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Potential of biotechnology for metals extraction in Zimbabwe: a review

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Synopsis

Zimbabwe is endowed with rich deposits of minerals such as diamonds, platinum, coal, uranium, lithium, gold, antimony, iron, and chrome. Bioleaching has been implemented as an efficient and low-cost method to extract metals such as copper, cobalt, and gold from sulphide and/or iron-containing ores and mineral concentrates in a number of countries around the globe. Zimbabwe, despite being a world leader in mineral wealth, has gone through years of economic stagnation which have brought with them energy shortages. Bioleaching is an innovative way to recover minerals from ores using relatively low-capital-cost and non-polluting technology. Principally, iron- and sulphur-oxidizing bacteria can be used to oxidize iron and sulphide to ferric iron and sulphuric acid, respectively, and the ferric iron oxidizes the insoluble metal sulphides to soluble metal sulphates that can be readily recovered from solution. Although some minerals such as gold are inert to biological reactions, they can be liberated using bacteria that act on certain types of ores and other minerals that co-occur with these minerals. The geology of the mineralized areas in Zimbabwe, rich in chalcopyrite / pyrite, allows a number of microorganisms to be used for the extraction of minerals by bio-oxidation. This paper reviews the potential of bioleaching in the country.

Keywords
bioleaching, bio-oxidation, gold, nickel, copper.

Introduction

Zimbabwe has rich deposits of minerals including diamonds, platinum, coal, uranium, lithium, gold, antimony, iron, and chrome. Bioleaching is defined as the use of microorganisms to facilitate the extraction of metals from sulphide or iron-containing ores or concentrates (Rawlings, 2004, 1997). Bioleaching has been shown to be an efficient (Blowes, Ptacek, and Jurjovec, 2003; Nordstrom and Southam, 1997; Schippers, 2004) and low-cost (Schippers *et al.*, 2010) method to extract minerals in many countries around the globe. For example, aerobic Fe(II)- and sulphur-oxidizing bacteria have been shown to be up to two orders of magnitude more efficient in the oxidation of pyrite than the chemical processes (Blowes, Ptacek, and Jurjovec, 2003; Nordstrom and Southam, 1997; Schippers, 2004). Additionally, bioleaching can be used to extract minerals from low-grade ores, sulphidic waste rock dumps, and tailings efficiently (Schippers *et al.*, 2010).

The process of bioleaching has been shown to occur largely by the indirect contact between microorganisms and ferric iron, the latter acting as an intermediate electron acceptor. 'Direct leaching' was believed to involve intimate microbial and mineral contact with direct enzymatic oxidation of the mineral under aerobic conditions (Berry and Murr, 1976; Bennet and Tributsch, 1978). However, the concept of direct leaching was disproved (Fowler and Crundwell, 1999). Bacterial leaching is believed to occur when bacteria attach to and accelerate the reaction of some minerals through the removal of sulphur, which would constitute a diffusion barrier in chemical leaching (Fowler and Crundwell, 1999). On the other hand, bacterial leaching can occur as a result of pH modifications at the mineral surface through bacterial action. The rate of dissolution of pyrite was shown to increase as a result of changes in the concentrations of ferric and ferrous ions and in pH due to bacterial action at mineral surfaces (Fowler and Crundwell, 1999; Zeng, Schumann, and Smart, 2013). The contact mechanism considers that bioleaching occurs through activities of the extracellular polymeric substances that are released into a mineral–bacteria interphase in biofilms that are formed when bacterial cells attach to the surfaces of sulphide minerals (Bobadilla Fazzini, Levican, and Parada, 2011; Sand and Gehrke, 2006). The oxidation of elemental sulphur by acidithiobacilli relies on oxygen as electron

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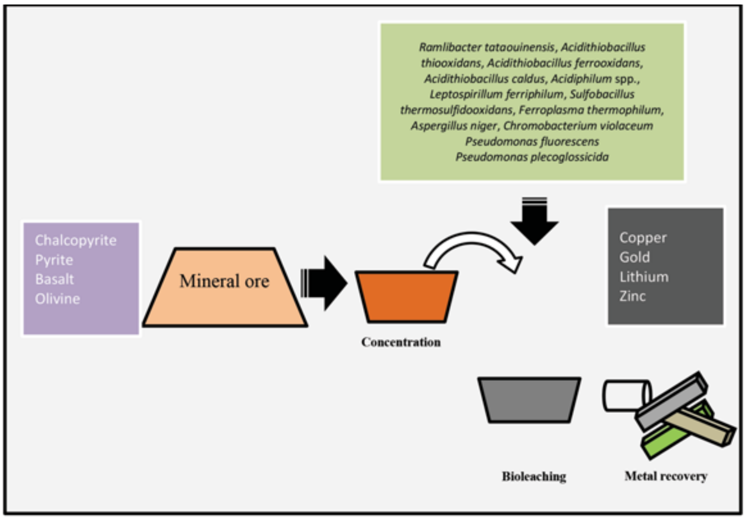

Figure 1—Graphical abstract showing bioleaching of mineral ores in Zimbabwe

acceptor, which assists the solubilization of metal sulphides present in the mineral surface (Rohwerder *et al*., 2003). *Pseudomonas fluorescens*, uses nitrate instead of oxygen as a final electron acceptor during anaerobic respiration (Samuelsson, Cadez, and Gustafsson, 1988), yielding cyanide which leaches minerals such as silver, gold, and platinum (Brandl *et al*., 2008; Pradhan and Kumar, 2012).

The capital cost of bioleaching is widely claimed to be considerably lower than that of conventional smelting (Dresher, 2004; Mintek, n.d.). No meaningful indications of the actual savings were found at this stage. Despite the demonstration of higher extraction efficiency and greater cost-effectiveness of the bioleaching process, its potential in the Zimbabwean geological and economic contexts has not been explored. Zimbabwe is going through economic challenges that affect its capacity to exploit its mineral wealth. The Zimbabwean mining sector continues to rely on energy- and cost-intensive mineral extraction methods, including smelting and chemical leaching. The geological formations that make up the principal mining areas of the country, concentrated along the Great Dyke, are rich in minerals that include platinum, uranium, lithium, gold, antimony, iron, and chrome. The rock types including orthopyroxenite, olivine basalt, gabbro, coarse websterite, fine websterite and olivine gabbro (Mukasa, Wilson, and Carlson, 1998; Oberthur *et al*., 2013). Of these, gold, base metal sulphides (including iron), and primary uranium are bioleachable (Johnson, Kanao, and Hedrich, 2012; Pal *et al*., 2010). The country's mineralization is divided into zones, namely the Sebakwean, Bulawayan, and Shamvaian, and granites and gneisses (Figure 2).

Potential for bioleaching in Zimbabwe

The Great Dyke

The Great Dyke (actually not strictly a dyke) is a linear lopolithic geological feature that spans approximately 550 km from its northern end to its southern end (Hughes, 1970) (Figure 2). The Great Dyke is rich in ore deposits, including gold, silver, chromium, platinum, nickel, and asbestos (Guilbert and Park, 1986). The Great Dyke consists of a group of layered ultramafic intrusions that are locally overlain by erosional remnants of gabbroic rock (Mukasa, Wilson, and Carlson, 1998). The sequence includes orthopyroxenite, olivine basalt, gabbro, coarse websterite, fine websterite, and olivine gabbro (Mukasa, Wilson, and Carlson, 1998) and chalcopyrite-bearing rocks (Li *et al*., 2007). The Main Sulphide Zone of the Great Dyke contains platinum-group element (Pt and Pd) sulphides, arsenides, tellurides, and base metal sulphide assemblages (Li *et al*., 2007). A number of microorganisms including *Ramlibacter tataouinensis, Acidithiobacillus thiooxidans* (Bobadilla *et al.*, 2011), *Acidithiobacillus ferrooxidans* (Karavaiko *et al.*, 1986), *Acidithiobacillus caldus* (Watling, *et al.*, 2015), *Acidiphilum* species (spp.) (Parada *et al.*), *Leptospirillum ferriphilum* (Fu *et al.*, 2008), *Sulfobacillus thermosulfidooxidans* (Stott *et al.*, 2000), *Ferroplasma thermophilum,* (Zhou *et al*., 2008) and *Aspergillus niger* (Aung *et al.*, 2005) have been shown to have great potential to leach the minerals that are found in the country.

Bioleaching of gold

Gold deposits (Figure 2). In arsenic-rich gold concentrates, the gold particles are enclosed in sulphide minerals, including arsenopyrite (FeAsS), pyrite (FeS_2), realgar (As_2S_2), or orpiment (As_2S_3) (Xie *et al*., 2013). In order to obtain satisfactory gold recoveries, oxidative pretreatment is required to break down the sulphide minerals (Xie *et al*., 2013). Gold is finely disseminated in refractory sulphide ores, which reduces the capacity of conventional cyanidation to recover gold (Lindstrom, Gunneriusson, and Tuovinen, 1992). In the bioleaching process, bacteria break down the sulphide minerals by oxidative dissolution, thus dissolving ferrous iron (Fe^{2+}) and exposing gold to the cyanide solution (Lindstrom, Gunneriusson, and Tuovinen, 1992). Biooxidation offers a cost-effective and efficient way to extract gold from refractory ores (Schippers *et al*., 2014). A number of pilot studies have demonstrated that biooxi-

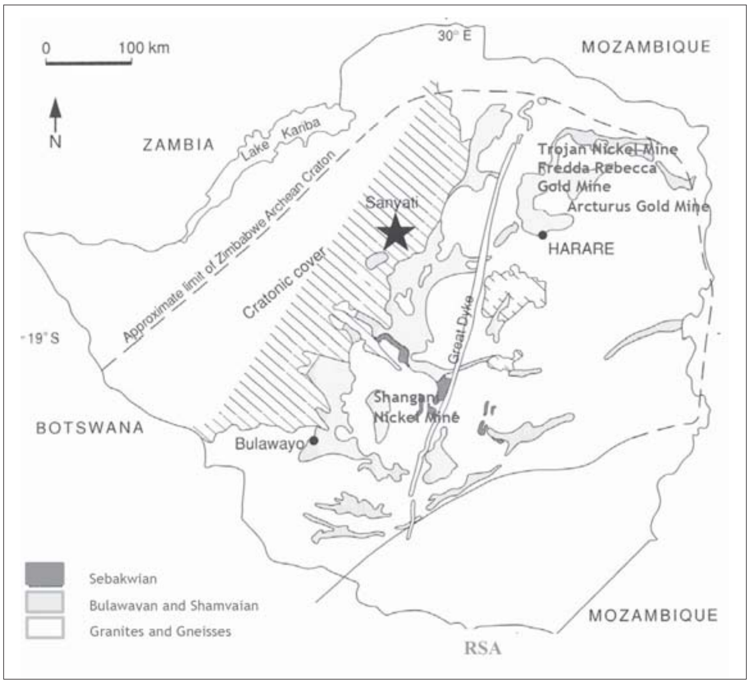

Figure 2—Mineralized areas of Zimbabwe (adapted from Oberthur and Koch, 1999)

dation can be used in the extraction of gold (Brierley, 1997; Gericke, Neale, and van Staden, 2009; Karavaiko *et al*., 1986; Marchant, 1986). Marchant (1986) demonstrated a 75% increase in gold recovery with partial bacterial oxidation of sulphide minerals, particularly arsenopyrite. A pilot study in the former USSR by Karavaiko *et al.*, (1986) demonstrated 90% gold recovery through the oxidation of arsenopyrite by *A. ferrooxidans*. The first commercial biohydrometallurgical process to extract gold in the world, patented as the Biox® process and involving the pretreatment of refractory gold-bearing arsenopyrite, was developed by Gencor SA Ltd (now BHP Billiton) at Fairview mine in South Africa (Brierley, 1997). The Biox® process has been shown to increase gold recovery by up to 95% (Brierley, 1997), depending on the mineralogy and gold deportment of each ore. Another biohydrometallurgical process, which operates at temperatures higher than those in the Biox® process, was developed and commercialized by Australian-based company BacTech (Brierley, 1997). Bactech, working in partnership with Mintek, established a Bacox™ bioleaching plant, in Tasmania (Gericke, Neale, and van Staden, 2009). In 2001, Bactech and Mintek established another bioleaching plant at the BioGold toll treatment facility located near the city of Laizhou, in the Shandong Province of PR China. Both of these plants remain in operation to date. (Gericke, Neale, and van Staden, 2009). Both the Biox® and Bacox™ processes are carried out in aerated stirred-tank reactors (Brierley, 1997), which are an alternative to heap leaching and Geobiotics processes. Biooxidation heap leaching is used by the Newmont Gold Company in Nevada, USA. Geobiotics Inc. built a demonstration facility in South Dakota, USA, which was based on the use of heaps of supporting rocks coated with an ore concentrate (Morin, 1995). Biooxidation of ore using the Geobiotics technology was shown to increase gold recovery by between 55% and 74% (Morin, 1995). However, the recovery of metals through the biooxidation of whole ores results in marginal economics (Gericke, Neale, and van Staden, 2009; Whitlock, 1997).

The Mazowe gold area

Gold mineralization in the Mazowe area, approximately 40 northwest of Harare, is hosted in a variety of lithologies of the Archean Harare-Bindura-Shamva greenstone belt (Figure 2) (Oberthur *et al*., 2000). The Mazowe gold mines are based on pyrite-rich reefs, the Bernheim group of mines are hosted on arsenopyrite-rich metabasalt ores, and Stori's Golden Shaft and the Alice mine are hosted in metabasalts containing sulphide-poor quartz veins (Oberthur *et al*., 2000). Notably, the sulphide-rich ores in Stori's Golden Shaft mine are characteristically low in gold content (Oberthur *et al*., 2000). Biooxidation may not be a viable option for the Stori ores due to the low sulphide content of the metabasalts and low gold concentrations in certain places. The bioextraction of gold from the pyrite-rich reefs in the Mazowe gold mines and Bernheim group of mines may be driven by bacteria that include *Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans, Acidithiobacillus caldus, Acidiphilium cryptum, Leptospirillum ferriphilum, Sulfobacillus thermosulfidooxidans, Ferroplasma thermophilum, and Sulfolobus* spp. The Biox® and Bacox™ processes may be viable technologies for the bioextraction of gold at the Mazowe gold mines.

The Arcturus-Harare gold area

The Arcturus gold mine, located within the Shamvaian Group (Figure 2), is hosted in the Iron Mask Formation, which comprises a succession of metamorphosed felsic volcanics and associated metasediments including prominent bands of sulphide-facies iron formation, phyllites, meta-arenites, and quartzose schists (Oberthur *et al.*, 2000). The mineralized shear zones in the Arcturus mine are characterized by silicification, biotite, and K-feldspar alteration. Gold mineralization is associated with pyrrhotite, arsenopyrite, and also occurs as free gold, which contributed up to 10% of production (http://metcorp.co.uk/operations/arcturus-mine.aspx). Biooxidation of the Arcturus ores may be possible using *A. ferrooxidans*, which reportedly oxidizes biotite (Bhatti *et al.*, 2011). Furthermore, the presence of sulphide-rich iron formation may allow for bioextraction of gold-bearing ores using *Acidithiobacillus ferrooxidans*, which is shown elsewhere to have this capacity (Dew, Lawson, and Broadhurst, 1998; Natarajan and Iwasaki, 1983). However, silica in the Arcturus ores may be a limiting factor due to the encapsulation of gold in silica, which locally inhibits biooxidation (Sherlock, 2010).

Shangani and Trojan nickel mines

Bindura Nickel Corporation (BNC) owns the Shangani and Trojan nickel mines, which are located within the Archaean greenstone belts in the Bulawayan and Shamvaian groups. Ore is processed at the Trojan concentrator, resulting in a nickel-in-concentrate recovery of approximately 71%, The company's Bindura Smelter and Refinery (BSR) complex, which is being re-opened, will produce high-quality nickel cathodes, copper sulphide, and cobalt hydroxide (ASA Resource Group, 2016). Generally BNC has recorded a nickel recovery capacity of between 70.7 and 88.8% (ASA Resource Group, 2016). The two nickel orebodies are rich in pyrite, and the biooxidation process could be adapted to recover nickel. Nickel sulphide heap bioleaching has been piloted at several sites, including the University of Cape Town (Rawlings, 2005). The successful implementation of bioleaching technologies for the extraction of nickel has been demonstrated by a cooperative agreement reached between Amsterdam-headquartered talc producer Mondo Minerals and South Africa's state-owned mineral technology research council Mintek, which has seen the construction of a nickel sulphide bioleach plant at Mondo's Vuonos talc processing site in Finland (Creamer Media, January 2015). Microorganisms such as *Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans, Acidithiobacillus caldus, Acidiphilium cryptum, Leptospirillum ferriphilum, Sulfobacillus thermosulfidooxidans, Ferroplasma thermophilum* and *Sulfolobus* spp. can facilitate the recovery of nickel.

Iron ore at Redcliff near Kwekwe

The area around Redcliff, the main iron-bearing area in Zimbabwe, is underlain by Archaean rocks of the basement complex (Geological Society of Zimbabwe, 2014). The Archaean rock formations, primarily a volcano-sedimentary pile, are flanked by granitic rocks of the Rhodesdale batholiths in the east and the Shangani batholiths in the west (Geological Society of Zimbabwe, 2014). The stratigraphy of the greenstone belt in the Redcliff area is divided into the Sebakwean, Bulawayan, and Shamvaian groups (Geological Society of Zimbabwe, 2014). The extraction of iron from these formations was primarily through smelting in energy-intensive blast furnaces (Geological Society of Zimbabwe, 2014). Energy shortages and economic challenges in Zimbabwe in recent years have resulted in the shutdown of operations.

Acidithiobacillus ferrooxidans reportedly increases the rate of the oxidation of ferrous ions by a factor of 106 (Singer and Stumm, 1970). *A. ferrooxidans* and *L. ferriphilum* can oxidize both sulphide and ferrous iron oxidation (using O_2 as a terminal electron acceptor) and ferric iron reduction (using reduced inorganic compounds like sulphur or hydrogen as electron donors), which allows them to grow under aerobic and anaerobic conditions (Ohmura *et al*., 2002; Pronk *et al*., 1992) (Figure 3). Hu *et al.* (2012) showed that Fe^{3+} ions are important for bioleaching of chalcopyrite. The presence of the bacterium can significantly increase the rate of sulphide leaching in the iron-bearing ores, thereby increasing the recovery of iron. It would be theoretically possible to extract iron using microorganisms such as *A. ferrooxidans.*

Despite this theoretical possibility, the use of this technology is limited since the solubilized iron precipitates as iron oxy-hydroxides / goethite (FeOOH) or equivalents (Parker, 2008)—the latter would require removal by smelting. Unless other biological technologies to leach iron can be developed, the use of iron bioleaching remains limited. Further research on this possibility is required.

Sanyati copper mine

The Sanyati orebody, located approximately 200 km west of Harare, is polymetallic and sulphidic (Oberthur and Koch, 1999) (Figure 2). The mineralization comprises zinc, copper, and lead sulphides (chalcopyrite, sphalerite, and galena) as well as pyrite, pyrrhotite, and arsenopyrite (Oberthur and Koch, 1999). A recent evaluation programme demonstrated that the Sanyati ore contains approximately 1.1% copper and 1.2% zinc (Oberthur and Koch, 1999). The Sanyati mine, recently opened by the Government of Zimbabwe, has capacity to produce at least 5000 tonnes of copper per annum using open pit mining, with a capacity of up to 40 kt of ore per month (Oberthur and Koch, 1999). Copper is extracted using solvent extraction and electrowinning (SX/EW), and

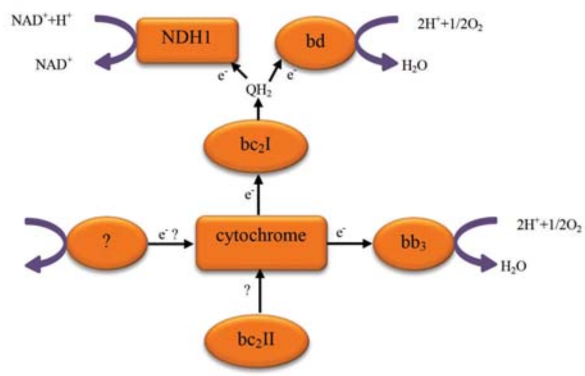

Figure 3—Oxidation pathway of Fe(II) by *L. ferriphilum* (adapted from Mi *et al.*, 2011). NDH1: type 1 NADPH dehydrogenase, bd: cytochrome bd-type quinol oxidase, bb3: bb3 type cytochrome oxidase, bcl2II: cytochrome bc1 complex, bc2I: cytochrome bc2 complex, NAD: nicotinamide adenine dinucleotide, QH2: dihydroquinone, Fe^{2+}: iron (II) ion, Fe^{3+}: iron (III) ion

the recovery of other minerals such as zinc, manganese and cobalt from the ore has been investigated (Oberthur and Koch, 1999). Bioextraction is seen as a complementary method to enhance the extraction of copper, zinc, and manganese from the Sanyati ore reserves. The sulphide-rich ores that are found in the Shamvaian Group, including Sanyati, are known to be readily oxidized by microorganisms such as *A. ferrooxidans* and *Sulfolobus* species to yield copper (Dew, Lawson, and Broadhurst, 1998; Natarajan and Iwasaki, 1983; Xia *et al.*, 2010) and cobalt (Dew, Lawson, and Broadhurst, 1998; Natarajan and Iwasaki, 1983).

Summary

Notwithstanding the fact that the species or strains of microorganisms reported herein are not metal-specific, their use may be convenient since the microorganisms are widely available. Given the geology of the mineralized areas of Zimbabwe and the availability of microorganisms with the capacity to extract metals through the oxidation of the ores containing minerals of interest, bioleaching could be a viable alternative to the energy- and cost-intensive extraction methods currently in use. Bioleaching can be used to facilitate the extraction of gold from the Mazowe gold district, including ores at Arcturus mine and Freda Rebecca gold mine, using such microorganisms as *A. thiooxidans, A. ferrooxidans, A. caldus, A. cryptum, L. ferriphilum, S. thermosulfidooxidans, F. thermophilum,* and *Sulfolobus* spp. Furthermore, methods such as the Biox® and Bacox™ processes could be viable, efficient, and cost-effective options for the bioextraction of gold in the Mazowe gold mines. The extraction of nickel at Shangani and Trojan nickel mines can also be enhanced through the use of such microorganisms such as *A. ferrooxidans* and *A. caldus*, which are known to oxidize the sulphide-rich ores that are found in the two mining areas. The potential of bioleaching to recover iron is not well established, however microorganisms such as *A. ferrooxidans* reportedly increase the rate of oxidation of ferrous ions by a factor of 10^6 (Singer and Stumm, 1970). The potential of bioleaching, relying primarily on *A. ferrooxidans* (Fowler and Crundwell, 1999), can be tapped to extract copper from ores at Sanyati copper mine. Bioleaching therefore has great potential for use as complementary technology to the conventional methods in the extraction of Zimbabwe's vast mineral wealth.

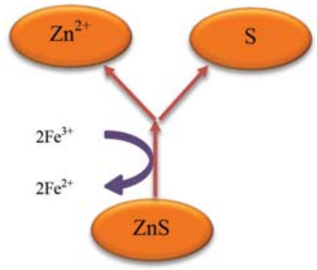

Figure 4—The classic reactions in the dissolution of sulphide by ferric sulphate to form zinc and ferrous ions in solution and elemental sulphur (adapted from Fowler and Crundwell, 1999)

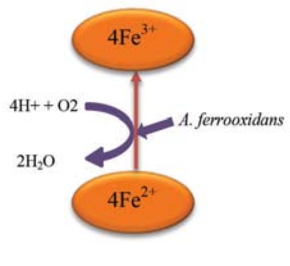

Figure 5—Formation of ferric ions in the leaching reaction by *A. ferrooxidans* (adapted from Fowler and Crundwell, 1999)

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