UNIT 16 MINING AND BIOLEACHING

Structure

16.1 INTRODUCTION

With the advent of industrialization as well as urbanization, there is an exponential increase in the demand of industrially important minerals along the exponential increase in world population. As the technology advances so does the need for minerals of industrial importance. The high-grade deposits of ores were easily available earlier as there were huge reserves however; many of them are either depleted or soon be depleted with their present rate of extraction and consumption. Hence, it becomes increasingly important to find innovative and economical methods to recover such metals from lower-grade deposits, which for technical or economic reasons have not been extracted for usage. Various physicochemical and biological methods are available and can play an important role in recovering of valuable minerals from low-grade ores. Among biological methods, microbes are used in recovering low-grade ores acting as biocatalyst in bio mining processes meeting some of the needs of industrialized society. Such recovery processes employ microbial metabolic activities to gain access to, rather than to produce, desired products; in the form of soluble minerals or metals, this process is called bioleaching. During bioleaching for the recovery of metals, methods modify the physicochemical properties of metallic ore, so that metals can be extracted. Bioleaching is unaffected by low concentrations of the metals in the solution. Currently, biomining is at the forefront of the accessible applied mining sciences. The techniques of biomining are inexpensive, nontoxic and efficient. Moreover, the techniques are environment friendly as bioleaching results in less air pollution and little disruption to geological formations, and the microbes used are naturally present. In short mining with microbe is both ecofriendly and economical.

Bioleaching (or biomining) is a biohydrometallurgy process that extracts valuable metals from a low-grade ore with the help of microorganisms. In other words, it is also defined as metal dissolution from their mineral resources by certain naturally occurring microorganisms or their utilization to change elements, so that when water is sifted through it, elemental extraction from a material is possible. Bioleaching generally refers to the transformation of metals via microorganisms into their water-soluble form. For instance, copper sulfide (CuS_2) is oxidized microbially to copper sulphate ($CuSO_4$) in case of copper (Cu), and metals are available in the fluid stage and remaining solids are disposed off. Conversely, bio-oxidation" (a type of bioleaching), defines the microbial oxidation of minerals, containing metal compounds of interest. Subsequently, metals stay in solid deposits in concentrated form. Additional terms such as bio-extraction, biomining, and bio-recovery are also used to describe metal mobilization from solid materials interceded by microorganisms or parasites or planktonic build-ups. Biomining, primarily concerns the wide-ranging implementation of microbial courses for economic metal regeneration in the mining sector.

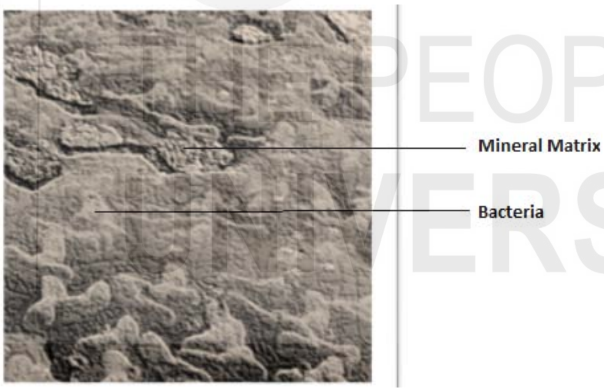
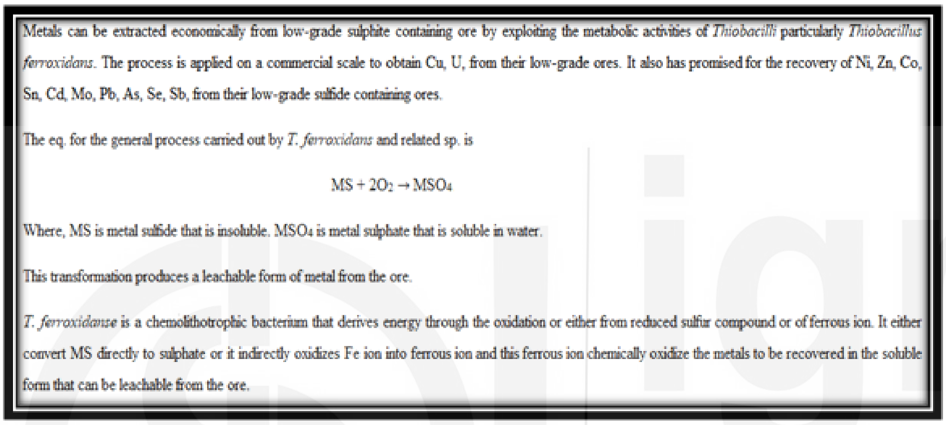


Fig.16.1: Electron microscopic view of bacteria embedded with mineral ore during bioleaching

16.2 BEGINNING OF BIOLEACHING PROCESS

Evidences shows that ancient people figured out, how to naturally recover the bioleached Copper. For example, one model was found at the hour of the Roman Empire, Spain, harking back to the eighteenth century, where recouping of copper from acidic water has been proved.However, this biotechnology development began in around 1950, after the isolation and characterization of bacteria capable of leaching Copper. This fundamental knowledge enabled the inception of understanding relationship between this unique microbial action and Cu disintegration, and its capability as an elective innovation for Copper recovery. Nowadays, this procedure is very popular in various countries with several thousand tons of extraction in case of Copper and other commercial metals. The extraction of metal sulfides was first demonstrated with the mobilization of zinc from zinc sulfide (ZnS). It was found that the transformation of ZnS to $ZnSO_4$ was microbially mediated. Later in 1947, *Thiobacillus ferrooxidans,* one the significant organism in bioleaching methods was found in an acid mine drainage. A first patent in this field of metal extraction was granted in 1958. Further exploration in this field continues which led to the popularization of this technique. Now biomining is used to recover lead (Pb), arsenic (As), antimony (Sb), nickel (Ni), molybdenum (Mo), gold (Au), silver (Ag) and cobalt (Co) in various countries esp. in India, China, Chile, South Africa, Australia, Iran, Mexico, and the United States.



Metals can be extracted economically from low-grade sulphite containing ore by exploiting the metabolic activities of *Thiobacilli* particularly *Thiobacillus ferroxidans*. The process is applied on a commercial scale to obtain Cu, U, from their low-grade ores. It also has promised for the recovery of Ni, Zn, Co, Sn, Cd, Mo, Pb, As, Se, Sb, from their low-grade sulfide containing ores.

The eq. for the general process carried out by *T. ferroxidans* and related sp. is

$$MS + 2O_2 \rightarrow MSO_4$$

Where, MS is metal sulfide that is insoluble. MSO_4 is metal sulphate that is soluble in water.

This transformation produces a leachable form of metal from the ore.

T. ferroxidanse is a chemolithotrophic bacterium that derives energy through the oxidation or either from reduced sulfur compound or of ferrous ion. It either convert MS directly to sulphate or it indirectly oxidizes Fe ion into ferrous ion and this ferrous ion chemically oxidize the metals to be recovered in the soluble form that can be leachable from the ore.

16.3 MICROORGANISMS IN BIOLEACHING

Bioleaching includes various ferrous iron and sulfur oxidizing bacteria, including one of the most commonly applied *Acidithiobacillus ferrooxidans* and *Acidithiobacillus* (formerly called *Thiobacillus*). It is a bacterium that is a non-spore forming, motile, rod-shaped and gram-negative. It is a chemo-lithotrophic bacterium which derives growth energy from sulfur or iron oxidation. It oxidizes ferrous iron (Fe^{+2}) into ferric form (Fe^{+3}), and convert soluble or insoluble sulfides, thiosulfate to sulfate ($SO^{2-}{}_4$).

T.ferrooxidans and *T. thiooxidans*, are synergistic bacteria and improves the efficiency of metal extraction from the ores when put together. Mixture of *Leptospirillum ferrooxidans* and *Thiobacillus organoparpus* can efficiently degrade pyrite (FeS_2) and chalcopyrite ($CuFeS_2$) to extract minerals of interest. Besides this, the other microbes used in bioleaching process are *Sulfolobus acidocaldarius* and *S. brierlevi.* These are thermophilic and acidophilic bacteria which grow in acidic hot springs and often used to extract Mo and Cu respectively from molybdenite (MoS_2) and $CuFeS_2$. *Pseudomonas aeruginosa*is also used in mining low grade Uranium (0.02%) ores. Among fungal strains *Aspergillus niger* can extract Cu and Ni while *Aspergillus oryzae* is employed for the extraction of Au. *Rhizopus arrhizus* is known to extract Uranium (U) from waste water. Bioleaching, in nutshell is the oxidative sulfide mineral solubilization interceded by microbial activity.

Chemolithotrophs, a group of microbes specifically use inorganic reduced compounds as a source of energy. These organisms are regularly utilized as acidophilic bioleaching microorganisms. They utilize Fe^{+2} or reduced sulfur composites as vitality source and commonly found chemical elements in ores, especially in Cu ores. The generation of ferric ion by the activity of microbes, is a strong Cu_2S oxidant, leading to the deliverance of metal into the solution. Reduced sulfur compounds are oxidized to sulfuric acid (H_2SO_4) via microbes during ferric attacks, upholding low pH, which is vital for acidophiles and the solubility of ferric iron. Microorganisms re-oxidize reduced iron, produced during mineral attacks at the end of the cycle.

16.4 OPERATING FACTORS THAT AFFECT THE PROCESS OF BIOLEACHING

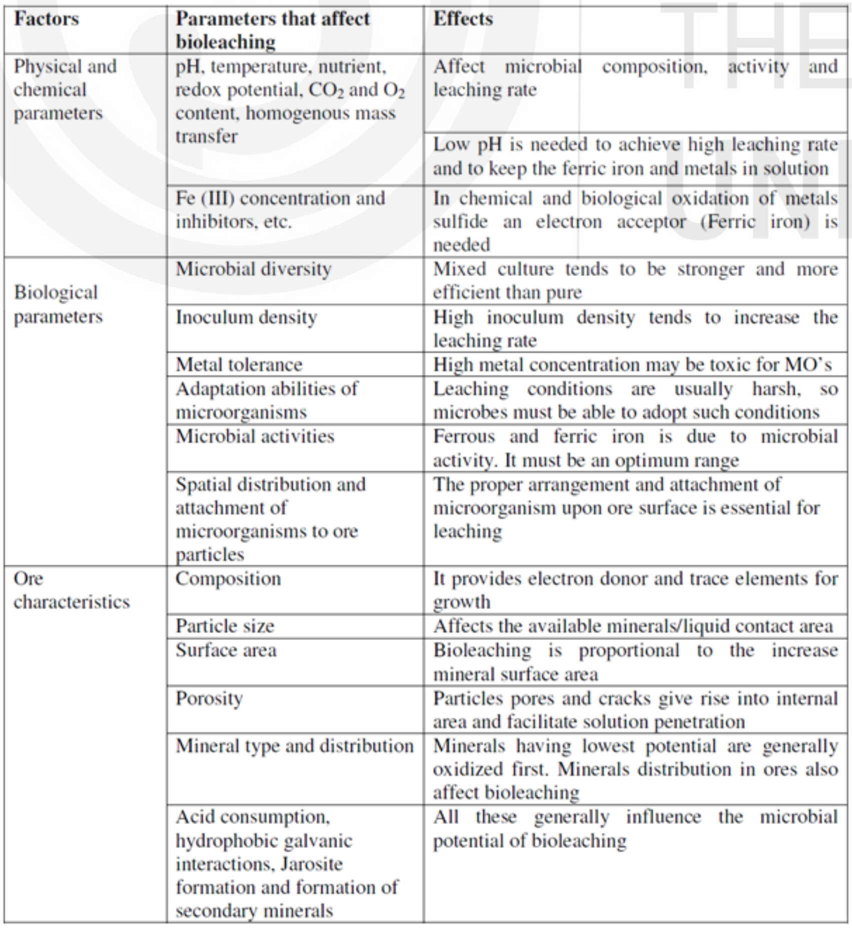
Microorganisms are undoubtedly, the primary performers in bioleaching. Since pile bioleaching is not conducted under aseptic settings, the process is taken care of by the mine site's in-situ mixed microbial consortia. A microbial consortium is a group of two or more organisms living together. A wide variety of microbes generally bacteria and archaea are available during heap bioleaching process. *.Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans*, and *Acidithiobacillus thiooxidans* are some of the most important and first recognized bioleaching bacteria. These microorganisms need nutrients for growth and to bioleach, which they must discover in their environment. A significant number of nutrients become accessible from similar ores and leaching solution, however, some of them like phosphorus and nitrogen may turn out to be rare and influence the bioleaching procedure. If economically practicable, these nutrients need to be supplemented to the leaching solution.

Bioleaching is profoundly influenced by biological, physicochemical, and environmental parameters, which in turn influence the yield of metal extraction. Two gaseous components are needed by the bioleaching microorganisms: carbon dioxide as an energy/carbon source, and oxygen as an electron acceptor. They must be shifted from gaseous phase to leaching solution, to become accessible to microorganisms. This implies that their accessibility will rely on the bioleaching framework's mass exchange characteristics.

Environmental factors like oxidation-reduction potential (ORP), pH, and temperature are significant operating conditions for microorganisms and sulfide oxidation done by ferric iron. Low pH (1-2) favors both the processes. While as, microbial tolerance fixes an upper limit in the event of temperature which obviously doesn't favor the sulfide ferric oxidation. High temperature loving organisms have appeared to get greater percentage of extraction than medium and low temperature organisms. While in ORP case, microbial action tend to increase the leaching solution as bioleaching continues. The speed of bioleaching process is more dependent on the kind of metal sulfide.

Generally primary Cu minerals ($CuFeS_2$, Enargite) are considerably harder to solubilize than the secondary ones (Chalcocite, Covellite, Bornite). Particle size influences the efficiency and degree of leaching in any extraction operation. The rate and stretch out of sulfide oxidation will rely upon the surface region presented to the leaching fluid. In turn, due to intensive smashing of the ore, elevated interface area is acquired. Diffusion phenomena control the solubilization with an enormous particle size. Initial bioleaching efforts were carried out in dump bioleaching mode, described by an exceptionally dissimilar solid bed, established by rocks as large as 1 m in distance across. In this context, the principle working factors are not controlled, resulting in low productivity. Heap is an improved and better framework, where homogeneous arrangement significantly increases the chances of bioleaching and the efficiency of the whole process. These are the contentions, why on industrial scale, it is utmost important. An outrageous circumstance is the utilization of unsettled reactors, where it is conceivable to apply tight compliance over temperature, accessibility of gaseous component, pH, and ORP. The effectiveness of bioleaching relies mainly on the expertise of microorganisms and the structure of mineralogical and chemical ores. Maximum metal extraction can be acquired only when leaching conditions are an optimal range of bacterial development conditions. Bioleaching factors and their related impacted have been listed in Table. 1

Table 16.1. Bioleaching factors and their impacts (adapted from Wasim and group, 2019)



Factors	Parameters that affect bioleaching	Effects
Physical and chemical parameters	pH, temperature, nutrient, redox potential, CO_2 and O_2 content, homogenous mass transfer	Affect microbial composition, activity and leaching rate
		Low pH is needed to achieve high leaching rate and to keep the ferric iron and metals in solution
	Fe (III) concentration and inhibitors, etc.	In chemical and biological oxidation of metals sulfide an electron acceptor (Ferric iron) is needed
Biological parameters	Microbial diversity	Mixed culture tends to be stronger and more efficient than pure
	Inoculum density	High inoculum density tends to increase the leaching rate
	Metal tolerance	High metal concentration may be toxic for MO's
	Adaptation abilities of microorganisms	Leaching conditions are usually harsh, so microbes must be able to adopt such conditions
	Microbial activities	Ferrous and ferric iron is due to microbial activity. It must be an optimum range
	Spatial distribution and attachment of microorganisms to ore particles	The proper arrangement and attachment of microorganism upon ore surface is essential for leaching
Ore characteristics	Composition	It provides electron donor and trace elements for growth
	Particle size	Affects the available minerals/liquid contact area
	Surface area	Bioleaching is proportional to the increase mineral surface area
	Porosity	Particles pores and cracks give rise into internal area and facilitate solution penetration
	Mineral type and distribution	Minerals having lowest potential are generally oxidized first. Minerals distribution in ores also affect bioleaching
	Acid consumption, hydrophobic galvanic interactions, Jarosite formation and formation of secondary minerals	All these generally influence the microbial potential of bioleaching

16.5 RECOVERY OF METALS

Bioleaching process is used to recover the metals from the ore's that are unsuitable for direct smelting because of their low-grade content. Under ideal laboratory conditions, nearly 97% recovery of Cu from the ores takes place by bioleaching, which is seldom attained in actual mining methods. Even 50 to 70% recovery of copper by bioleaching from an ore that would otherwise be completely unproductive would be an important achievement.

If the ore establishment is enough porous and over layers a water-impermeable stratum, the mineral can be leached in situ without first mining it. An appropriate boreholes pattern is created, with some holes used for leaching liquor injection and others used for leachate recovery. More often, though, this bioleaching method is accomplished after mining, splitting, and piling of the material in heaps on a water-resistant surface or on a specially constructed apron. Water is then pumped to the top of the heap and runs down through the ore of the apron. The leaching water and ore usually supplies enough dissolved mineral nutrients to satisfy the needs of *T. ferroxidans,* but in some cases, minerals such as ammonia and phosphate must be added. In most of these bioleaching operations, the leached metal is then extracted with an organic solvent and subsequently removed by stripping from the solvent. The leaching liquor and the solvent are recycled.

The characteristics of the ore have an important effect on its susceptibility to bioleaching. The rate of leaching is determined in large part by the size of the mineral particles. Increasing the surface area, accomplished by crushing and/or grinding, generally increases bioleaching however, must also be conductive for efficient leaching to occur. Optimal conditions for bioleaching use *T. ferroxidans* area temperature of 30 to 50 °C, a pH of 2.3 to 2.4, and an iron concentration of 2 to 4 g/L of leach liquor. Available oxygen and nutrients such as ammonium, nitrogen, phosphorus, sulfate and magnesium are essential for the growth of *T. ferroxidans*.

The oxidative activities of *Thiobacilli* can produce high temperature in some mineral deposits and may increase the tolerance limits of the species being used. Obviously, this would lead to decreased bioleaching activity and mineral production. Because of these high temperatures, thermophilic sulfur-oxidizing microorganisms may be useful for some bioleaching processes. Members of the genus *Sulfolobus* are obligate thermophiles that oxidizes Fe^{+2} and sulfur in a way, like that of the members of the genus *Thiobacillus*. These acid-tolerant thermophilic bacteria can oxidize inorganic substrates and are used in the bioleaching of metallic sulfides. *Sulfolobus* has been used for MoS_2 (Molybdenum sulfide) bioleaching, whereas *Thiobacillus* is not tolerant to high Mo, mercury, and Ag concentrations. Two methods of sulfide mineral oxidation have been proposed and relay on its composition. The suggested pathway for thiosulfate oxidizes species like FeS_2, MoS_2, and tungstenite (WS_2), while sphalerite ((Zn, Fe) S), $CuFeS_2$, arsenopyrite

(FeAsS), and galena (PbS) are oxidized by means of polysulfide pathway.

16.6 METHODS IN MINERAL RECOVERY

Methods play a key role in the leaching of metals from mineral bearing rocks but their activities were discovered only recently. *Thiobacillus ferroxidans* was isolated from coalmine drainage in 1947 and was subsequently associated with most of the natural and artificial leaching sites. Methods are used for recovery of minerals from low-grade ores and they do metal leaching without polluting the atmosphere. Besides *T. ferroxidans*, other acidophilic chemolithotrophic bacteria that are believed to be important to the leaching processes are *T. thioxidans*, *Leptospirillum*, *ferroxidans* and species belonging to genus *sulphobus.T. ferroxidans* is a small gram-positive straight rod-shaped bacterium. It grows best in acidic solution at pH range 1.5-2.5 with an optimal temperature range of 10-30 °C and upper limit of 37 °C. It obtains energy by the oxidation of ferrous to ferric form and the reduced form of sulfur to H_2SO_4 using oxygen as a terminal electron acceptor. It uses CO_2 as a carbon source. Other *thiobacillus* sp. that also plays a role in leaching include *T. thioxidans*, *T. acidophilus* and *T. organoborous*. Many commercial minerals of utilities are MS (metal sulphite) that are extremely insoluble. Microbial activity causes solubilization of metals from their ores either by direct leaching or by indirect leaching. These methods can be employed together for efficient recovery of the metals (Fig.2).

Direct leaching:

In this process, the microbe act directly on the ore to extract metal. *T. ferroxidans* become attached to mineral particles. Enzymes associated with the cell walls catalyze oxidative attack on crystal lattice of the MS and oxidation of mineral occurs in two steps.

$$Cu\,S + 0.5\ O_2 + 2H^+ \rightarrow Cu^{+2} + S^o + H_2O$$

$$S^o + 1.5\ O_2 + H_2O \rightarrow H_2SO_4$$

T. thioxidans and *T. ferroxidans* cooperate in leaching of sulphite mineral. When sulfide minerals are oxidized to Cu^{+2}, the S^o (elemental sulfur) is formed as a byproduct and coats the (covering Cu) remaining mineral particles and limit the further access of Cupric to mineral sulfide.*T. thioxidans* attacks this “passivating” sulfur layer and enhances the leaching process by exposing the mineral surface and by generating H_2SO_4. *Leptospirillum ferroxidans* is somewhat more acidophilic than *T. ferroxidans* and grows at pH 1.2 on FeS_2 and at temperature up to 40 °C. *Archaebacteria* of genus *sulphobolus* may also contribute to the leaching process; the organisms grow autotrophically at pH 1-3 and at temperature ranging 50-90 °C.

Indirect leaching:

In this process the microbe produce certain substances or oxidizing agents such as ferric iron or sulphuric acid which solubilize the metal for extraction. For indirect leaching acidic environment is important to extract metals. It depends on the ability of various species of acidophilic sp. like *Thiobacillus ferroxidans* to generate metabolic energy by oxidizing ferrous or sulfide leading to ferric sulphate production according to following equation:

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4$$

$$2FeSO_4 + 0.5\ O_2 + H_2SO_4 \rightarrow Fe_2\ (SO_4)_3 + H_2O$$

Ferric sulphate is a potent oxidizing agent capable of dissolving many essential minerals of copper sulfide.

$$CuFeS_2 + 2Fe_2\ (SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^o$$

(Chalcopyrite)

$$Cu_2S + 2Fe_2\ (SO_4)_3 \rightarrow 2CuSO_4 + 4\ FeSO_4 + S^o$$

(Chalcocite)

$$Cu_5FeS_4 + 6Fe_2\ (SO_4)_3 \rightarrow 5CuSO_4 + 13FeSO_4 + 4S^o$$

(Bornite)

Leaching by ferric sulphate is called as indirect because it is independent of presence of oxygen or microbial activity; an acidic pH is required for dump leaching. In its absence, the oxidation of ferrous is very slow and hence mineral leaching would be very slow. Thus, the indirect leaching means that the microbial activity supply necessary conditions and efficiency to the process. *T. ferroxidans* also derive energy by oxidizing sulfur generated in the process and give H_2SO_4.

$$2S^o + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

H_2SO_4 maintains low pH that is optimal for acidophilic *T. ferroxidans* and suppresses the loss of ferric sulphate by hydrolysis.

$$Fe_2\ (SO_4)_3 + 2H_2O \rightarrow 2Fe\ (OH)SO_4 + H_2SO_4$$

H_2SO_4also leaches several copper oxide minerals for eg:

$$Cu_3\ (OH)_2(CO_3)_2 + 3H_2SO_4 \rightarrow 2CuSO_4 + 2CO_2 + 4H_2O$$

(Azurite)

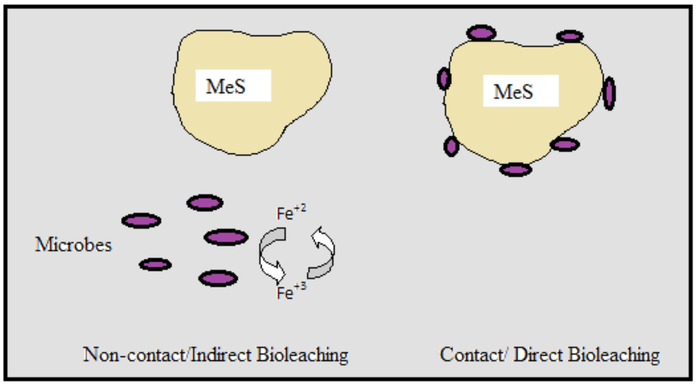


Fig. 16.2: The Indirect and direct mechanism of bioleaching

16.7 COMMERCIAL PROCESSES OF BIOLEACHING

The natural process of bioleaching is very slow. In order to increase the efficiency of the process, various methods are used commercially for maximum extraction of the minerals. The type of resource is the main factor that decides about the process involved in bioleaching. Generally three main methods are used according to the ore to be processed (Fig. 3).

a) Slope/ Dump Leaching:

It is one of the most commonest and cheap method in which the finely powdered ore are made into large piles along the slopes of a range, and water containing microbes (*Thiobacillus*) is continuously sprinkled over the slope. The collected water at the bottom is used to extract the metals. After extraction, the microbial population is regenerated in an oxidation pond.

b) Heap Leaching:

This method is used to extract low grade minerals from ore. The powdered ore is arranged in a big heap on an impervious natural surface, and then the same process of metal leaching is followed as in case of slope leaching.

c) *In-Situ* Leaching:

This process takes place at the point of generation of ore, hence called as *in-situ* process. The ore is exposed through sub surface blasting and passages for acidic water are drilled through this ore. The acidic water is pumped along with the microbe (*Thiobacillus* sp.) through these passages. A pit is made at the bottom of the ore surface to collect this percolating water. This water rich in minerals is pumped out for extraction of desired minerals. After extraction the water is reused for generation of microbial species.

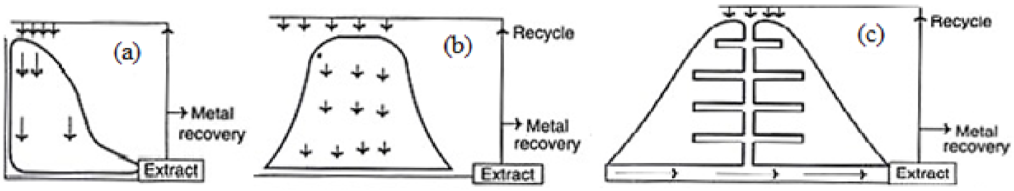


Fig. 16.3: Commercial processes of bioleaching (a) Slope (b) Heap (c) *In-situ*

Case studies:

Copper bioleaching

Copper, an element with high thermal conductivity and ductility has always been in elevated demand for electricity, construction, transportation and other industries. With its increased demand there has always been a felt a limited supply of this resource hence, bioleaching has been commonly applied to extract this mineral from low grade ores in many countries like the United States, Australia, Canada, Mexico, South Africa and Japan. The United States alone produces 10% of total copper through bioleaching. Types of copper ores used in bioleaching processes are Covellite, chalcocite and Chalcopyrite. These ores also contain fractions of other elements such as Chalcopyrite contains 26% copper, 25.9% iron, 20.5% zinc and 33% sulphur. *Thiobacillus ferrooxidans* oxidizes insoluble $CuFeS_2$ and transforms it into soluble copper sulfate ($CuSO_4$). Sulphuric acid, a byproduct produced in this reaction, maintains an acidic environment (low pH) necessary for microbial growth.

During the oxidation of Chalcopyrite the following reaction occurs:

$$2CuFeS_2 + 8\,\tfrac{1}{2}\,O_2 + H_2SO_4 \rightarrow 2\,CuSO_4 + Fe_2\,(SO_4)_3 + H_2O$$

Similarly covellite is oxidized to copper sulphate:

$$CuS + 2O_2 \rightarrow CuSO_4$$

In copper leaching processes, the action of *Thiobacillus* includes both direct and indirect oxidation of CuS via generation of ferric ions from ferrous sulfide (FeS). FeS is present in most of the important copper ores, like $CuFeS_2$. Copper is recovered by solvent extraction or by using scrap iron. In the latter case, Cu replaces Fe according to the equation:

$$CuSO_4 + Fe^0 \rightarrow Cu^0 + FeSO_4$$

16.8 RECOVERY OF COPPER BY DUMP LEACHING:

Copper ore containing more than 0.5 % of Cu is prone to smelting whereas Cu in lower grade ore is recovered by dump or heap leaching. A method in which broken rocks are piled 100 or more feet high on an impermeable surface and water. The same water is repeatedly circulated and recirculated through pile of the rock. Same time FeS_2 oxidize causes ore to become strongly acidic and rich in ferric sulphate. This water slowly percolates down through the pile and creates the applicable conditions for the growth of *T. ferroxidans* within the pile.

The effluent becomes progressively enriched in metals such as Cu. Finally the metal rich effluent is pumped in to a basin called as launder and iron scraps are added to precipitate the copper by following eq.:

$$Cu^{+2} + Fe^0 \rightarrow Cu^0 + Fe^{+2}$$

This Fe^{+2} rich solution is transferred to shallow oxidation ponds when *T. ferroxidans* rapidly oxidizes ferrous to ferric and forms some additional H_2SO_4 by oxidation of sulfur compounds. Much of Fe^{+3} formed in oxidation ponds precipitate as $Fe(OH)_3$. The acidic supernatant $Fe_2(SO_4)_3$ solution is then pumped back to top of dump. A dump can be view as a continuous flow reactor in which solubilization of metal is performed by bacteria attached to ore particles.

The bacteria thus play roles at two places:

(i) in the leached dump

(ii) in oxidation pond

At present, large-scale Cu bioleaching is mostly conducted by heaps percolation. Minerals are squashed to a particle size of about 1 cm or more in few smashing stages, healed with diluted H_2SO_4 and agglomerated before stacking into tiny mechanically resistant spheres. Using drip irrigation or sprinkling, an acid solution is applied over heaps and rehashed many times as needed to get the ideal extraction and concentration of Cu. To facilitate percolation of leaching solution, and flow of upcoming gas inoculated at bottom, it is critical to construct a homogenous heap with a high void portion to provide necessary oxygen and CO_2. Loaded liquor at that point enters the recovery segment, comprising of solvent extraction unit, which purifies and concentrates fluid in Cu and Cu recuperation by means of electrowinning. The duration of leaching may last two months or more. The schematic diagram of a typical Cu heap bioleaching operation is shown in Fig.16. 4.

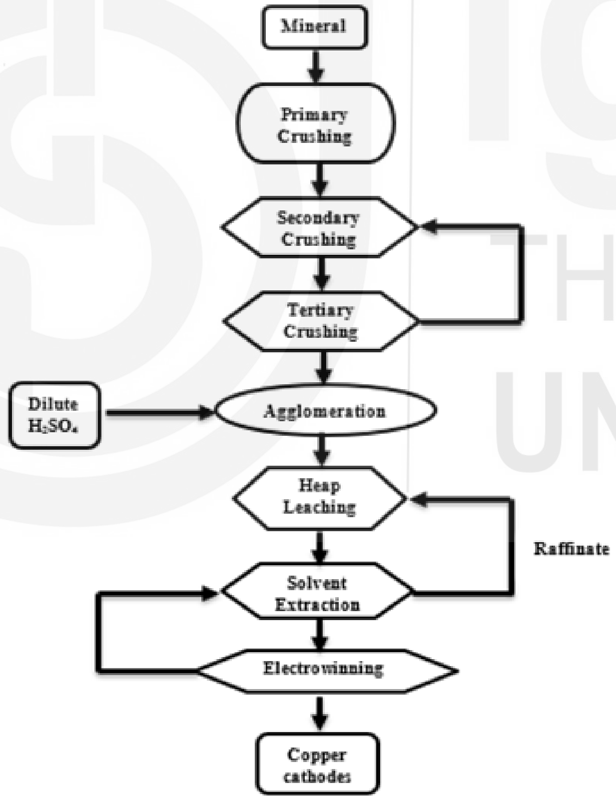


Fig. 16.4: The schematic diagram of a copper heap bioleaching operation (adapted from Gentina, 2013)

16.9 URANIUM BIOLEACHING

Uranium (U) bioleaching is commonly used in Canada, the United States, India and many other nations. This process helps to recover U from low grade ores (0.01 to 0.5% U) and low-grade nuclear wastes. The recovery of

Uranium, a fuel required by the nuclear power generation industry, can easily be enhanced by microbial activities. The microbial recovery of Uranium from otherwise useless low-grade ores is helpful in overcoming the international energy shortage. Nuclear safety and waste disposal problems, as well as the limited supply of Uranium, render current nuclear fission generators controversial; for all of these reasons, it may very well be only a stopgap solution to the international energy problem. Although bioleaching cannot influence safety considerations, this process can have an immediate and direct bearing on the economics of nuclear power production by providing a mechanism for commercial use of low-grade nuclear waste. Recovery of Uranium from radioactive wastes is extremely important because it overcomes the problem of waste disposal, a major shortcoming of using nuclear power generators.

Bacterial leaching of Uranium is most feasible in geological strata where the ore is in the tetravalent state. Insoluble tetravalent Uranium oxide (UO_2) occurs in low-grade ores. Although there is no evidence for the direct oxidation of UO_2 by *T. ferroxidans*, UO_2 can be converted to the leachable hexavalent form (UO_2SO_4) indirectly by the action of this microorganism.

Uranium ore occurs not as sulfide but as oxide UO_2 and is frequently associated with FeS_2 minerals. The Uranium is leached from ore by indirect mechanism. *T. ferroxidans* oxidizes Fe^{+2} in FeS_2 (which often accompanies the U ores) to ferric iron. The oxidized iron acts as an oxidant, converting UO_2 chemically to UO_2SO_4, which is then recovered through leaching. The optimal conditions for extraction of Uranium are: 45-50 °C temperature, 1.5-3.5 pH, and around 0.2% of incoming CO_2 air. The soluble form of U from the leach liquor is extracted into organic solvents (tributyl phosphate) which is then precipitated and recovered through ion exchange chromatography. Uranium recovery through this leaching process ranges from 30-90%.

$$UO_2 + Fe_2(SO_4)_3 + 2H_2SO_4 \rightarrow [UO_2\,(SO_4)_3]^{-4} + 2FeSO_4 + 4H^+$$

The technical and economic feasibility of employing *Thiobacillus* for the recovery of Uranium and copper minerals depends on various factors. The geological formation in which the minerals occur is also important in determining the suitability of the bioleaching process. In situ bioleaching is ideal when there is a natural drainage system, as through a fault with an impermeable basin, that will permit economic recovery of the minerals. However, recovery of Uranium is much higher in heap leaching method.

Check Your Progress 1

Notes: a) Use the Space given for your answer.

b) Check your answer with the one given at the end of this unit.

1. Explain methods of mineral recovery?

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1. Discribe Uranium biobleaching.

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16.10 BIOLEACHING OF OTHER METALS

Bioleaching technique is also used for extraction of other metals such as gold, silver, nickel, molybdenum, cobalt and antimony. This method has been considered as most promising in case of precious metal ores like Au and Ag. Removal of iron is again significant here, prior to the actual process of leaching. This is done by using the organism *Thiobacillus ferrooxidans* which precipitate iron under aerobic conditions. Au is acquired through bioleaching of arsenopyrite/FeS_2 ore and its cyanidation process. Ag is more easily solubilized than Au during microbial leaching of iron sulfide. Bioleaching is also helpful in removing certain impurities from the metal rich ores. The microorganisms such as *Rhizobium* sp. and *Brady rhizobium* sp. can remove silica from bauxite (aluminium ore) in metal purification process

Advantages of Bioleaching process

- Bioleaching is simple and effective technique in recovering metals from low grade ores.
- It is an ecofriendly and cost effective technique as compared to smelting process.
- It can used to concentrate metals from dilute mixtures and wastes.
- Compared to other processes this process does not produce any toxic emissions and other health risk to miners
- Bioleaching also offer different ways to extract valuable metals from low-grade ores that have already been processed.

However, the process has a major limitation or disadvantage due to its very slow speed in recovering metals through biological processes. Though researches are going on to make the process faster and efficient.

16.11 MICROBIAL SORPTION IN METAL RECOVERY

In the field of biotransformation and biogeochemical cycling, metal and mineral transformations by microbes are significant. Different microbial properties can cause changes in metal speciation, toxicity and mobility, along with formation, dissolution or deterioration of minerals. Among these properties, biosorption is most important in case of microbial transformation of metals. Biosorption is commonly referred to as the mechanisms involved in extracting metals from solution through microorganisms and related materials. A wide range of microorganisms (bacteria, algae, yeasts, molds) are used for biosorption of metals.

The cell membranes of microorganisms possess negatively charged ions due to presence of hydroxyl (OH^-), phosphoryl ($PO^{3-}{}_4$), carboxyl (COO^-) and sulfhydryl (HS^-) groups. Metals being positively charged ions are easily adsorbed on microbial cell surfaces. Several potential microbial metal biosorbents are members from *Bacillus, Pseudomonas, Streptomyces, Aspergillus, Trichoderma, Yarrowialipolytica, Rhizopus*, and *Penicillium sp. Rhodospirullum* sp. can bioaccumulate Cd, Hg and Pb. *Bacillus circulans*is used to bioadsorb metals such as Cd, Co, Cu and Zn. Among fungal species, immobilized fungal biomass has been widely used in metal biosorption due to mechanical strength, increased density, and resistance to chemical environment. *Aspergillus niger, A. oryzae, Mucor haemalis, Penicillium chrysogenum* helps in selective adsorption of several metal ions like Uranium, Thorium. *Pencillium lapidorum*, *P. spimuiosum* are useful for the bio sorption of metals such as Hg, Zn, Pb, Cu. Several species of fresh water or marine algae are also known to bio accumulate metals. For example, *Chlorella vulgaris* and *C. regularis* can accumulate metals like Pb, Hg, Cu, Mo and U. All these processes are confirmed by use of electron microscopy, which record the deposition of metals on the microbial cell walls which proves the composition of cell wall plays a key role in the metal adsorption.

16.12 OIL RECOVERY

Bioleaching of oil shales (oil containing rocks) likewise can possibly enhance hydrocarbons recovery. Many oil shales contains huge amount of carbonates and FeS_2, and evacuation of these minerals builds the porosity of the shale, indirectly enhancing oil recovery. Acid dissolves the carbonates and can be produced by *Thiobacillus* species growing on the sulfur and iron in FeS_2. Such microbial leaching appears to have the potential for making recovery of hydrocarbons from oil shales economically feasible.

Recovering oil involves two to three stages. Primary recovery is a stage where 12% to 15% of the oil in the well is recovered without need of any external agent. Secondary recovery involves the use of water and other substances to extract 15-20 % of more oil from well. The tertiary oil recovery is the utilization of biological and chemical agents to improve oil recovery from oil shales. Tertiary recovery of oil employs solvents, surfactant, and polymers to dislodge oil from the geological formations (Fig.5). The tertiary recovery has the potential for recovering 60 to 120 billion barrels of oil in the United States reserves alone that otherwise could not be recovered. Xanthan gum produced by bacteria such as *Xanthomonas campestries*, is a promising compound for the tertiary recovery of oil. Such polymers have higher viscosity and flow characteristics that enables them to move in the rock layers containing oil deposits through small pores. When introduced during operations of aqueous flooding, that is, injected into petroleum reservoirs to force out the oil, Xanthan gums help push the oil toward the production wells. These polymers are formed through conventional fermentation processes in which *X. campestries* is grown and the xanthan gums are retrieved.

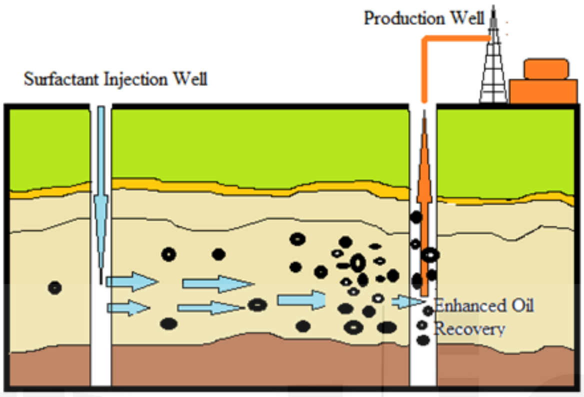

Fig. 16.5. Tertiary oil recovery process using surfactant injection method

16.13 PETROLEUM PROSPECTING

Petroleum prospecting is one of the most interesting way in which these methods aid to the petroleum industry. Associated with liquids and solid part of petroleum, a gaseous fraction also occurs. It consists of methane, ethane and propane. In petroleum producing region, these gases may seep to the surface and provide nutrient for the growth of specific hydrocarbons utilizing bacteria. When one find bacteria capable of oxidizing these gases there is a strong suggestion that a petroleum deposit is nearby. However, CH_4 utilizing bacteria are not the indicator of petroleum because CH_4 is produced biologically in many systems that are not related to petroleum (by cattle and rice field). However, C_2H_6 is not produced biologically in significant amounts and it is almost always associated only in with petroleum. Detection of C_2H_6 utilizing methods can be used as an indication of petroleum resources. Since geological methods of locating petroleum deposit are adequate, microbiological prospecting at present is not in much use. However, it may become more important in future as petroleum is getting depleted.

16.14 LET US SUM UP

In this unit we have discussed about bioleaching process, microorganisms in bioleachingand various operating factors that affect the process of bioleaching. The unit also covers recovery of metal and prospects of commercial processes of bioleaching.

16.15 KEY WORDS

Biobleaching: Bioleaching process is used to recover the metals from the ore’s that are unsuitable for direct smelting because of their low-grade content.

16.16 SUGGESTED FURTHER READING/ REFERENCES

- Douglas E. Rawlings (Ed.) Biomining Theory, Microbes and Industrial Processes. Springer Science & Business Media. 2013
- Edgardo R. Donati, Wolfgang Sand. Microbial Processing of Metal Sulfides. Springer Science & Business Media. 2007
- Pradipta Kumar Mohapatra. Textbook of environmental biotechnology, I K International. 2006
- K A Natarajan. Biotechnology of Metals Principles, Recovery methods and Environmental Concerns. Elsevier. 2018

16.17 ANSWERS TO CHECK YOUR PROGRESS EXERCISE

Check Your Progress 1

1. Refer Section Number 16.6
2. Refer Section Number 16.9