Feasible bioprocessing technologies for low-grade iron ores

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Abstract

With increasing demand for steel and depletion of high-grade iron ore deposits, more research efforts are being directed toward extending the life of existing ore reserves and developing technology to treat low-grade iron ore resources. Among all the reported technologies, biotechnologies in mineral processing – specifically bioleaching and microbially induced flotation – have emerged to be considered as low-cost, environmentally friendly potential alternatives to many of the current mineral processing techniques. This paper provides a comprehensive review of current research on the use of microorganisms for iron ore beneficiation and, further, discusses the applicability of bioleaching, bioflotation and bioflocculation for the beneficiation of low-grade iron ores.

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Introduction

Increasing global demand for raw materials has led to diminishing resources of high-grade iron ore. As a result, the mining and utilization of low-grade hematite, limonite, specularite, siderite and goethite ores have attracted more and more attention. However, these types of iron ores are of complex paragenesis and fine disseminated grain size, and often contaminated by phosphorus in the form of solid solution. The distribution of phosphorus throughout the iron mineral crystals prevents the effective use of physical separation techniques, and these complex ores are at present largely untapped due to a lack of cost-effective and efficient processing methods. Chemical leaching and roasting-magnetic separation approaches have been mainly tested only on the laboratory scale and are all either cost prohibitive or ineffective when used on low-grade complex iron ores.

Bioprocessing is considered one of the most promising solutions for low-grade complex ores, compared with other reported processes such as pyrometallurgy or chemical metallurgy. Mostly due to the rising costs of milling and concentration for low-grade ores, bioprocessing has been shown to require less capital, lower operating cost, and fewer skilled operation and maintenance personnel than the traditional pressure-oxidation or roasting techniques for nonferrous and precious metal extraction. In addition to holding the promise of dramatically reducing capital costs, bioprocessing offers an opportunity to reduce environmental burdens. Biological processes are carried out under mild conditions, usually without the addition of strong

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acids or bases. The products of biological processes end up in aqueous solution, which is more amenable to containment and treatment than gaseous waste.

Bioprocessing technologies

Bioprocessing refers to the removal of undesirable mineral components from an ore through interactions with microorganisms that bring about their selective removal either by bioleaching or biobeneficiation processes and thereby enrich the desired mineral constituent in the solid ore matrix, mediated by a number of surface chemical and physiochemical phenomena. There are three broad categories of biologically assisted mineral beneficiation process, based on the microorganism-mineral interactions and roles of mineral-specific bioreagents:

1. Selective dissolution of mineral phases in an ore matrix.
2. Sorption, accumulation and precipitation of ions and compounds.
3. Alteration of surface chemistry of minerals or generation of surface active chemicals.

Figure 1 shows the bioprocessing routes derived from the interactions between microorganisms and minerals. Through microbially assisted reduction or oxidation, the extraction of metals can be realized by transforming solid compounds into soluble and extractable elements, which can then be recovered. This process is called bioleaching, and it is an industrially important process that has been commercially applied in recovering nonferrous metals like copper, zinc, uranium, nickel, cobalt and gold from their sulfide minerals. The other important bioprocessing route is biobeneficiation, which refers to the selective removal of undesired elements or mineral constituents from iron ores through interactions with microorganisms. Depending on the interaction mechanism between the microorganisms and minerals, biobeneficiation can be divided into two processing routes: biodephosphorization/ biodesulfurization and bioflotation/bioflocculation.

Bioleaching can be categorized into two segments: whole ore, and concentrate systems. Whole ore can be further subdivided into in situ or ex situ processes. Concentrate systems are always ex situ processes.

In situ bioleaching refers to the process where ore is treated without mining to remove the overburden rocks. This process relies on fracturing the ore by blasting or natural processes, thus producing voids and porosity to allow free solution flow. The solution is collected generally at the bottom of the mine and then processed for metal recovery by solvent extraction and electrowinning. The biological system receives its oxygen from the solution. The application of this process has not spread widely as it requires very specific orebody characteristics: high-permeability ore with low-permeability host rock. Additionally, recoveries are typically low and the time required is long.

Ex situ bioleaching refers to processes where the ore is pre-treated or concentrated before the bio-treatment process. Depending on the leaching method, it can be categorized as stirred tank, dump, heap or vats leaching. Bacterial oxidation of ground mineral slurry can be carried out in aerated and agitated vessels when the value of the metal is sufficient to justify the cost of installing and operating the equipment. The application of this process to ores has been rather limited due to the large size of the vessels, often making it cost prohibitive. However, its oxidation kinetics are much higher than for in situ or heap systems. Heap bioleaching is typically conducted by stacking crushed ores into constructed piles on prepared impervious pads that have a sloped base to allow solution to flow by gravity into collection drains. Oxygen can be added to the system to enhance the rate of oxidation by blowing low-pressure air into the heap base. This system was first employed for secondary copper minerals in large dumps using run of mine ores. Acidic solutions carry away the biooxidized products such as copper or iron. Recent advances in whole ore heap leaching have seen the use of closely sized ore particles to aid the oxidation rate, under heap piping for better air distribution and agglomeration, and pre-inoculation to aid in permeability and oxidation rate. Additionally, whole ore systems are now applied to a wide range of ore types including refractory gold ores, copper sulfides, nickel sulfides, cobaltiferrous ores and zinc sulfides. In vats leaching, which is a combination of heap and stirred tank leaching, the ore is immersed in solution for

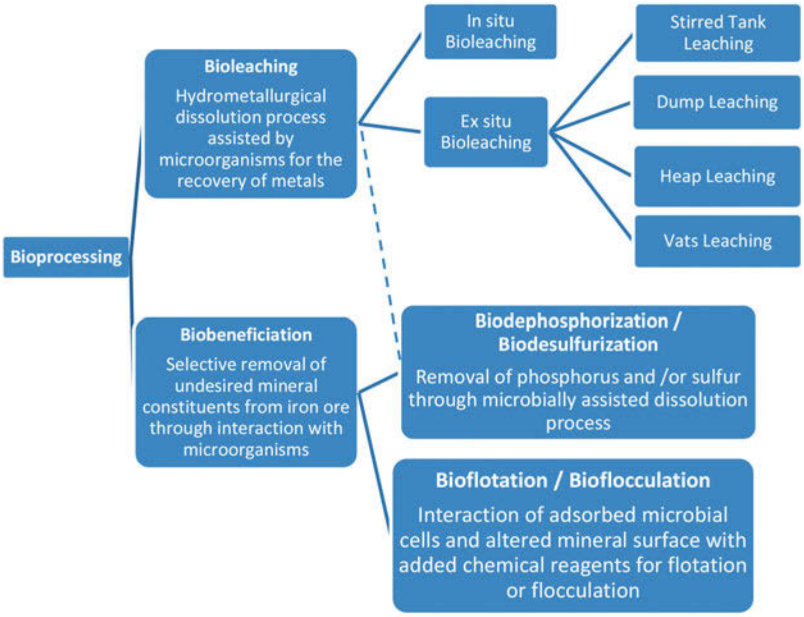

Figure 1 — Bioprocessing routes for low-grade iron ores.

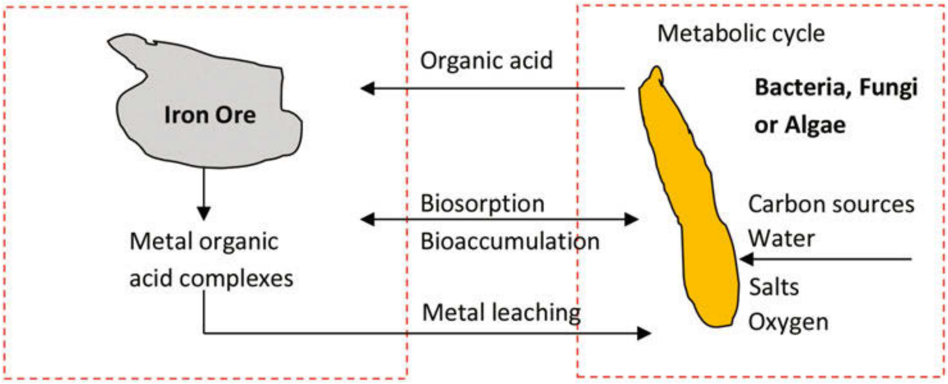

Figure 2 — Mechanism of microorganism interactions with iron ores.

all or part of the treatment process. The vats provide for better control of the biooxidation environment while not having the requirement of expensive agitation and air distribution. This process is not widely employed as the biooxidation rate and metal recovery are often low.

The heap leaching approach is suitable for the treatment of low-grade orebodies and overburdens because it is easy to construct and operate. But the inability to maintain constant pH gradient, temperature, selective microbial colony, homogeneous mineral and nutrient composition, and hence the desired reaction rate is a major roadblock to the commercialization of such processes in many instances. Gold and copper from their sulfide ores are commercially produced in Uzbekistan, Australia, Greece and Chile through the bio-oxidation process using the proprietary Gold Fields BIOX process and BHP Billiton BIOCOP process, supplied by Biomin South Africa and BHP Billiton, respectively. The Kasese plant in Uganda uses BRGM (Bureau de Recherches Geologiques et Minieres) technology for the recovery of cobaltiferous pyrite. A major challenge is to find a match between an orebody and a suitable bioleaching/beneficiation technology. For instance, the technology of recovery of nickel from its sulfide ore using the BIONIC process has been theoretically tested, but an orebody of suitable concentration and size has yet to be identified that would allow economic recovery at the prevailing nickel price. Commercial heap leaching units have been in operation for quite some time for the recovery of copper mainly from their sulfide ores in countries like Chile, the United States and Australia. Copper recovery from bioleaching accounts for about 25% of world copper production (Dresher, 2004).

Bioflotation and bioflocculation refer to flotation and flocculation that use microorganisms to bring about the selective separation of minerals. Recent literature shows that microbial species can be used as flotation reagents in the selective separation of iron ores, such as hematite-quartz and corundum-quartz (Deo and Natarajan, 1998) and apatite-dolomite (Zheng et al., 1998). Bacteria, yeast and their excreted metabolites can also be excellent flocculating agents and in some cases can function as selective flocculating agents (Misra et al., 1993; Raichur et al., 1995, 1996; Schneider et al., 1994; Smith et al., 1994). Although numerous laboratory studies have demonstrated that it is possible to use microbial species as flotation or flocculating reagents in the selective separation of minerals, the roles of microorganisms and their metabolites in altering the surface chemistries of object minerals such as hematite, limonite and specularite and the gangue minerals of quartz, kaolinite, chlorite, calcite, pyrophyllite and dolomite are still not very clear.

Microorganism-mineral interactions

Biosorption and bioaccumulation are based on the interactions of microbial cells and soluble metals and metalloids. Microbial cell surfaces and organelles offer a large number of active functional groups and possible physicochemical mechanisms of interactions. The result is the immobilization of the metals and metalloids on the microbial biomass. Biosorption is defined as the selective or nonselective sequestering of dissolved metals by microbial cells and refers mostly to the passive physicochemical mechanisms of inactive (nonmetabolizing) metal uptake by microbial biomass. Bioaccumulation is referred to as active absorption (as opposed to passive physicochemical adsorption-retention by biosorption). Passive adsorption is rapid and independent of the presence of specific nutrients, whereas active adsorption is slow and nutrient dependent.

The presence of functional nonpolar groups (hydrocarbon chains) and polar groups (carboxyl, hydroxyl, phosphates) at the microbial cellular surfaces or metabolic products give the microbial culture characteristics similar to those of surfactant molecules. Therefore, the microorganisms can modify the mineral surfaces, either directly or indirectly. The direct mechanism involves the adhesion of cells to mineral particles while the indirect mechanism refers to the biological reagents such as excreted metabolites acting as surface-active reagents (Sharma and Rao, 1999) or as soluble fractions of the microorganisms derived from their rupture (Schneider et al., 1994; Raichur et al., 1997).

Several types of autotrophic and heterotrophic bacteria, fungi, yeasts and algae may be involved in mineral bioprocessing processes. The microorganisms have been reported to solubilize different alumina silica, titanium, copper and sulfur compounds found in nature. Heterotrophic microorganisms degrade aluminosilicates by means such as soluble low-molecular-weight metabolites, organic acids and amino acids. The metabolites can dissolve metals from minerals through the displacement of metal ions from the ore matrix by hydrogen ions and formation of soluble metal complexes and chelators. Figure 2 represents the mechanism of heterotrophic bacterial interactions with iron ores.

Microorganisms relevant to bioprocessing low-grade iron ores

Many types of microorganisms including autotrophic and heterotrophic archaea, bacteria, eukarya, fungi and yeasts can act as reagents, collectors or modifiers to bring about the beneficiation of iron ores. Table 1 summarizes the reported microorganisms used in biobeneficiation; most of these microorganisms are present ubiquitously in many iron ore deposits. Generally, the microorganisms that catalyze the dissimilatory oxidation or reduction of iron ore can be subdivided into four main physiological groups: (1) acidophilic, aerobic; (2) neutrophilic, aerobic; (3) neutrophilic, anaerobic (nitrate dependent); and (4) anaerobic photosynthetic. Among these microorganisms, *Gallionella spp.* and *Leptothrix spp.* are invariably associated with biogenic iron oxides at neutral pH in oxygen-rich zones. In acidic environments, *Acidithiobacillus spp.* brings about ferrous iron oxidation. Iron-oxidizing archaea such as *Thermoplasmales* could be identified in extreme acidic environments. Bioreagents such as exopolysaccharides and proteins are secreted by iron bacteria during the process of iron biogenesis and conversion. Microorganisms capable of producing polyphosphate granules, sulfur granules and other intracellular and intercellular inorganic polymers have also been located in mining environments. Many iron-bacteria exhibit magnetotaxis and are implicated in the biosynthesis of magnetite (Liu et al., 2006). An iron-reducing bacterium like *Shewanella putrefaciens* is capable of producing intracellular particles of iron minerals (Roberts et al., 2006). With reference to banded iron formations, iron-oxidizing bacteria can produce and precipitate iron-rich sediments on a large scale.

Bioleaching of low-grade complex iron ores

For the selective dissolution of iron minerals, iron-reducing bioleaching processes are the most effective methods due to the fact that the reduced (Fe^{2+}) form of iron has higher solubility than oxidized Fe^{3+} compounds. Using a reductive microorganism, iron can be converted into Fe^{2+} (ferrous) iron salts that are considerably more soluble than ferric iron salts, and so will dissolve under only mildly acidic conditions. Iron dissolution can also be accelerated by the use of organic acids that can complex iron and increase its solubility. Some of these organic acids, particularly oxalic acid, can convert Fe^{3+} into a soluble ferric oxalate [$Fe(C_2O_4)_3{}^{-3}$], allowing the iron to be dissolved at moderate pH without chemical reduction (Panias et al., 1996).

Table 1 — Summary of potential microorganisms for the bioprocessing of low-grade iron ores, studied by various investigators.

Domain	Organism	Nutrition type	Main iron minerals	Main application	pH range	Reference
Archaea	*Sulfolobus acidocaldarius*	Chemilithoautotrophic	Pyrite	Bioleaching of iron ore	0.9-5.8	Acuna et al. (1992)
	Ferroplasma acidarmanus	Chemilithoautotrophic	Pyrite	Bioleaching of iron ore	0.35-2.20	Dopson et al. (2004)
	Thermoplasma acidophilum	Chemilithoautotrophic	Pyrite	Bioleaching of iron ore		Johnson (1998)
Bacteria	*Leptospirillum ferrooxidans*	Chemilithoautotrophic	Goethite and magnetite	Dephosphorization of iron ore	2.5-3.0	Chime (2013)
	Shewanella putrefaciens	Chemilithoautotrophic	Magnetite	Bioleaching of iron ore	1.4-6.0	Roberts et al. (2006)
	Bacillus subtilis	Neutrophilic	Hematite	Selective flotation of hematite, corundum, calcite and quartz		Poorni et al. (2013, 2014)
	Desulfovibrio desulfuricans	Chemilithoautotrophic	Hematite	Hematite and quartz separation		Sabari Prakasan and Natarajan (2010)
Eukarya	*Actinomucor sp.*	heterotrophic	Not applicable	Not applicable		Muller (1964)
Fungi	*Aspergillus terreus*	Heterotrophic	Goethite and magnetite	Dephosphorization of iron ore		Anyakwo and Obot (2010)
	Aspergillus niger	Heterotrophic	Hematite and goethite	Dephosphorization of iron ore		Delvasto et al. (2007)
	Penicillium sp.	Heterotrophic	Hematite	Removal of potassium and phosphorus from iron ore		Adeleke et al. (2010)
Yeasts	*Saccharomyces cerevisiae*	Heterotrophic	Hematite	Separation of quartz from hematite and calcite		Natarajan and Padukone (2012)
Algae	Not identified					
Protozoa	Not identified					
Amoebae	Not identified					

Eisele and Gabby (2014) recently reviewed iron-reducing anaerobic bacteria and their potential application in the processing of low-grade iron ores. Experiments conducted on the laboratory scale have shown reductive iron leaching to be most effective for dissolving the more hydrated and amorphous iron oxides, with low dissolution rates for highly crystalline oxides such as hematite. If given sufficient adaptation and leaching time, selected microorganisms can produce iron-bearing solutions containing as much as 1,800 mg of Fe^{2+} per liter.

Iron-oxidizing bioleaching processes are mostly applied in sulfide mineral leaching, as the products of oxidizing sulfide minerals are significantly more soluble than the original sulfides (Brombacher et al., 1997). Lacey and Lawson (1970) reported that the iron (II) oxidation by *Acidithiobacillus ferrooxidans* was half a million to a million times faster than abiotic chemical oxidation by dissolved oxygen. As a result of this study and similar work later by others, copper bioleaching was initiated in 1980, and several commercial-scale copper bioleaching operations have been set up since then.

It should be noted that the direct bioleaching of iron minerals may not be an economically feasible processing route for low-grade iron ores due to difficulties in iron recovery from aqueous iron-bearing solution. Available technology such as iron electrowinning has not been successfully applied because of low current density and low current efficiency resulting from parasitic hydrogen evolution. Mostad et al. (2008) discussed the electrowinning of iron from sulfate solutions. High-purity iron deposits were obtained from an electrolysis tank equipped with a diaphragm between the cathode and anode compartments, with Glauber salt ($Na_2SO_4 \cdot 10H_2O$) added into the sulfate solution to increase conductivity. Acceptable current yield and product quality were achieved, but detailed evaluation of market considerations for this process showed unfavorable results due to high production costs and limited saleable product quantity.

Biodephosphorization of iron ores

Besides the direct leaching of iron from iron ores, the bioleaching approach may have better potential as a way to remove phosphorus from iron ores. Phosphorus minerals such as apatite and phosphorus-containing goethite and limonite are commonly found in many iron ore deposits. High-phosphorus iron ores generally contain a few times or even hundreds of times more phosphorus than common iron ores. Vast amounts of high-phosphorus iron ores have been reported worldwide. In China, high-phosphorus iron ores account for 15% of total reserves and are estimated to amount to 7.45 Gt (Xia et al., 2011). Although conventional hydrometallurgical processes (roasting and chemical leaching) have demonstrated high efficiency in phosphorus removal for these iron ores, they involve energy-consuming steps as well as large environmental footprints. Most importantly, the relatively lower value of iron ore cannot always justify the cost of additional facilities for dephosphorization in iron ore processing plants.

Phosphorus separation can be achieved by bacterial-mediated solubilization, providing a more environmentally friendly and cost-effective alternative to the traditional metallurgical treatments that involve roasting and acid or alkali leaching (Delvasto et al., 2005). Phosphorus is an essential nutrient for all living organisms as it is a major component of nucleic acids and the energy-storing molecules of cells. In the environment, microorganisms (particularly fungi) play an important role in the phosphorus cycle: they solubilize mineral phosphates through the production of organic and inorganic acids, making these available for plant growth. Thus, many microorganisms, especially those in nutrient-limited environments, are capable of mobilizing the phosphorus contained in minerals (Banfield et al., 1999; Nautiyal, 1999).

A study of the phosphorus-mobilizing bacteria *Burkholderia caribensis* from a Brazilian high-phosphorus iron ore deposit showed that the bacteria can be used to liberate mineral phosphate from iron ore (Delvasto et al., 2007, 2008). The production of gluconic acid and exopolysaccharides and the formation of biofilms were implicated in the proposed mechanisms by which the bacteria extracted the phosphorus contained in the ore. The major disadvantage reported for this process is the slow dephosphorization rate compared with conventional hydrometallurgical processes. It may only be applicable to the long-term leaching treatments of marginal high-phosphorus iron ores in heaps or ponds.

The effects of ore particle size on selectively bioleaching phosphorus from high-phosphorus iron ore were studied. The average contents of phosphorus and iron in the iron ore were 1.06 and 47.90% (w/w), respectively. The particle sizes of the ores used ranged from 58 to 3,350 microns. It was found that the indigenous sulfur-oxidizing bacteria from municipal wastewater could grow well in the slurries of solid high-phosphorus iron ores and municipal wastewater. The minimum bioleaching pH reached for the work was 0.33. The phosphorus content in bioleached iron ore reduced slightly with decreasing particle size, while the removal percentage of iron decreased appreciably with decreasing particle size. The optimal particle size fraction was 58-75 micron, because the phosphorus content in bioleached iron ore reached a minimum of 0.16% (w/w), the removal percentage of phosphorus attained a maximum of 86.7%, while the removal percentage of iron dropped to a minimum of 1.3% and the iron content in bioleached iron ore was a maximum of 56.4% (w/w) in this case. The iron ores thus obtained were suitable for use in the iron-making process.

Technical feasibility of bioprocessing low-grade iron ores

The technical feasibility of bioleaching has already been established for various metals on the laboratory scale. Commercial-scale bioleaching operations have been reported for the extraction of valuable gold and base metals like copper, zinc and cobalt from their sulfide ore bodies. For lean-grade iron ores and tailings, which will be the resources of the future, bioprocesses are still in their infancy or confined to the laboratory scale. The potential of heterotrophs for leaching/beneficiation is yet to be fully exploited, and major challenges in process design remain unresolved. The ideas nurtured and expertise developed in laboratories should find their ways to transformation into feasible technology; only then can the commercialization of such processes to recover metals from lean-grade iron ores or overburdens be considered as reaching reality.

The inputs to the process of bioleaching mainly depend on the type of microorganism used and should be extremely favorable for the dissolution of the targeted minerals. They include the following:

- Iron ore or concentrate to provide energy for the bioleaching microorganisms
- Proper air conditions to suit the microorganisms, based on whether they are aerobic or anaerobic
- Carbon dioxide because bioleaching microorganisms need the macronutrient carbon to build cell mass
- Nitrogen, phosphorus, potassium and magnesium: nutri-

Table 2 — Important factors influencing the bioleaching of low-grade iron ore.

Factors	Parameters	Preferred range
Physicochemical	Temperature	15-30°C
	pH	2.0-4.5
	Redox potential	
	Oxygen potential and availability	
	Carbon dioxide content	
	Nutrient availability	
	Iron (III) concentration	
	Presence of inhibitor	None
	Pressure	1 atm
	Surface tension	Low
Microbiological	Microbial diversity	
	Population density	
	Microbial activities	
	Spatial distribution of microorganisms	
	Metal tolerance	High
	Adaption abilities of microorganisms	High
Mineralogy	Mineral type	Hematite, magnetite and goethite
	Mineral composition	
	Mineral dissemination	
	Grain size	
	Surface area	
	Porosity	
	Hydrophobicity	
	Galvanic interactions	
	Formation of secondary minerals	
Processing	Leaching mode (in situ, heap, dump or tank leaching)	
	Pulp density	
	Stirring rate (tank leaching)	
	Heap geometry (heap leaching)	

ents needed by bioleaching microorganisms

- pH regulators, as some microorganisms need highly acidic environments while others need highly alkaline conditions
- Bioleaching microorganisms, such as *S. putrefaciens*
- Methods to cultivate bioleaching microorganisms for inoculation
- Temperature control mechanisms
- Distribution systems, stirring (in tanks), sprinklers, airflow, tubes that allow for the circulation of microorganisms
- Reaction catalysts, if needed

The microbial leaching of iron in acidic environments is affected by a number of factors (Table 2). The physicochemical as well as microbiological parameters of the leaching environment are the determining factors for leaching rates and efficiencies. The properties of the iron ore to be leached are also of major importance. For example, pH and particle size were identified as major factors for pyrite bioleaching by *Sulfolobus acidocaldarius* (Lindstrom et al., 1993). Optimal conditions were pH 1.5 and particle size of < 20 μm. The influence of processing parameters such as leaching mode, heap design and geometry, and temperature are equally important for the bioleaching rate.

Microbially induced iron ore flotation and flocculation

It has been widely reported that microorganisms, both living and dead, and products derived from the microorganisms, can function as flotation and flocculation agents. They can act as flotation collectors, depressants and activators depending on their interactions and adhesion of relevance to minerals, which typically change the surface chemistry of the minerals, modify the mineral surfaces (hydrophobic or hydrophilic), and selectively dissolve minerals.

Much of the focus of fundamental bioflotation and bioflocculation research had centered on the beneficiation of nonferrous sulfide minerals. Until recently, very little research effort had been expended to determine their use in the beneficiation of oxide minerals such as iron ores. Deo and Natarajan (1999) reported that bacteria such as *Bacillus polymyxa* and their metabolic products, such as exopolysaccharides, and bioproteins interact effectively with oxide minerals and bring about

Table 3 — Flotation of minerals after microbial interactions at neutral pH (7.0).

Minerals	Flotability (wt%) Control	*B. polymyxa*	*P. polymyxa*	*B. subtilis*	*S. cerevisiae (adapted)*	*D. desulfuricans (adapted)*	*R. opacus*
Reference	Deo and Natarajan (1998)	Deo and Natarajan (1999)	Deo and Natarajan (1998)	Poorni and Natarajan (2013, 2014)	Natarajan and Padukone (2012)	Sabari Prakasan and Natarajan (2010)	De Mesquita et al. (2003)
Quartz	4-19	60-80	60	96	95	78	6
Hematite	4-7	2-4	8	4	8	9	72
Kaolinite	38	80-90	-	-	-	-	-
Corundum	5	2-20	-	-	-	-	-
Calcite	8	7-8	-	-	-	-	-

significant surface chemical changes. Detailed electrokinetic studies have shown that these bacteria's interactions with quartz, hematite, calcite, kaolinite and corundum result in significant shifts in isoelectric points. Bacterial cells adsorb on the mineral surfaces to different degrees of coverage, and along with metabolite products form a biofilm. The adsorption tendency of the bacterial cells follows the sequence reported earlier (Deo and Natarajan, 1998), that is, kaolinite > calcite > corundum > hematite > quartz. The adsorption was also found to be almost independent of pH between 2 to 10, indicating that nonelectrostatic forces are responsible for the bacterial mineral adhesion.

Sarvamangala et al. (2012) reported that quartz surfaces are rendered more hydrophobic after bacterial interaction, while hematite and corundum become more hydrophilic. Similar tests indicated that kaolinite behaves similar to quartz while calcite surfaces are rendered more hydrophilic after bacterial interaction. Such microbially induced mineral surface chemical changes can be beneficially used to bring about the selective flotation/flocculation of minerals.

Table 3 shows the flotation of quartz and hematite in weight percent before and after interactions with cell and cell free metabolites. It was observed that quartz flotation was enhanced greatly in the presence of microorganisms either in the form of cells or cell free metabolites. Such an enhancement in hydrophobicity of quartz is due to mineral-induced proteins secreted by various microorganisms into the cell free metabolites during growth in the presence of quartz. It should be noted that under all conditions whether interacted with cells or cell free metabolites, hematite flotation was significantly impaired.

De Mesquita et al. (2003) conducted microflotation tests on a synthetic mineral mix of hematite and quartz using only *Rhodococcus opacus* cells as flotation reagent. The test results indicated that recovery of about 70% of hematite can be obtained with a concentrate grade of 49% for a head grade of 35% (total Fe). The results demonstrate the potential of using *R. opacus* cells as a collector at neutral pH in systems for the direct flotation of hematite where iron grade is low.

Natarajan (2003) studied the settling rates of various minerals at different pH values in the presence of bacterial cells and bacterial metabolite. It was found that the settling rates of hematite, calcite and corundum particles were increased after interaction either with the bacterial cells or the metabolites, while those of quartz and kaolinite were significantly decreased. Therefore, the selective flocculation of hematite, calcite and corundum and dispersion of quartz and kaolinite can be facilitated by bacterial interaction. Various polysaccharides such as starches and dextrans are used as depressants for iron oxides in iron ore flotation. The selective flocculation of iron oxide with dispersion of silica can be achieved by the addition of the above polysaccharides. Biopolymers such as those containing exopolysaccharides can interlink the mineral particles through polymer bridging and flocculate the mineral fines selectively. The increased affinities of bacterial cells and excreted polysaccharides toward hematite and corundum result in their selective flocculation, facilitating their rapid settling in an aqueous solution.

The results of selective flocculation tests carried out with mineral mixtures substantiate the above conclusion. It is possible to efficiently separate silica and silicates from alumina, calcite and iron oxide through bioflocculation. However, it is difficult to separate alumina from hematite efficiently using ordinary bacterial cells since bacterial interaction brings about similar surface-chemical changes on both of them. Tests with hematite–corundum mixtures have shown that both the minerals settled down faster in an aqueous medium after bacterial interaction without any selectivity. However, it has been observed that through the use of corundum-adapted strains of *B. polymyxa*, the efficient separation of alumina from iron oxides can be achieved.

The use of genetically modified microorganisms may also provide enhanced selectivity over the use of indigenous bacteria. Farahat and coworkers (2008) recently reported the potential application of molecular cloning in bioflotation. In their study, a genetically modified strain of *Escherichia coli* was used as a collector and surface modifier for quartz. The modified strain carries and expresses the silica-induced protein gene, which gives the cell a positive surface charge under acidic conditions, allowing it to adhere strongly to the negatively charged quartz. Under acidic conditions, the adsorption of the bacteria onto mineral surfaces renders the mineral hydrophobic, allowing recovery by flotation. Using the bacteria alone, the authors demonstrated that 60% recovery could be achieved by bacterial conditioning with the silica-induced protein-*E. coli* strain. Using sodium dodecyl sulfate for the anionic flotation of quartz, recoveries of up to 85% were achieved with the modified *E. coli* strain.

The laboratory experimental investigations showed that the microorganisms and iron oxide particles below 10 microns can coagulate effectively. Furthermore, it was shown that bioflotation is suitable for the separation of iron oxide minerals. However, the successful development of a bioflotation method for iron ore entails many steps. The identification of potential microorganisms is a major part of the development process. Factors such as the difficult adaptation of nonindigenous microorganisms, biofilm formation, and a lack of cheap carbon sources have hindered the scaling up of this technology. Although problems associated with large-scale and rapid bacteria culturing may be overcome by the use of genetically modified strains, its application may be considerably limited by the costs associated with modifying the microorganisms.

With the depletion of high-grade iron ores, the removal of alumina-containing minerals and phosphorus from low-grade iron ores could be the first area of application of bioflotation in the iron ore industry. The flotation behavior of kaolinite is generally opposite to that of quartz, and special care has to be taken for the successful removal of the clay minerals. The surface properties of gibbsite are similar to that of iron oxides, which makes it refractory to treatment using conventional flotation methods. The mineralogy of phosphorus in iron ore depends on the type of iron minerals. In magnetite, phosphorus is often found in the form of discrete apatite minerals, which can be removed by flotation using anionic collectors. In hematite and goethite ores, phosphorus tends to be incorporated in the lattice of iron minerals and has to be rejected by chemical methods.

Capital and operating cost estimates

The profit potential and viability of bioprocessing technology can be assessed by all financial factors in the mining process and mineral beneficiation processes. Such a feasibility study can better screen and evaluate various choices and options involved in biobeneficiation processes. This is especially true for the development of low-grade iron ore deposits, since the paramount concern is the best method of extracting the iron value.

Smith and Miettinen (2006) described major costs associated with materials and reagents for bacterial culturing as well as additional capital costs associated with the integration of bacteria or bacterial reagents in current beneficiation processes as some of the challenges that must be overcome before this technology may be applied commercially on a large scale.

In the case of in situ bioleaching, especially, the feasibility study plays a highly significant role since the percentage recovery of iron is extremely difficult to predict. Even if laboratory or pilot plant tests indicate a certain recovery, such as 60-70%, there is no guarantee that the specified recovery would be possible to attain in actual practice. In such cases it is critical for mine management to carry out the feasibility study and cash flow analyses at 60, 50, 40, 30, 20 and 10% recovery levels. If the cash flow and thus the economic viability of the process do not appear to be favorable at 50 or 40% recovery levels, then it would be preferable to reconsider the project or undertake additional laboratory and field studies in order to increase the confidence level of the economically acceptable recovery figure. On the other hand, if the feasibility study appears favorable at 30 or 20% recovery levels, all efforts should be made to initiate the in situ bioleaching operation as soon as possible.

Table 4 shows the estimated operating costs for various unit operations encountered in the in situ leaching extraction of copper and iron. As can be seen, the solvent extraction-electrowinning (SX-EW) cost for iron is considerably lower than that for copper. The primary reason for this difference is the additional cost of refining required for high-purity cathode copper, which is not required for iron because iron can be used as scraps for blast-furnace or electric-arc-furnace processes.

In addition to the known factors contributing the operating costs of bioleaching, the economics of bioleaching are strongly governed by the trade-off between the slow rate and limited extent of leaching from large particles and the cost of crushing to a finer particle size. Rawlings et al. (2007) studied the feasibility of a bioleaching project (BIOX) for the treatment of refractory gold concentrates. The bio-oxidation section contributes to more than 50% of the total BIOX plant equipment cost. The capital and operational costs of the BIOX reactors and agitators comprise the major portion of the project cost.

Table 4 — Preliminary cost comparison: Direct operating cost per ton of ore.*

Unit operations	Conventional iron ore (strip ratio 1:1.6)	Reference	In situ leaching		
			Copper	Reference	Iron
Grade	25-35%	Raman (2011)	0.4-1.2%	Dresher (2004)	15-25%
Drilling	$5-10	Raman (2011)	-	-	-
Blasting	$5-10	Raman (2011)	-	-	-
Hauling	$10-20	Raman (2011)	-	-	-
Dumping	-	-	-	-	-
Crushing	$5-7	Raman (2011)	$75 - 227	Dresher (2004)	$5-7
Ore handling	$5-7	Raman (2011)	-	-	$5-7
Concentrating	$20-50	-	-	-	-
Leaching	-	-	$125-375	Dresher (2004)	$125-375
Metal recovery	$150-250 (BF)	-	$250-350 (SX) $350-550 (EW)	Dresher (2004)	$200-400 (SX)† $300-500 (EW)†
Total cost per ton	$250-350	-	$1,000-2,000	Dresher (2004)	$650-1,300

*Cost numbers may vary depending on copper or iron recovery, energy and reagent costs, production capacity, etc.

†Estimated number based on copper solvent extraction and electrowinning (SX-EW) process.

The reactor cost depends mainly on the retention time required and material of construction.

The economics of bioflotation are relatively unknown due to the fact that few studies have utilized microorganisms isolated from ore deposits, and even fewer still have conducted flotation and flocculation experiments on real ore samples. Changing culturing conditions, cell concentration, mineral adaptation and interactions with conventional collectors and modifiers also need to be examined with respect to the production of bioreagents and utility of the microorganisms themselves for mineral beneficiation. Moreover, detailed characterizations of the extracellular and cell surface bioproteins and polysaccharides have yet to be investigated. Separating large-scale bacterial culturing from the flotation and flocculation process by utilizing cell free extracts as reagents will reduce the complexity involved, removing issues related to the large-scale culturing of microorganisms at an industrial processing plant.

Compared against a typical iron ore flotation process, the unknown overall economics of processes using microorganisms as flotation or flocculation agents can be broken down as follows:

1. Materials and operating costs for microorganisms as reagents, including:
    - The microorganisms themselves
    - Carbon source
    - Trace nutrients
    - Frothers
    - pH control
    - Dispersants, activators, depressants
    - Collector(s) if the bacteria are to be used as activators or depressants
    - Chelating agents for Ca(II) and Mg(II) control
    - Laboratory analyses
2. Capital equipment costs:
    - Flotation cells
    - Conditioning tanks and holding tanks
    - Mixing and blending
    - Pipes, conveyors, pumps, etc.
    - Flow measurement, sampling equipment, online monitoring equipment, online analytical equipment (bacteria, pH, nutrients, etc.)
    - Fermenters and associated equipment

All of these items could contribute to the cost of bioflotation process. What costs might be less than those in conventional flotation? Probably many of the materials and operating costs aside from the production and handling of the microorganisms would be comparable. Also, the capital equipment costs should be comparable except for the fermenters and associated equipment. For autotrophic bacteria (probably for use in oxide mineral flotation), the costs should be as for bioleaching. For heterotrophic bacteria, the cost of the bacteria depends on the cost of the carbon source and various nutrients, major and trace. Thus, much depends on the availability of cheap, possibly waste carbon sources.

Conclusions

It is clear from the literature discussed that microbially induced iron ore beneficiation is one of the most promising technologies for the processing of low-grade iron ores. However, much of the fundamental research had focused on the beneficiation of sulfide minerals until recently, when more research efforts have been directed toward its application in the beneficiation of iron oxide minerals.

At present, the most promising area for potential commercialization is in the treatment of iron ores containing alumina and/or phosphorus. The "niche" area for the first applications of iron ore bioprocessing is likely to be in the processing of iron ore fines that are contaminated with phosphorus and therefore unsuitable for the conventional blast-furnace ironmaking process. The bioprocessing methods that are feasible for handling high-phosphorus iron ores are bioflotation/bioflocculation and bioleaching of phosphorus. Both methods have been proven to be effective on the laboratory scale.

The estimated operating costs for bioleaching iron ore showed that the cost of iron produced by bioleaching would be less than copper produced by bioleaching due to lower requirement in product purity. However, this cost estimation is influenced significantly by the production scale, price of metal, and downstream iron recovery methods, so it is necessary to carry out pilot- or larger-scale tests to verify the economics. The economics of the biodephosphorization and bioleaching of phosphorus from iron ores are more difficult to estimate due to a lack of experimental data with actual iron ores, not to mention pilot- or larger-scale operating data. Nevertheless, biodesphosphorization is expected to be the most promising area for potential commercialization in the iron ore industry.

In conclusion, it is believed that the increasing requirement for cost-efficient and environmentally clean process technologies for low-grade iron ores will be a major incentive for adopting bioprocessing technology. A long-term pilot plant study and independent costing exercises will be necessary to support technical and economic process viability. A larger-scale demonstration plant will be required to confirm positive findings and to advance the bioprocessing of low-grade iron ore toward commercialization.

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