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TOPIC-BACTERIL LEACHING

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BIOLEACHING

- Bioleaching is the extraction of metals from their ores through the use of living organisms. This is much cleaner than the traditional heap leaching using cyanide.
- Bioleaching is one of several applications within bio-hydrometallurgy and several methods are used to recover copper, zinc, lead, arsenic, antimony, nickel, molybdenum, gold, silver, and cobalt.

- In nature sulfidic ores are decayed by weathering under the influence of oxygen and water
- Several bacteria, are able to solubilize heavy metal minerals by oxidizing ferrous to ferric iron as well as elemental sulfur, sulfide and other sulfur compounds to sulfate
- leaching of heavy metals from sulfidic ores under aerobic conditions about 104 fold or more compared with weathering without bacteria

- Bioleaching can involve numerous ferrous iron and sulfur oxidizing bacteria, including Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans
- □ As a general principle, Fe³⁺ ions are used to oxidize the ore. This step is entirely independent of microbes. The role of the bacteria is the further oxidation of the ore, but also the regeneration of the chemical oxidant Fe³⁺ from Fe²⁺.

Pyrite leaching (FeS2): In the first step, disulfide is spontaneously oxidized to thiosulfate by ferric ion (Fe3+), which in turn is reduced to give ferrous ion (Fe2+):

$$\mathrm{FeS_2} + 6 \; \mathrm{Fe^{3+}} + 3 \; \mathrm{H_2O} \longrightarrow 7 \; \mathrm{Fe^{2+}} + \mathrm{S_2O_3^{2-}} + 6 \; \mathrm{H^+}$$
 spontaneous

The ferrous ion is then oxidized by bacteria using oxygen:

$$4 \text{ Fe}^{2+} + O_2 + 4 \text{ H}^+ \longrightarrow 4 \text{ Fe}^{3+} + 2 \text{ H}_2\text{O}$$
 (iron oxidizers)

Thiosulfate is also oxidized by bacteria to give sulfate:

$$S_2O_3^{2-} + 2 O_2 + H_2O \longrightarrow 2 SO_4^{2-} + 2 H^+$$
 (sulfur oxidizers)

The ferric ion produced in reaction (2) oxidized more sulfide as in reaction (1), closing the cycle and given the net reaction.

 $2~{\rm FeS_2} + 7~{\rm O_2} + 2~{\rm H_2O} \longrightarrow 2~{\rm Fe}^{2+} + 4~{\rm SO_4^{2-}} + 4~{\rm H^+}$ Call/Whatsapp-8804777500 ?www.MINEPORTAL.in www.fb.com/mineportal.in

- The net products of the reaction are soluble ferrous sulfate and sulfuric acid.
- The microbial oxidation process occurs at the cell membrane of the bacteria.
- The electrons pass into the cells and are used in biochemical processes to produce energy for the bacteria while reducing oxygen to water.
- The critical reaction is the oxidation of sulfide by ferric iron. The main role of the bacterial step is the regeneration of this reactant.

The principal bacterium in ore leaching is Thiobacillus ferrooxidans, which is capable of oxidizing ferrous iron as well as sulfur and sulfur compounds. Biomining is an approach to the extraction of desired minerals from ores. Microorganisms are used to leach out the minerals, rather than the traditional methods of extreme heat or toxic chemicals, which have a deleterious effect on the environment. Using Bacteria such as Acidithiobacillus ferrooxidans to leach copper from mine tailings has improved recovery rates and reduced operating costs.
 Moreover, it permits extraction from low grade ores - an important consideration in the face of the depletion of high grade ores

The potential of thermophilic sulfide-oxidizing archaea in copper extraction has attracted interest due to the efficient extraction of metals from sulfide ores that are recalcitrant to dissolution. Microbial leaching is especially useful for copper ores because copper sulfate, as formed during the oxidation of copper sulfide ores, is very watersoluble. Approximately 25% of all copper mined worldwide is now obtained from leaching processes

□ The oxidation of the ferrous ion (Fe²⁺) to the ferric ion (Fe³⁺) is an energy producing reaction for some microorganisms. As only a small amount of energy is obtained, large amounts of (Fe²⁺) have to be oxidized.

copper

- Acidithiobacillus ferrooxidans is able to oxidize the Cu+ in chalcocite (Cu2S) to Cu2+, thus removing some of the copper in the soluble form, Cu2+, and forming the mineral covellite (CuS).
- This oxidation of Cu+ to Cu2+ is an energy yielding reaction (such as the oxidation of Fe2+ to Fe3+).
- Covellite can then be oxidized, releasing sulfate and soluble Cu2+ as products.

A second mechanism, and probably the most important in most mining operations, involves chemical oxidation of the copper ore with ferric (Fe3+) ions formed by the microbial oxidation of ferrous ions (derived from the oxidation of pyrite). Three possible reactions for the oxidation of copper ore are

$$\Box$$
 $Cu_2S + 1/2 O_2 + 2 H^+ \rightarrow CuS + Cu^{2+} + H_2O$

$$\square$$
 CuS + 2 O₂ \rightarrow Cu²⁺ + SO₄²⁻

$$\square$$
 CuS + 8 Fe³⁺ + 4 H₂O \rightarrow Cu²⁺ + 8 Fe²⁺ + SO₄²⁻ + 8 H⁺

- The copper metal is the recovered by using Fe⁰ from steel cans:
- \Box Fe⁰ + Cu²⁺ \rightarrow Cu⁰ + Fe²⁺

Uranium

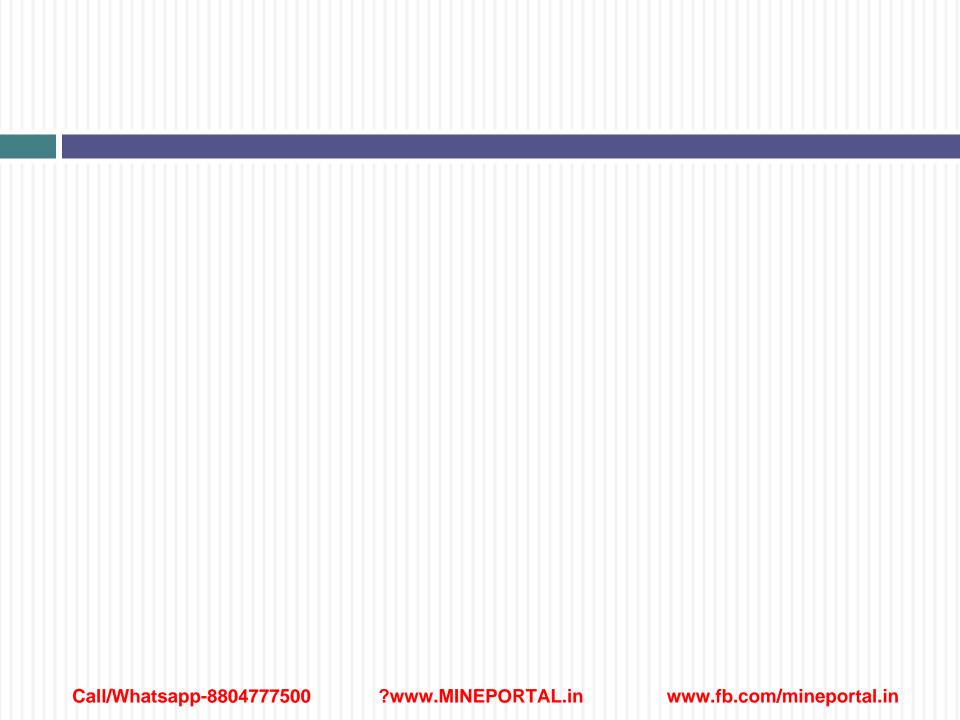
□ Acidithiobacillus ferrooxidans can U⁴⁺ to U⁶⁺ with O₂ as electron acceptor. However, it is likely that the uranium leaching process depends more on the chemical oxidation of uranium by Fe³⁺, with At. ferrooxidans contributing mainly through the reoxidation of Fe²⁺ + to Fe³⁺ + as described above.

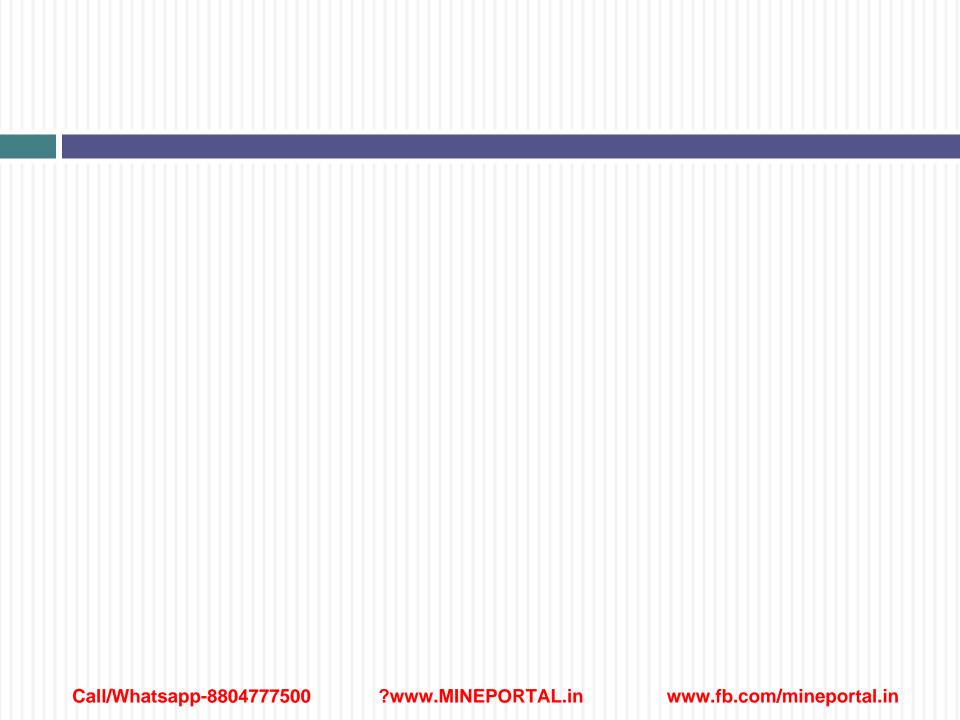
 \square UO₂ + Fe(SO₄)₃ \rightarrow UO₂SO₄ + 2 FeSO₄

Gold

□ Gold is frequently found in nature associated with minerals containing arsenic and pyrite. In the microbial leaching process At. ferrooxidans and relatives are able to attack and solubilize the arsenopyrite minerals, and in the process, releasing the trapped gold (Au):

□ 2 FeAsS[Au] + 7 O₂ + 2 H₂O + H₂SO₄ \rightarrow Fe(SO₄)₃ + 2 H₃AsO₄ + [Au]





Bacterial ore leaching can be applied to extract heavy metals from low grade ores, industrial wastes and other materials on an industrial scale by different procedures: dump leaching, in situ leaching, tank leaching, leaching in suspension.

- Microbial leaching of ores depends primarily on bacterial processes which are the essential causes of natural weathering of sulfidic minerals.
- If sulfidic heavy metal minerals come into contact with air and water they begin to decay with the formation of sulfate, sometimes sulfuric acid, and water soluble heavy metal cations.

Weathering of an ore body results in a typical picture

An upper oxidation zone, being in contact with atmospheric oxygen and rain water, which contains secondary minerals formed by oxidation of the primary ore minerals and in most cases a remarkable enrichment of ferric iron minerals (limonite and others).

- an underlying cementation zone just below the groundwater level, in which minerals, formed by the reaction of primary ore minerals with the constituents of the leaching solution descending from the oxidation zone, are accumulated.
- A zone in which the primary ore minerals are unchanged.

Microbiology of ore leaching

Thiobacilli

- The principal bacteria which play the most important role in solubilizing sulfidic metal minerals at moderate temperatures are species of the genus Thiobacillus. They are gramnegative rods, either polarly or nonflagellated.
- Most species are acidotolerant, some even extremely acidotolerant and acidophilic. Some grow best at pH 2 and may grow at pH 1 or even at pH 0.5. Most species are tolerant against heavy metal toxicity

Thiobacillus ferrooxidans

- In addition to the oxidation of sulfur and sulfur compounds Thiobacillus ferrooxidans is able to oxidize ferrous to ferric iron and so derive its energy from this exergonic reaction. In this reaction hydrogen ions are consumed and so the pH of the medium should rise.
- But at pH values higher than 2 the ferric iron precipitates as ferric hydroxide, jarosites or similar compounds and this results in the formation of hydrogen ions, so that the pH of the medium is lowered as is the case with oxidation of sulfur compounds:

$$2Fe^{++} + 2H^{+} + \frac{1}{2}O_{2} ----> 2Fe^{+++} + H_{2}O$$

 $2Fe^{+++} + 6H_{2}O$ ----> $2Fe(OH)_{3} + 6H^{+}$
 $2Fe^{++} + 5H_{2}O + \frac{1}{2}O_{2}$ ----> $2Fe(OH)_{3} + 4H^{+}$

Thiobacilli and sulfidic minerals

- Some Thiobacilli, especially T. ferrooxidans, are able to oxidize sulfide and some heavy metals mainly iron but also copper, zinc, molybdenum and presumable some other metals in the form of sulfidic heavy metal minerals which are of very low solubility in water, practically insoluble.
- These oxidations result in a solubilization of the minerals. This is often seen in the case of pyrite or marcasite, both FeS2, minerals which are oxidized very easily by Thiobacilli

FeS₂ + H₂0 +
$$3\frac{1}{2}O_2$$
 \rightarrow Fe⁺⁺ + 2 SO₄⁻⁻ + 2 H⁺

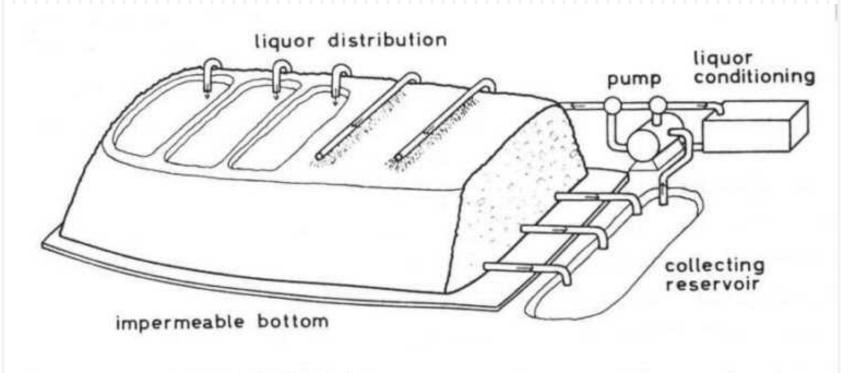
Me^{II}S + $2O_2$ \rightarrow Me⁺⁺ + SO_4 ⁻⁻

Dump leaching

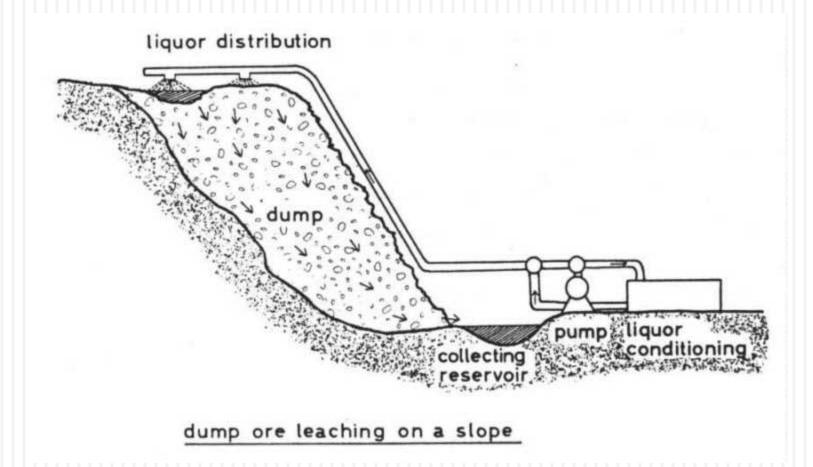
- The most commonly applied method is that of the percolator principle. Big dumps of ore are set up on an impermeable ground.
- The grain size has to be so that on the one hand the leaching liquor can percolate through the dump and air may enter from the sides, and on the other hand the distances for mass diffusion inside the grains are as short as possible.

- The leaching liquor is distributed on the top of the dumps by sprinklers or by intermittent flooding of ponds.
- At the bottom the liquor is collected, in some cases by a drainage system, and conducted to a collecting reservoir from which it is pumped back on top of the dump.
- Before pumping back to the dump the whole liquor or a part of it may be conditioned, that means extracting the dissolved metal (for instance copper by cementation with iron scrap), addition of sulfuric acid if the pH is too high and addition of nutrient salts if desired.

- In the industrial microbial leaching process popularly known as bioleaching, low grade ore is dumped in a large pile (the leach dump) and a dilute sulfuric acid solution (pH 2) is percolated down through the pile.
- The liquid coming out at the bottom of the pile, rich in the mineral is collected and transported to a precipitation plant where the metal is reprecipitated and purified.
- The liquid is then pumped back to the top of the pile and the cycle is repeated



dump ore leaching



- Copper from ores which contain sulfides are leached on the whole by dump leaching. Chiefly copper ores of the porphyric type (disseminated copper ores) with low concentrations of copper (below 0.6% Cu) are leached in this way.
- For instance in some states of the U.S.A. at some open pit mines, in which low grade copper ores are excavated, big dump leaching facilities are operated.
- □ The height of the dumps ranges from 20 m to about 200 m and they may contain up to 10° t of ore at one mine. The grain size is up to 1 m³, the copper concentration is 0.1 to 0.6%.

- □ The pH of the circulating liquor is about 2.0 3.5, its iron concentration about 35 60 mmol/l. In the on-flowing liquor the iron is almost completely ferrous iron, whereas in the outflow only 108 to 40%, sometimes 70%, of the iron is ferrous iron.
- So we can conclude, that iron is oxidized by the bacteria almost exclusively inside the dump.

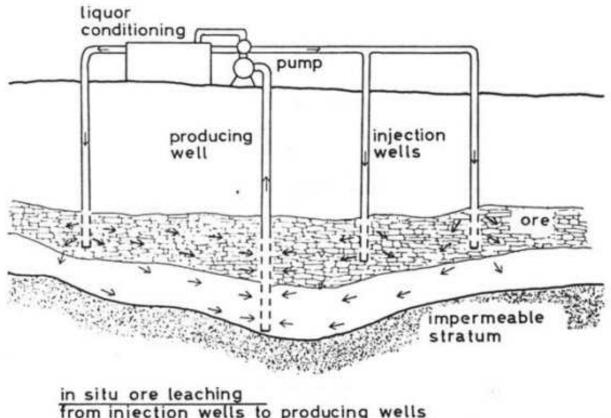
- In most cases the addition of nutrients is not necessary because Thiobacilli are lithoautotrophs and need only some inorganic nutrients besides an energy source.
- The required inorganic nutrients may be taken from the ore. The nitrogen source may be an exception for ores usually contain only small amounts of nitrogen compounds

□ Operating big dumps the circulation rate is about 5000 m^3 of liquor per hour (20 -30 l × m⁻² × h⁻¹). The copper concentration of the out-flowing liquor is about 8 mmol/l (500 g/m³).

- Bacterial leaching is a very slow process. Around 3 to 10% of the copper content is leached out of a low grade sulfidic copper ore per year. So dumps may be operated 10 to 20 years.
- But on the other hand dump leaching is a simple and cheap method. It needs only a little capital investment, has low operating costs, requiring-little labor, and is well-suited to low grade ores if they contain the metal in sulfidic minerals or if sulfides are contained in addition

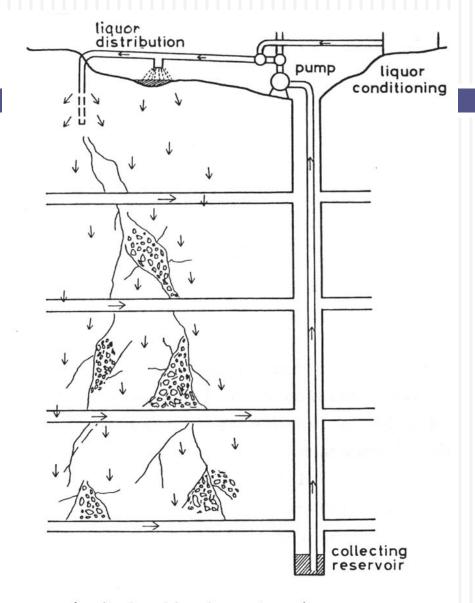
In situ leaching

- In a few cases it has been attempted to leach ores by means of bacteria without excavating the ore prior to leaching.
- At first sight it seems advantageously to leach ores on the spot were they are, for excavating costs can be saved.
- But difficulties arise if the ore body is impermeable or if there are only a few channels through which the leaching liquor would stream downwards without percolating the ore body entirely. In such cases the ore body has to be cracked by explosions.



in situ ore leaching from injection wells to producing wells

- Moreover there may be some difficulties connected with the geological situation because it is necessary to collect the liquor after it has passed through the ore body. Unsuitable siting may lead to large amounts of the leaching fluid escaping underground.
- To my knowledge bacterial leaching in situ, in a strict sense, has not yet been performed. In the U.S.A. uranium deposits were leached in situ underground as shown in the picture



in situ leaching in a mine

- But these leachings were done abiotic without using bacteria. There are some bacterial leaching set-ups which in a broader sense can be called in situ leaching. To this belongs the percolating of a worked-out mine with residues of ore as is schematically shown.
- In Canadian uranium mines after they were workedout the walls, roofs and floors were hosed down at intervals of several months. The water was collected and the uranium extracted.

Problems

Advantages of bioleaching

- Economical: Bioleaching is in general simpler and, therefore, cheaper to operate and maintain than traditional processes, since fewer specialists are needed to operate complex chemical plants.
- Environmental: The process is more environmentally friendly than traditional extraction methods. [citation needed] For the company this can translate into profit, since the necessary limiting of sulfur dioxide emissions during smelting is expensive. Less landscape damage occurs, since the bacteria involved grow naturally, and the mine and surrounding area can be left relatively untouched. As the bacteria breed in the conditions of the mine, they are easily cultivated and recycled.
- Ore concentration: Bioleaching can be used extract metals from ores that are too poor for other technologies. It can be used to partially replace the extensive crushing and grinding that translates to prohibitive cost and energy consumption in a conventional process.

Disadvantages of bioleaching

- Economical: The bacterial leaching process is very slow compared to smelting. This brings in less profit as well as introducing a significant delay in cash flow for new plants.
- Environmental: Toxic chemicals are sometimes produced in the process. Sulfuric acid and H+ ions that have been formed can leak into the ground and surface water turning it acidic, causing environmental damage. Heavy ions such as iron, zinc, and arsenic leak during acid mine drainage. When the pH of this solution rises, as a result of dilution by fresh water, these ions precipitate, forming "Yellow Boy" pollution. For these reasons, a setup of bioleaching must be carefully planned, since the process can lead to a biosafety failure. Unlike other methods, once started, bioheap leaching cannot be quickly stopped, because leaching would still continue with rainwater and natural bacteria.

