BIO-HYDROMETALLURGY FOR EXTRACTION OF NONFERROUS METALS

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INTRODUCTION

The advent of microbial leaching process has opened scope for supplementing the availability of different non-ferrous metals globally, and has made the exploitation of poor grade and discarded ores/tailings, refractory ores, dirty concentrates and complex resources possible for metal recovery. The importance of various types of micro organisms has been recognised in the origin of minerals and metals beneath earth crust and in dissolution of various sulfidic and oxidic ores and concentrates. Since over a decade, *Acidithiobacillus ferrooxidans* has been commercially exploited in recovery of copper and uranium from ores, and gold and silver from refractory sulfide/arsenopyrite concentrates. Biotechnology is poised to have an explicit role in mineral processing in the next millennium.

PROGRESS IN BIOLEACHING

Most of the nonferrous metals are extracted by hydrometallurgical route. They contribute more than half to the world production especially with respect to aluminium, zinc, copper, nickel, uranium etc. From the historical milestone of isolation of *Acidithiobacillus ferrooxidans* by Colmer and Hinkle in 1947 [1] to the bioleaching at copper mine of Rio-Tinto in Spain and ongoing commercial practices worldwide for extraction of various metals, the advent of microbial world in metallurgy is unequivocally felt. The role of autotrophic bacteria in sulfide dissolution has been recognized only after 1947's breakthrough, but it has been operative unknowingly ever since the advent of copper hydrometallurgy. Throughout the world, bioleaching processes are now becoming an imperative alternative. Bio-leaching on a large scale for recovering strategic metals from the low grade reserves is currently being practised by several nations like USA, Chile, Australia. For instance, nearly 10% of copper produced in USA since 1990 is through this technology [2]. Commercial applications of bioleaching in South Africa, Canada and Australia are increasing since the last 20 years. The application of biotechnology in non-ferrous extractive metallurgy is not restricted to leaching alone, but encompasses all facets of metal production, mining, beneficiation, extraction, and waste disposal.

BIOHYDROMETALLURGY - AN INHERENT WORTH

With the recognition of the interactions between the biosphere and the lithosphere, a new scientific field was opened, which is referred to as biohydrometallurgy. Today, biohydrometallurgy is an interdisciplinary subject combining geomicrobiology, microbial ecology, microbial biogeochemistry and hydrometallurgy. The advantages of controlled microbiological processing of ore low-grade mineral resources are evident such as low energy costs, the economical treatment of low-grade metal-containing materials for a cost-effective recovery of valuable metals, and the application of an industrial process that is similar to the global biogeochemical cycles in the biosphere [3].

The expected shortage of raw materials is one of the essential problems currently faced by the world. In general, the perception is focussed on the depletion of oil as an energy source, thereby neglecting the exhaustion of mineral ore deposits that are necessary to obtain metals. Since high-grade ore deposits are becoming rare, the importance of processing low-grade ore has been recognized since the seventies. Although many investigations involving high-volume low-value raw materials have been completed in recent years, biohydrometallurgy is still a very important field of research.

Bio-leaching has of late emerged as an important processing tools and sometimes only option to recover metals from the lean grade ores and discarded materials, off-grade concentrates and complex/refractory resources, because of advantages such as low cost of production, low energy consumption and eco-friendly nature. With the advent of bio-processing, several such resources have become viable leading to supplement the production of metals such as copper, uranium, gold/silver, nickel etc. Several other metals such as zinc, manganese, cobalt etc are also being considered for their recovery, besides bio-beneficiation of different ores, desulphurisation of coals and bio-sorption/ bioremediation for effluent/waste treatment [3]. For large scale bio-leaching, native microorganisms derived from the ore bodies, mainly mesophilic bacteria -*Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans*, and certain thermophiles, are mostly used to achieve intended objectives. Undoubtedly, microbial processes are slow but they are competent enough to treat the large reserves of hither to unexploited ores.

THE LEACHING MICRO-ORGANISM

Table-1 below enlists complete information about the microorganisms that plays the vital role in bioleaching.

Microorganism	Characteristic	Leaching agent requirement	Carbon Req.	Oxygen (Opt)	pH (Optimum)	Temp
Acidithiobacillus ferrooxidans	Oxidize : Fe ₂ +, S ⁰ , U ⁴⁺ , Cu ⁺ , Se ²⁺ , Thiosulfate, Tetrathionate, S ⁺	Fe ³⁺ , H ₂ SO ₄	0.C	A	1.2 - 6.0 (2.5 - 28)	5 -40 (28 - 35)
Acidithiobacillus thiooxidans	Oxidize : S ⁰ , Thiosulfate, Tetrathionate	H ₂ SO ₄	0.C	S.A	0.5 - 6.0 (2.0 - 3.5)	10-40 (28 - 30)

Table-1: Usefu	l micro-organisms in	biohydrometallu	rgy of mineral and ores
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Acidithiobacillus acidophilus	Oxidize : S ^o , organic compounds	H ₂ SO ₄	O.C	A	1.5 - 6.0 (3.0)	5-35 (25 - 30)
Leptospirillum ferrooxidans	Oxidize : Fe ²⁺ , pyrite	Fe ³⁺	0.C	A	1.5 - 4.5 (2.5 - 3.0)	20-40 (30-35)
Leptospirillum thermoferro- oxidans	Oxidize : Fe ²⁺ , pyrite	Fe ³⁺	0.C	A	1.0 - 3.5 (1.7-1.9)	30-50 (45-50)
Leptothrix Sp	Oxidize : Fe ²⁺ , S 0	$\mathrm{Fe}^{3+},\mathrm{H}_{2}\mathrm{SO}_{4}$	F.A	A	5.8-7.8 (6.8-7.2)	5-40 (30-35)
Sulfolobus acidocaldarius	Oxidize : Fe2+, S 0	Fe^{3+} , H_2SO_4	F.A	A	2 .0 - 7.0 (2.0-3.0)	55-85 (70 - 75)
Sulfolobus thermosulfio- oxidans	Oxidize : Fe ²⁺ , S ⁰ , S ²⁻	Fe^{3+} , H_2SO_4	F.A	A	1.9-3.0 (1.9-2.4)	20-60 (50)
Metalloshaera sedula	Oxidize : Fe ²⁺ , S ⁰ , S ²⁻	$\mathrm{Fe}^{3+},\mathrm{H}_{2}\mathrm{SO}_{4}$	0.C	A	0.5-3.0 (1.5-2.0)	45-75 (75-80)
Acidianus brierleyi	Oxidize : Fe ²⁺ , S ⁰ , yeast extract	H ₂ SO ₄	F.C	S.A	1.6 - 6.0 (1.5 - 2.0)	45 - 75 (70)

The most important player in the bioleaching process is *Acidithiobacillus ferrooxidans* (*A.ferrooxidans*). It is a chemoautotrophic acidophile, meaning that it obtains its energy from inorganic sources and fixes its own carbon while growing in an acidic medium. Its unique ability to oxidise ferrous to ferric, and sulphur and reduced sulphur compounds to sulfuric acid, leads to leaching of metals from their oxide and sulfide ores. These properties make it most attractive for commercial leaching operations. Due to its specific attributes, *Acidithiobacillus ferrooxidans* has been the most studied one [4]. A detailed understanding of the ecology, physiology, and genetics of this microorganism involved in bioleaching is necessary to enable their efficient utilisation in biomining processes.

Microbiology

The typical characteristics of *Acidithiobacillus ferrooxidans* depicted in Fig.1 are summarised in Table-2 below.

Condition	Characteristic		
Optimum growth pH	1.3-4.5		
Temperature range	10-37°C		
Optimum temperature	30-35°C		
Motility	0 to several polar or peritrichous flagella		

Table-2 : Characteristics of Acidithiobacillus ferrooxidans

Mol% G+C	56-59		
Gram staining	Gram-negative		
Spore formation	None		
Shape	Rod, 0.5-1 micrometers		
Trophy	Obligate chemolithoautotroph*		
Energy pathway	Oxidation of Fe ²⁺ and reduced sulfur**		
Oxygen requirements	Obligate aerobe*		
Electron acceptor	Oxygen*		
Nitrogen source	Ammonium salts, nitrate, fix dinitrogen		
Oxygen requirements	Obligate aerobe*		
Intracellular Granules	Polyphosphate granules, Sulphur granules, Carboxysomes		
Source of Energy	S ⁰ ,S ₂ O ₃ ²⁻ ,S ₄ O ₆ ²⁻ ,Fe ²⁺ ,S ²⁻ ,U ²⁺ ,Cu ¹⁺		

**A. ferrooxidans* is generally assumed to be obligately aerobic, but under anaerobic conditions, *A. ferrooxidans* can be grown on elemental sulfur using ferric iron as an electron acceptor. These results indicate that *A. ferrooxidans* can be considered a facultative anaerobe playing an important role in the iron and sulfur cycles in acidic environments. The ability of *A. ferrooxidans* to grow in oxygen deficient environments may have important implications in bioleaching processes where anaerobic conditions may often exist.

***A. ferrooxidans* may also obtain energy from oxidizing Cu⁺ and Se²⁻ and from the oxidation of tetrathionate, molecular hydrogen, formic acid, antimony compounds, uranium compounds, and molybdenum compounds.

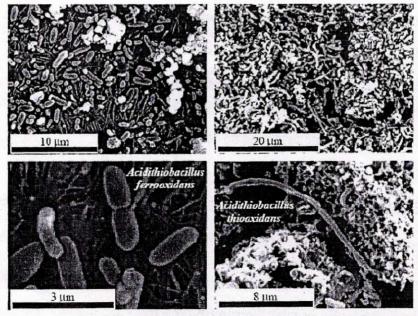


Fig.1 : SEM micrographs of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans

Leaching factors

The following are the physico-chemical and microbiological factors that contributes to the growth and activity of bioleaching microbes: -

- Physicochemical parameters of a bioleaching environment temperature :- pH, Redox potential, Oxygen content, Carbon dioxide content, Mass transfer, Nutrient availability, Iron (III) concentration etc.
- B. Microbiological parameters of a bioleaching environment microbial diversity:-Population density, Microbial activities, Metal tolerance, etc.

THE MECHANISM OF BIOLEACHING

Many base metals and a few precious metals as well as some metalloids can be enzymatically or non-enzymatically concentrated and dispersed by microorganisms in their environment. Some of these activities are commercially exploited or have a potential for it. Such metals or metalloids are present in the form of their cations or oxy-anions. These ions can be playing several roles. In few cases, they have structural or functional roles (for eg. Ca and Mg). For such functions a small concentration is sufficient. Metals also act as electron accepter or donor and thus plays a role in energy metabolism, but for this function cations or oxy-anions should be available in higher concentration.

Some of the interactions between microbes and metals are -

- 1. Structural or catalytic interaction.
- 2. Metals may act as electron donor or accepter in energy metabolism
- 3. Enzymatically microbial detoxification of harmful metals and metalloids.
- 4. Anaerobic enzymatically catalyzed Bio-corrosion of metals

Mineralytic effects of bacteria and fungi on minerals are based mainly on three principles, namely acidolysis, complexolysis, and redoxolysis. Microorganisms are able to mobilize metals by:-

- (1) The formation of organic or inorganic acids (protons);
- (2) Oxidation and reduction reactions; and
- (3) The excretion of complexing agents.

Sulfuric acid is the main inorganic acid found in leaching environments. It is formed by sulfuroxidizing microorganisms such as Thiobacilli. A series of organic acids are formed by bacterial (as well as fungal) metabolism resulting in organic acidolysis, complex and chelate formation.

The mechanisms generally involved during bioleaching are namely, Direct, Indirect and Galvanic Conversion [5].

1. **Direct Mechanism :** Cells have to be attached to the mineral surface and a close contact is needed. The adsorption of cells to suspended mineral particles takes place within minutes or hours. Cells adhere selectively to mineral surfaces occupying preferentially irregularities of the surface structure. In addition, a chemotactic behavior to copper, iron, or nickel ions has been demonstrated for *Leptospirillum ferrooxidans*. Genes involved in the chemotaxis were also detected in *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. It can be explained by the following reaction:

 $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$

3

2. Indirect Mechanism : It is mediated by ferric iron (Fe³⁺) originating from the microbial oxidation of ferrous iron (Fe²⁺) compounds present in the minerals. Ferric iron is an oxidizing agent and can oxidize, e.g., metal sulfides and is (chemically) reduced to ferrous iron which, in turn, can be microbially oxidized again. In this case, iron has a role as electron carrier. It was proposed that no direct physical contact is needed for the oxidation of iron. In many cases it was concluded that the "direct" mechanism dominates over the "indirect" mostly due to the fact that "direct" was equated with "direct physical contact". This domination has been observed for the oxidation of covellite or pyrite in studies employing mesophilic *A. ferrooxidans* in bioreactors which consisted of chambers separated with dialysis membranes to avoid physical contact. How-ever, the attachment of microorganisms on surfaces is not an indication for the existence of a direct mechanism. The term "contact leaching" has been introduced to indicate the importance of bacterial attachment to mineral surfaces.

$$4FeSO_4 + O_2 + 2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2S$$

$$2S + 3O_2 + H_2O \longrightarrow 2H_2SO_4$$

3. **Galvanic Conversion :** It is an inherent phenomenon which operates automatically in a heterogeneous system or wherever two or more different phases co-exist. Contact between different minerals can be an important factor in the general process of mineral oxidation. In addition, it was earlier recognised that the solubility of mineral sulfides increased in presence of pyrite. Minerals with a comparatively lower rest potential value behave anodically and undergo dissolution (oxidation) whereas the mineral with the higher rest potential acts as cathode at which reduction of oxygen occurs.

Anodic reaction (on active sulfide sites)

MS $M^{2+} + S^{\circ} + 2e$ O₂ + 4H⁺ + 4e \rightarrow 2H₂O

During anodic dissolution, elemental sulphur is formed due to the oxidation of sulfide mineral which covers the mineral surface and thus forms a physical barrier for further dissolution. But in presence of bacteria, elemental sulphur gets converted into sulfate further promoting the

anodic dissolution. Thus, the presence of sulphur oxidising bacteria accelerate the galvanic dissolution process.

The galvanic series for a few important base mineral sulfides in bioleaching in presence and absence of bacteria (*A. ferrooxidans*) is shown in Table-3. Among the four sulfide minerals, pyrite is the noblest with sphalerite being the most electrochemically active. Under the circumstances, sphalerite, galena and chalcopyrite bio-oxidation can be enhanced in presence of pyrite. The role of bacteria is to be an electrochemical catalyst. Relative surfaces of noble and active minerals which are in contact in anodic area determine the rate of selective dissolution. Choice of appropriate weight ratios of different sulfide minerals in mixture would govern the selective dissolution rates.

Mineral	Redox Potential, mV (SCE)		
	(-) Microbe	(+) Microbe	
Pyrite	300	450	
Chalcopyrite	200	310	
Galena	10	175	
Sphalerite	-35	-10	

Table-3:	Galvanic	series of	sulfide	minerals
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Pyrite Oxidation by Bacteria

Pyrite, FeS_2 , is the most common sulfide mineral. It is found in magmatic and igneous rocks, sedimentary deposits, and hydrothermal deposits. Pyrite has iron and sulphur, both of which can be used by this acidophilic and iron oxidizing species. In general, the rate of oxidation of pyrite increases with the concentration of ferric ions, and decreases with the concentrations of ferrous and H+ ions. The dissolution of pyrite is an oxidation-reduction reaction since the pyrite is oxidized and the ferric ions and oxygen are reduced at the pyrite surface.

The overall reaction can be written in terms of the half reactions for the oxidation of pyrite and the reduction of ferric ions.

These half-reactions are the anodic oxidation of pyrite: -

 $FeS_2 + 8H_2O$ \longrightarrow $Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^-$

And the cathodic reduction of ferric ions or dissolved oxygen,

$$Fe^{3+} + e^{-}$$
 \longrightarrow Fe^{2+}

 $O_2 + 4H^+ + 4e^- \longrightarrow 2H_0$

The overall reaction generates acid, which helps in the growth of acidophiles.

APPLICATION OF BIOHYDROMETALLURGY

In the context of bioleaching, most microbiological research is conducted utilizing known iron- and sulphur oxidising bacteria, either as single strains or in mixed cultures. However, in many instances, bacteria indigenous to the ore are not excluded and may thus contribute to

bioleaching. Indeed, it is often noted that indigenous bacteria, being acclimatised to high levels of selected metals in their environment, are more effective as bioleaching catalysts. The acclimatisation of bacteria to a particular mineral system by subjecting them to progressively greater amounts of the major elements present is common practice in test work. In addition, there have been many fundamental studies on the tolerance of single strains and cultures to base metal ions. Table-4 below details the metal tolerance of *A.ferrooxidans* to some common metal ion.

Metal	Use Tolerance (g/L)	After adaptation (g/L)		
Zn	10	120		
Cu	1	55		
Ni	10	72		
U ₃ O ₈	0.7	13		

Table-4 : Metal Tolerance in Acidithiobacillus ferrooxidans

a) Bioleaching of Copper

Extensive research studies have been carried out on the use of *A.ferrooxidans* for recovery of copper from low grade ores [6]. The process was initiated at the Kennecott Copper Corporation (USA) and practised on mine wastes which contained as little as 0.25-0.5% Cu.

In the commercial practice of biohydrometallurgy, the common type's viz., In-situ, Dump, Heap, Percolation, and Agitation/Vat Leaching are used. Fig.2 shows the hierarchy of importance of each type.

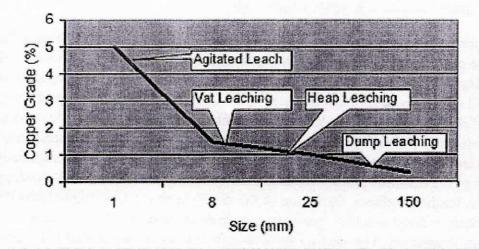


Fig. 2 : Preferential Hierarchy for commercial practice in copper bioleaching

World copper production has increased steadily in the period 1984-2007, from 9Mt to 18Mt per annum, and is predicted by the Australian Bureau of Agricultural and Resource Economics (ABARE) to reach close to 18 Mt in 2006. More than 20% of that copper is now produced via hydrometallurgy. An indirect indicator of the notable increase in hydrometallurgical copper production over recent years is the increased overall capacity of solvent extraction-

electrowinning (SX-EW) plants producing cathode copper. Copper production from SX-EW rose from 0.8 to 3.0 Mt in the period 1993 to 2007. While world demand for copper is growing, the minerals industry is increasingly faced with the need to process low grade ores, overburden and waste from current mining operations. The economic extraction of copper from lowgrade ores requires low-cost processing methods such as in situ, dump and heap leaching. Bacterially-assisted heap leaching of low-grade copper sulfides is a developing technology that has been applied successfully to the extraction of copper from secondary sulfide minerals such as chalcocite at a number of operations worldwide. However, heap bioleaching of the refractory primary copper sulfide, chalcopyrite, has yet to be implemented at commercial scale. The most successful copper heap leaching operations have been those processing copper oxides and secondary copper sulfides. Chalcocite (Cu,S) is the main copper sulfide mineral mined at bioleaching operations. Some of the chalcocite heap operations began as oxide (chemical) leach operations and were converted to bioleach (oxidative) operations by heap aeration and/ or inoculation, when the oxidised ore was depleted. However, even if bacterial activity is not facilitated, microbial assisted air oxidation of iron(II) and sulphur will contribute to copper extraction if sulfide minerals are present in a heap. Millions of tonnes of low-grade ore and copper-rich tailings await the development of an efficient and economic bioleach process for chalcopyrite (CuFeS,).

Leaching chemistry of Chalcopyrite

The extraction of selected metals from mineral sulfides such as chalcopyrite can be an oxidative process in which ferric ions are the oxidant and the sulfide component of the mineral is oxidized to elemental sulphur.

$CuFeS_{2} + 4Fe^{3+} \longrightarrow 5Fe^{2+} + Cu^{2+} + 2S^{\circ}$

The reaction is known to be sensitive to redox potential; and surprisingly, higher dissolution rates have often been measured at lower potentials, in the range 0.45- 0.65 V. The main disadvantage of (bio-)leaching of sulfides is that the process is perceived to be slow relative to pyrometallurgical process routes and other high-intensity hydrometallurgical processes. In the case of chalcopyrite, both sulphur- and iron containing reaction products have been invoked as the cause of slow dissolution. On the basis of the sulphur speciation, a mechanism for the ferric ion oxidation of chalcopyrite has been proposed. A key feature of the mechanism is the oxidation of the disulfide phase, which forms rapidly on freshly fractured chalcopyrite and persists on leached surfaces. Oxidation of the disulfide phase directly produces thiosulfate which is then oxidized to sulfate, generating the basic ferric sulfate that then acts as a template for jarosite formation. The jarosite layer then builds to the point that it hinders further chalcopyrite oxidation. The slow and incomplete extraction of copper from chalcopyrite concentrates and ores can be overcome when the ore/concentrate is finely ground. Small volume particles combined with a high surface area promoted rapid copper extraction. By the time the "inhibiting layer" had developed to the point of hindering further reaction, copper extraction was all but complete. The dissolution of copper sulfides in aqueous system can also be better correlated with the Pourbaix Diagram of copper sulfide in aqueous system as in Figure-3 below: -

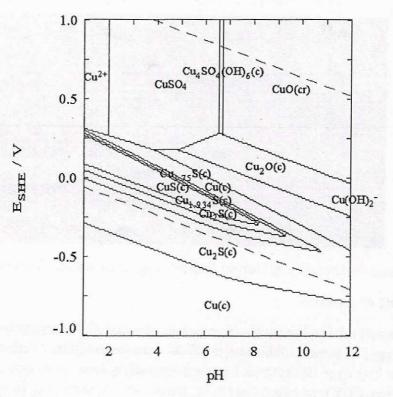


Fig. 3 : Pourbaix Diagram of Copper sulfide in water at 25°C

It is well known that the bioleaching of chalcopyrite proceeds more rapidly if the temperature is raised above about 55°C. Greater copper extraction is achieved before leaching rates are slowed by the formation of inhibitory layers on the mineral surface. The exploitation of thermophiles in the bioleaching of base metal concentrates represents a breakthrough development for the bioleaching of chalcopyrite. Some of them (Fig.4) are as follows: -

- Straits Resources operated a test heap with chalcopyrite ore in parallel with their copper oxide/chalcocite heap leach operation at Girilambone with promising results. Titan Resources operated a trial mixed nickel sulfide and chalcopyrite heap at their Radio Hill deposit with some success.
- Currently, Mintek, with the National Iranian Copper Industries Company (NICICO), are undertaking a large-scale pilot test of Mintek's heap bioleaching technology for Darehzar chalcopyrite ore at the Sarcheshmeh Copper Complex in southern Iran.
- The GEOCOAT process was evaluated as a low cost alternative for chalcopyrite bioleaching. Experiments were carried out at moderate temperature (35-45°C) using a mixed mesophilic bacterial culture, and at elevated temperature (70°C) using thermophilic archaea (extreme thermophiles). The use of thermophilic archaea at 70°C resulted in 94% extraction of the concentrate copper, and 86% of the total copper, in 90 days. The improved leaching at elevated temperatures supports the contention that chalcopyrite bioleaching at lower temperatures is limited by the formation of a heat labile passivation layer. The best result at moderate temperature was 97% copper removal achieved with the addition of 0.1% silver sulfate, compared to 19.2% without silver.

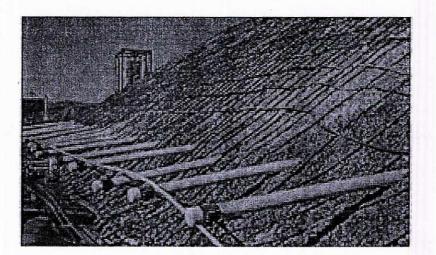


Fig. 4 : Commercial practice of Copper Bioleaching at Kennecott Corporation, USA

b) Bioleaching of uranium

Like copper, uranium ore leaching is also an example of successful commercial application of biohydrometallurgy [7]. In most of the ores, uranium occurs as a mixture of minerals containing uranium in either U (IV) or U(VI) state. Uranium is mostly soluble in its most oxidized state, that being U(VI) ion. U(IV) can be oxidized to the soluble form by ferric ion. Uranium extraction by direct acidulation is not effective and therefore oxidation of UO₂ to its hexavalent form is required which is expected in presence of Fe³⁺. Acidic ferric sulfate is used commercially as an oxidant for uranium bioleaching. A pH 1.0-3.0 is considered suitable for the bioleaching however, for rapid uranium extraction kinetics, a high Fe³⁺/Fe²⁺ ratio is necessary which determines the redox potential(Eh) of the leach liquor. For the leaching to be effective it must reach the potential (Eh) above 400 mV in accordance with Pourbiax diagram that is Fe²⁺ produced in the course of leaching must be re-oxidized to Fe³⁺ and recycled (Fig. 5).

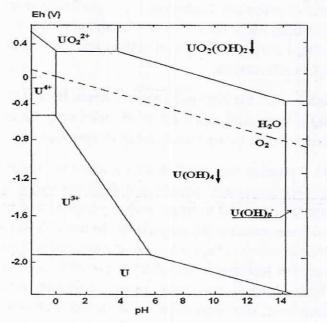


Fig. 5 : Pourbaix Diagram of Uranium in water at 25°C

In bioleaching, Fe³⁺ can be bacterially generated from the iron bearing minerals such as pyrite, which can act as an ideal lixiviant for uranium minerals indicating the uranium bioleaching to be indirect.

 $FeS_{2} + H_{2}SO_{4} + \frac{1}{2}O_{2} \longrightarrow FeSO_{4} + H_{2}O + 2S^{\circ}$ $FeSO_{4} + H_{2}SO_{4} + O_{2} \longrightarrow Fe_{2}(SO_{4})_{3} + H_{2}O$

The sulphur obtained may simultaneously be oxidized to sulfuric acid by *A.ferrooxidans* thereby maintaining acidic environment. The bioleaching of uranium from its ore involves oxidation of U(IV) to the water-soluble U(VI) and ferrous sulfate being re-oxidised to Fe(III) by bacteria.

 $UO_2 + Fe_2(SO_4)_3 \longrightarrow UO_2 SO_4 + 2FeSO_4$

2

Commercial application of bioleaching of uranium from low-grade ores has been practiced since the 1960s. The seven leading uranium producing countries in descending order are Canada, Australia, Niger, the Russian Federation, Kazakhstan, Namibia and Uzbekistan. The two largest producers viz., Canada and Australia alone account for over 50% of global production. In 1977, Canada produced about 70,000 lb of U_3O_8 using A. ferrooxidans at Agnew Lake Mine from its ore. To date commercial scale experience is limited to at Denison's Elliot Lake operations (85% uranium recovery in 20 weeks using -8mm particles) in the 1980's. Much faster leaching rates of 90% in 30 hours were demonstrated using a six-stage continuous ferric leach bacterial regeneration process. Pilot plant tests were run on feed with 0.1% U3O8 with recoveries up to 95% in ten days. However, Canada has been slower to adapt biotechnology at commercial mining operations as compared to United States, South Africa, Chile, Australia, countries in Europe and elsewhere. It was in 1975 that the Denison mines in Ontario were found ideal to bioleaching operations and simultaneously practised with in-situ and stope leaching.

c) Bioprocessing for refractory gold ores :

Refractory gold ores (sulfidic or carbonaceous) cannot be efficiently extracted by floating or direct cyanide leaching at a reasonable cost. Gold is usually contained in arsenopyrite and pyrite of primary refractory sulphidic ores and is commonly present in forms of submicroscopic particles or impregnated ores (quantity usually less than 2-3 gram/T of gold). One of potential advantage of biooxidation over the commonly applied techniques is that this specific technology allows large quantities of low grade ores (less than 1 gram/T of gold) in the world to be extracted without pre-concentration, and which otherwise, would be too costly to be considered by conventional methods [8]. The first stage of development in the application of biotechnology in treatment of refractory gold-bearing sulfide concentrates was a plant at the Fairview mine that could treat 10 tons per day (tpd) concentrate of the 40 tpd full capacity. Known as BIOX®, the process used mesophilic microorganisms (approximately 40 °C) to oxidize sulfide minerals to liberate gold in refractory sulfide gold concentrates. The minerals involved were mainly pyrite, pyrrhotite and arsenopyrite. The leaching was carried out in stirred reactors with oxygen supplied through air injection and temperature control by immersed cooling coils. Construction of the Ashanti Sansu BIOX® plant in 1994 established stirred tank bioleaching as a process suitable for very large-scale application within the gold mining industry. Developments in reactor design allowed operating volumes to approach 1000 m³ and with multiple reactors installed at Ashanti, capacity increased to approximately 1000 tpd of concentrate. This was a hundred-fold increase in capacity over the initial BIOX[®] plant at Fairview. The latest plant to be commissioned is at Fosterville in Victoria, Australia. The Navoi Mining and Metallurgical Kombinat in Uzbekistan is planning to build the largest BIOX[®] plant to date at Kokpatas.

The Hutti Gold Mines Company Limited, India with IISC-Bangalore assessed the amenability of bio-processing of refractory gold ores of Karnataka. The material contained 30 gm/ton of gold and 800 gm/ton of silver. In presence of Acidithiobacillus ferrooxidans isolated from the Hutti Gold Mines, prior biotreatment enhanced gold and silver recovery by ~ 50% at 100kg/d capacity in continuous bioreactor operations.

Major challenges existing in bio-processing of gold ores are as follows: -

- Beneficiation of low grade and high sulfidic gold-bearing ore
- Bio-oxidation of gold-bearing sulfide minerals to liberate bound gold
- Direct solubilisation of gold
- Recovery of Au, Ag etc. from cyanide effluents
- Biodegradation of cyanide wastes

It should be understood that bio-processing of sulfidic gold bearing a mineral is aimed at liberation of locked-up gold particles. In absence of prior treatment, even grinding has shown marked improvement in recovery. A typical flow sheet incorporating bio-oxidation and cyanidation is illustrated in Fig.6 below.

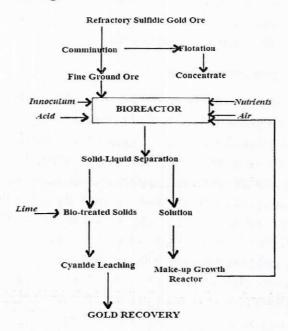


Fig. 6 : Flow-sheet for biotreatment and cyanidation of gold.

d) Biohydrometallurgy in Environmental Protection

Heavy-metal pollution represents an important environmental problem due to the toxic effects of metals, and their accumulation throughout the food chain leads to serious ecological and

health problems [9]. Metal remediation through common physico-chemical techniques is expensive and unsuitable in case of voluminous effluents containing complexing organic matter and low metal contamination. Biotechnological approaches that are designed to cover such niches have, therefore, received great deal of attention in the recent years. Biosorption studies involving low-cost and often dead/pretreated biomass have dominated the literature and, subsequently, extensive reviews focusing on equilibrium and kinetics of metal biosorption have also come up. However, the low binding capacity of biomass for certain recalcitrant metals such as Ni and failure to effectively remove metals from real industrial effluents due to presence of organic or inorganic ligands limit this approach. At times, when pure biosorptive metal removal is not feasible, application of a judicious consortium of growing metal-resistant cells can ensure better removal through a combination of bio-precipitation, biosorption and continuous metabolic uptake of metals after physical adsorption. Such approach may lead to simultaneous removal of toxic metals, organic loads and other inorganic impurities, as well as allow optimization through development of resistant species. However, sensitivity of living cells to extremes of pH or high metal concentration and need to furnish metabolic energy are some of the major constraints of employing growing cells for bioremediation. The efforts to meet such challenges via isolation of metal-resistant bacterial/fungal strains and exploitation of organic wastes as carbon substrates have began. Recent studies shows that the strains (bacteria, yeast and fungi) isolated from contaminated sites possess excellent capability of metal scavenging. Some bacterial strains possess high tolerance to various metals and may be potential candidates for their simultaneous removal from wastes. Evidently, the stage has already been set for the application of metal-resistant growing microbial cells for metal harvesting.

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REFERENCES

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- 1. Colmer, A.R. and Hinkle, M.E., Science, 106, 1947, 253-256.
- 2. Ehrlich, H.L., Hydrometallurgy, 59, 2001, 127-134.
- 3. Brierley, J.A. and Brierley, C.L., Hydrometallurgy, 59, 2001, 233-239.
- 4. Silverman, M. P., and Lundgren, D. G., Journal of Bacteriology, 77, 1959, 642-647.
- 5. Sand, W., Gehrke, T., Jozsa, P.G., and Schippers, A., Hydrometallurgy, 59, 2001, 159-175.
- 6. Watling, H.R., Hydrometallurgy, 84, 2006, 81-108.
- Tuovinen, O.H. and Bhatti, T.M., Minerals & Metallurgical Processing, 16(4), 1999, 51-60.
- Curreli, L., Loi, G., Peretti, R., Rossi, G., Trois, P. and Zucca, A., Minerals Engineering, 10(6), 1997, 561-576.
- 9. Volesky, B., Water Research, 41, 2007, 4017 4029.