.

Deeper mining and increasing population: As ore head grades decline and mines become deeper, open-pit and underground mining will no longer be profitable, because of increased cost of production.

The earth is currently home to 7.2 billion people and the current projection is that the earth will need to support a population of 9.6 billion by 2050 and 11 billion by 2100 (NRC 2014). Increasing population points to two matters of concern for mining:

- The amount of land throughout the world that is not populated by humans is decreasing. Consequently, mining activities are increasingly located near villages or larger population centers (Silver 2008)
- Most people envision a future with a greater standard of living than on average we currently have. This means a greater consumption of resources including metals (NRC 2014)

These two factors—deeper mines and increasing population—place significant challenges on the mining sector to reduce the footprint of mining, to cost effectively extract the metals necessary to sustain an increasing world population that expects a good quality of life, and to protect the environment. Practicable in situ (borehole) mining techniques must be developed to enable cost-effective mining of refractory and complex, low-grade metals at depth, protect groundwater, and reduce surface impacts. Commercially viable in situ leaching for metallic minerals in pristine formations entails making subsurface rocks permeable to solutions, containing solutions in underground mineral formations, controlling chemistry to selectively dissolve metals of value while leaving other subsurface material behind, and successfully returning the metal-bearing solutions to the surface for value recovery. Advancing in situ leaching for base and precious metal recoveries requires developments in: characterizing the ore body with minimal invasion; directional drilling of hard rock ore bodies; fracturing technology to enhance permeability; sensing technologies to monitor solution flow and chemistry; protecting groundwater; and robust extractive processes. Biological processes are expected to be an important technology for minimally invasive extraction technology.

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