Microbes and mineral recovery: Bioleaching of copper, gold and uranium.

Dr. Yogender Pal Khasa
The elements or compounds, which occur naturally in earth's crust are known as MINERALS.

At some places, minerals contain a very high percentage of a particular metal and the metal can be profitably extracted from it. These are called ORES.
- **Smelting**: it is a form of extractive metallurgy; to produce a base metal from ore. It uses heat & chemical reducing agent to decompose the ore, driving off other gases or slag & leaving just the metal behind.

- Discharge large amount of carbon dioxide, sulphur dioxide & other toxic materials such as arsenic.

- **Roasting**: roasting is a metallurgical process involving solid-gas reactions at elevated temperature with the aim of purifying the metal component.

- It is a serious source of pollution.

- These methods are very intensive & require high concentration of elements in ores.
Conventional smelting processes discharge large amount of CO₂, SO₂ and various toxic materials such as arsenic... rising cost of environmental protection throughout the world.

They require high energy and capital input as Ores with low metal content are not suitable for direct smelting.

As the high-grade deposits of certain metals are being depleted, there is a pressing need to find innovative and economical procedure to recover metals from low grade deposits.

There is urgent need to develop alternate technologies to recover metals from low grade ores and minerals.

Microorganisms can play an important role in meeting some of these needs.
BIOLEACHING

- **Bioleaching** is the extraction of metals from their ores through the use of living organisms where “the dissolution of metals from their mineral sources by certain naturally occur microorganisms”

- Bioleaching refers to the conversion of solid metal values into their water soluble forms by the use of microorganisms.

- Conversion of insoluble metal sulfides into water-soluble metal sulfates.

- Copper sulfide is microbially oxidized to copper sulfate and metal values are present in the aqueous phase and the remaining solids are discarded.

- Bioleaching is an important field of biohydrometallurgy.
Why bioleaching...?

- Reduce fixed capital cost and environmental problems
- Carried out under ambient conditions without addition of toxic materials
- The process of bioleaching takes place at atmospheric pressure and lower temperatures than smelting. Thus, the energy consumption at the mining site is less.
- Products of these process usually ends up in aqueous solution—more amendable to containment & treatment.
Bioleaching is the extraction of a metal from sulfide ores or concentrates using materials found native to the environment.

Bioleaching is the commercialization of the ability of certain bacteria and archaea, found in nature, to catalyze the oxidation of sulfide minerals.

The leaching of sulfide minerals distinguishes bioleaching from conventional acid leaching.

Bioleaching involves the use of microorganisms to catalyze the oxidation of iron sulfides to create ferric sulfate and sulfuric acid.

Bioleaching is used today in commercial operations to process ores of copper, nickel, cobalt, zinc and uranium.
• Recovery of metals from low and lean grade ores using conventional techniques is very expensive due to high energy and capital inputs required.

• Another major problem is environmental costs due to the high level of pollution from these technologies.

• Biological leaching is regarded as one of the most promising and certainly the most revolutionary solution to these problems.

• It holds the promise of dramatically reducing the capital costs and environmental pollution.

• Biological processes are carried out under mild conditions, usually without addition of toxic chemicals.

• The products of biological processes end up in aqueous solutions which is easier to treat than gaseous waste.
**Advantages**

**Economical**: bioleaching is generally simpler and therefore cheaper to operate and maintain than traditional processes.

**Environmental**: The process is more environmentally friendly than traditional extraction methods. Liquid effluent generated can be neutralized and no sulphur dioxide emission.

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.

**Disadvantages**

**Not economical**: the bacterial leaching process is very slow compared to smelting.

**Not environmental**: Toxic chemicals are sometimes produced in the process. Sulfuric acid and H⁺ ions formed can leak into the ground and surface water turning it acidic, causing environmental damage.
Microorganisms Involved

- A consortium of microorganisms namely *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans*, *Burkholderia*, *Erwinia*.

- Thermophilic bacteria including *Sulpholobus thermosulphidoxidans* and *Sulpholobus brierleyi* are known to be involved in bioleaching.

- The most important microorganism in the bioleaching process is *Thiobacillus ferrooxidans* (now called *Acidithiobacillus ferrooxidans*) isolated by A R Colmer and M E Hinkle in 1947.

- 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 sulphuric acid, leads to leaching of metals from their oxide and sulphide ores.

- *Thiobacillus thiooxidans*, a sulphur oxidising bacterium works in association with *A. ferrooxidans* in bioleaching process. It is an autotrophic bacterium which produces sulphuric acid and facillitates the growth of other metal leaching species.
Mechanisms

A generalised reaction can be used to express the biological oxidation of a mineral sulphide involved in leaching:

\[ \text{MS} + 2\text{O}_2 \rightarrow \text{MSO}_4, \]

where M is a bivalent metal.

There are two major mechanisms of bacterial leaching:
1) involves the ferric-ferrous cycle (indirect mechanism)
2) involves physical contact of the organism with the insoluble sulphide (direct mechanism).

An important reaction mediated by \textit{Acidithiobacillus ferrooxidans} is:

\[
4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}.
\]

Ferric sulphate is a strong oxidising agent capable of dissolving a wide range of metal sulphide minerals. Leaching brought about by ferric sulphate is termed indirect leaching because it proceeds in the absence of both oxygen and viable bacteria.
This mode is responsible for leaching several minerals:

\[
\begin{align*}
\text{CuFeS}_2 (\text{chalcopyrite}) + 2\text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{S}^2, \\
\text{FeS}_2 (\text{pyrite}) + \text{Fe}_2(\text{SO}_4)_3 & \rightarrow 3\text{FeSO}_4 + 2\text{S}^2, \\
\text{UO}_2 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4 & \rightarrow \text{UO}_2(\text{SO}_4)_4 + 2\text{FeSO}_4 + 4\text{H}^+. 
\end{align*}
\]

Elemental sulphur generated by indirect leaching can be converted to sulphuric acid by *Acidithiobacillus ferrooxidans*:

\[
2\text{S}^2 + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 .
\]

In the direct mechanism of leaching by bacteria, intimate contact and adhesion to the mineral takes place prior to enzymatic attack by the organism. The direct mechanism is inferred from scanning electron micrographs which demonstrate bacterial adhesion on mineral surfaces.

The direct mechanism is further confirmed by the leaching of synthetic sulphides free of iron, where only the direct attack of the bacteria can lead to leaching:

\[
\begin{align*}
\text{CuS (covellite) + 2O}_2 & \rightarrow \text{CuSO}_4 , \\
\text{ZnS (sphalerite) + 2O}_2 & \rightarrow \text{ZnSO}_4 .
\end{align*}
\]
History of bioleaching

- Copper recovery from mine waters in the Mediterranean area 3000 years ago

- Heapleaching in Spain in big scale 300 years ago the process was seen as natural degradation

- The role of bacteria in bioleaching was shown in first time in 1947

- In the beginning of 1950’s *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* were indentified (currently *Thiobacillus* has been renamed to *Acidithiobacillus*)

- In 1950´s copper dump leaching

- In 1960´s the first industrial copper heap leaching operation

- First industrial gold bioleaching plant in 1980´s

- Nowadays about 40 plants in industrial use for copper, gold, zinc, cobalt, uranium
### MICROORGANISMS INVOLVED

- Bioleaching can involve numerous **ferrous iron and sulfur oxidizing bacteria**

<table>
<thead>
<tr>
<th>Mesophilic range</th>
<th>Thermophilic range</th>
<th>Hyperthermophilic range</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Acidithiobacillus albertensis</em></td>
<td><em>Acidimicrobium ferrooxidans</em></td>
<td><em>Acidianus brierleyi</em></td>
</tr>
<tr>
<td><em>Acidithiobacillus ferrooxidans</em></td>
<td><em>Acidithiobacillus caldus</em></td>
<td><em>Metallosphaera sedula</em></td>
</tr>
<tr>
<td><em>Acidithiobacillus thiooxidans</em></td>
<td><em>Sulfoabacillus acidophilus</em></td>
<td><em>Sulfolobus acidocaldarius</em></td>
</tr>
<tr>
<td><em>Leptospirillum ferrooxidans</em></td>
<td><em>Sulfoabacillus thermosulfidooxidans</em></td>
<td><em>Sulfolobus acidophilus</em></td>
</tr>
<tr>
<td><em>Leptospirillum ferrphilum</em></td>
<td><em>Sulfoabacillus thermotolerans</em></td>
<td><em>Sulfolobus metallicus</em></td>
</tr>
<tr>
<td><em>Thiobacillus prosperus</em></td>
<td><em>Ferroplasma acidiphilum</em></td>
<td><em>Sulfolobus thermosulfidooxidans</em></td>
</tr>
</tbody>
</table>
<30 °C
1. *Thiobacillus* spp.
2. *Acidithiobacillus* spp.

30-50 °C
1. *Ferroplasma* spp.
2. *Leptospirotillum* spp.
4. Eukaryotes

> 50 °C
2. 

\[
\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} \\
\rightarrow \text{heat} + 16\text{H}^+ + 2\text{SO}_4^{2-} + 15\text{Fe}^{2+}
\]
The method used to extract a metal from its ore depends on the reactivity of the metal.

**Most reactive**

- K
- Na
- Ca
- Mg

| Very reactive metals – extracted using **electrolysis** |

**Al**

| More reactive metals – usually extracted by **reduction** – heating with carbon to remove oxygen |

| C |
| Zn |
| Fe |
| Sn |
| Pb |

| Unreactive metals – little or no extraction needed |

| H |
| Cu |
| Ag |
| Au |
| Pt |

*Sometimes non-metals are included for reference.*
Factors affecting bioleaching

<table>
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<th>Factor</th>
<th>Effect</th>
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<tr>
<td><strong>Physicochemical</strong></td>
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<td>Population density</td>
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<td>cracks and pores in the particles give rise to the internal area</td>
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Factors Affecting Bioleaching

**Physicochemical**

**Temperature and pH**
- affects leaching rate, microbial composition and activity
  - needs to be low to obtain the fastest leaching rates and to keep ferric iron and metals in solution
  - electron acceptor needed in chemical and biological oxidation

**Microbiological**

- **Microbial diversity cultures**
  - mixed cultures tend to be more robust and efficient than pure

- **Population density**
  - high population density tends to increase the leaching rate

- **Metal tolerance**
  - high metal concentrations may be toxic to microorganisms
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<td>Presence of other metal sulfide</td>
<td>mineral having the lowest potential is generally oxidized first</td>
</tr>
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</table>
Contact Leaching

- The bacteria oxidise ferrous iron (Fe2+) and sulphur (S) to produce ferric iron (Fe3+) and sulphate (SO42-)
- The Fe3+ in turn reacts with the sulphide minerals to produce Fe2+ and S
Microorganisms exerts bioleaching in following ways..

**Direct**
- It is viewed as a process by which components within the bacterial membrane interact directly with the metal and sulfide moieties of the mineral by using an enzymatic type of mechanism.

**Indirect**
- Refers to a chemical attack by ferric iron or protons on a mineral sulfide that results in the dissolution of the mineral.
- Iron oxidizing microbes use the ferrous iron as an electron donor, reoxidizing it to ferric iron, thereby regenerating the reactant.
- Ferric iron in turn chemically oxidizes the metal to be recovered.
• Bacterial dissolution of sulphide minerals is thought to involve 2 mechanisms:

a) **DIRECT LEACHING** – bacteria attach themselves to the metal sulphide crystals within the rock and then oxidise the metal sulphide crystals to soluble sulphates through oxidation..thus dissolving the metals

b) **INDIRECT LEACHING** – bacteria need not be in contact with the mineral. The role of the bacteria is to oxidise the ferrous iron to the ferric form which then oxidises the sulphide minerals producing ferrous iron. The bacteria only have a catalytic function.
Diversity of microbes and Bioleaching
selection pressure

 adaptation

 transferred to next generation

 of microbes with the "right"

 "constructive" genetic changes become fixed in the

 methods for control & investigation

 cultivation identify/ characterize

 anthropogenically optimized molecularly by investigating

 growth/fission multiply during

 genome/gene pool

 continuously change

 genetic variation cause?

 environment/community

 detoxification & excretion of metals

 metal resistance

 geological agent because of

 metabolism may cause

 Bioleaching Bioprecipitation Other processes

 Bioaccumulation Biorosorption Biocoagulation Biotransformation

 Cell

 microbially-mediated mineral transformations

 will affect
Mobilization

1. Oxalate, siderophores
2. S(0), Fe(II)
3. H₂SO₄, Fe(III)

Bioleaching (e.g., Au, Cu, Ni, Co, U)
(i) Heterotrophic leaching
(ii) Chemolithotrophic leaching
(iii) Reductive mineral dissolution

Bioreduction (e.g., Ag, Au, Pd, Se, Te, U)

Biosorption (e.g., Ag, Au, Dy, Ru, U)

Bioaccumulation (e.g., U, Dy)

Bioprecipitation (e.g., Ca, Cd, Zn, Sr, U)

Immobilization

Poly phosphate

Me(aq)

- NH₂, -HPO₄²⁻, -COOH, -OH

Me(s), Me(aq)-chelate

Me(aq)

Me(s), Fe(III)

Me(s), Fe(III)

Me(s)

Me(aq), Fe(II)

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Au-bearing refractory ore (or) low-grade Au ore

- Crushing & Grinding
- Screening & Flotation
- Nutrient solutions & inoculum
- Bio-oxidation (Pre-treatment)
- Pregnant solution with base metals and impurities
- Solvent stripper
- Pregnant solution with gold
- Bio-cyanidation
- Electro-winning
- Smelting & bullion

Residual ore (carbon acid wash)
- Pre-treated ore
- Nutrient solutions & inoculum
- Tailing pond
- Electro-winning
- Smelting & bullion
- Gold
- Base metal
Fig. 16.2. Froth flotation process
WEATHERING OF AN ORE BODY

Water oxygen

Goethite $\alpha$-FeOOH
Siderite FeCO$_3$
Azurite Cu$_3$[OH$_2$CO$_3$]$_2$
Malachite Cu$_2$[(OH)$_2$]CO$_3$
Cerussite PbCO$_3$
Smithsonite ZnCO$_3$
Anglesite PbSO$_4$
Goslarite ZnSO$_4$·7H$_2$O
Melanerite FeSO$_4$·7H$_2$O
Chalcanthite CuSO$_4$·5H$_2$O
Silver Ag
Argentite Ag$_2$S
Copper Cu
Covellite CuS
Pyrite FeS$_2$
Chalcopyrite CuFeS$_2$
Chalcocite Cu$_2$S
Galena PbS
Sphalerite ZnS

oxidation zone

groundwater level

cementation zone

unchanged primary ore
Bioleaching strategies

- HEAP BIOLEACHING
- STIRRED TANK BIOLEACHING
- DUMP BIOLEACHING
- INSITU BIOLEACHING (hole-to-hole leaching)

What method is followed depends on:

- The ore type
- Its geographical location
- Metal content
- Specific minerals present
Heap bioleaching

- The soil on a slightly sloping ground is first compacted and then covered with an impermeable pad like an asphalt layer or a flexible plastic sheet.

- Crushed ore is stacked in big heaps on the pad. Fine particles are agglomerated to increase permeability.

- The heap is sprayed with leaching reagent.

- As the reagent percolates through the heap the wanted metals are solubilised.

- The leachate (metal containing solution) drained from the heap is collected in a pond and the solution is subsequently sent for metal recovery.

- Compared to stirred tank reactors, heap reactors form undesired gradients of pH and reagent levels.
Heap leaching followed by solvent extraction and electrowinning
Copper leachate from heap to pond
Advantage:

- Simple equipment and operation,
- Low investment and operation costs,
- Acceptable yields
- Environment friendly

Disadvantage:

- The piled material is heterogeneous and practically no close process control can be exerted, except for intermittent pH adjustment and the addition of some nutrients.
- Heap reactors are more difficult to aerate efficiently and
- Undesirable formation of gradients of pH and nutrient levels as well as liquor channeling are difficult to manage.
- Moreover, the rates of oxygen and carbon dioxide transfer that can be obtained are low, and extended periods of operation are required in order to achieve sufficient conversion
Copper recovery process using bio-mining technology

1. Dumped low-grade sulfide copper ore
2. Heap bio-leaching
3. Leaching solution
4. Solvent extraction / electrowinning (SX/EW)
5. Copper cathodes

Steps:
- Cultivation / inoculation of bacteria
- Sulfuric acid
Tank bioleaching:

- Known as **stirred tank process** (major form)
- Requires construction of large aerated tanks, generally arranged in series so that the reactor can operate in a **continuous flow mode** with fresh ore being added in the 1st tank while run off from the last tank is removed and treated.
- The ore is crushed so that solids remain suspended in liquid medium.
- Used for highly valuable materials (high cost of tanks).
- The process is used as a pretreatment to remove low valuable sulphide material from higher valuable materials such as gold.
Stirred tank process

- Stirred-tank processes use highly aerated, continuous-flow reactors

- Finely ground mineral concentrate or ore is added to the first tank together with inorganic nutrients in the form of ammonia- and phosphate-containing fertilizers

- The stirred suspension flows through a series of pH- and temperature-controlled aeration tanks in which the mineral decomposition takes place

- Mineral decomposition takes only days in stirred-tank reactors compared with weeks or months in heap reactors.

- Stirred-tank reactors that operate at 40 and 50 °C have proven to be highly robust, and very little adaptation is required for the treatment of different mineral types.
Figure. Stirred tank biooxidation. The slurry of crushed ore and liquid ore is moved from tank to tank to ensure adequate time for arsenopyrite oxidation. The last tank is a settling tank where the solids containing gold are removed and extracted using cyanide.
The diagram illustrates the process of extracting copper from leached ore. The chemical reaction involved is:

$$2\text{Fe}_2(\text{SO}_4)_3 + \text{CuFeS}_2 + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$$

The process involves leaching the ore, followed by precipitation of copper. Air is introduced to facilitate the oxidation reaction. Leptospirillum bacteria aid in the conversion of FeSO4 to Fe2(SO4)3.
2. **Continuous bioreactor**

The ore is placed into the reactor and water pumped through on a continuously recirculating basis as shown below.
The mineral **is extracted directly from the mine instead** of collecting the ore and transferring to an extracting facility away from the site of the mine.

Rarely, under favorable geological conditions, microbes maybe induced to release the metals into solution without any mechanical mining.

If the **ore formation is sufficiently porous and overlies water-impermeable strata**, a suitable pattern of boreholes is established. Some holes are used for injection of leaching liquor and others for recovery of leachate (HOLE – TO – HOLE LEACHING).

**In situ** leaching involves pumping of solution and air under pressure into a mine or into ore bodies made permeable by explosive charging.

The resulting metal-enriched solutions are recovered through wells drilled below the ore body.
**In situ leaching** This is only practical under favorable geological conditions. Wells are drilled, the outer wells are used to apply leach liquor, and the center well is the recovery shaft.

In all cases, the leached metal can be recovered by electrolysis.

But the majority of metal recovery operations use a solvent or lixivient extraction.

The lixivient is a kerosene-like material that contains a metal-chelating agent.

The metal partitions into the lixivient layer and out of the water phase.

The metal is then recovered from the lixivient.
in situ ore leaching from injection wells to producing wells
in situ leaching in a mine
DUMP BIOLEACHING:

- Same as heap bioleaching except for the fact that the uncrushed ore is piled up.
- Dump leaching involves uncrushed waste rock which is piled up.
- These dumps generally contain about 0.1-0.5% copper, too low to recover profitably by conventional procedures.
- Some of these dumps are huge, containing in excess of 10 million tons of waste rock.
- Essentially, dump leaching involve the application of the lixiviant to the top of the dump or heap surface and the recovery of metal laden solution that seeps to the bottom by gravity flow.
- The dilute sulphuric acid sprinkled on top percolates down through the dump, lowering the pH and promoting the growth of acidophilic microorganisms.
- The acid run-off is collected at the bottom of the dump, from where it is pumped to a recovery station.
- Copper is extracted from the acid run-off by solvent extraction or electrowining.
Figure 30

**Dump Leaching**

Uncrushed stones of low-grade oxide or sulfide ores (a) are hauled from the mining pit to a dump (b), where they are sprayed with a water solution (c). The influent solution, aided by the growth of sulfur- and metal-oxidizing bacteria, leaches metal salts from the ore. The salt-rich leachate is collected in an effluent pond (d) and either recycled immediately (e) to pick up more of the metal-containing salts or pumped (f) to the processing plant for removal of the metal.
dump ore leaching on a slope
<table>
<thead>
<tr>
<th>Factor</th>
<th>Parameter</th>
</tr>
</thead>
</table>
| Physicochemical parameters of a bioleaching environment | temperature  
pH  
redox potential  
water potential  
oxxygen content and availability  
carbon dioxide content  
mass transfer  
nutrient availability  
iron(III) concentration  
light  
pressure  
surface tension  
presence of inhibitors  
microbial diversity  
population density  
microbial activities  
spatial distribution of microorganisms  
metal tolerance  
adaptation abilities of microorganisms  
mineral type  
mineral composition  
mineral dissemination  
grain size  
surface area  
porosity  
hydrophobicity  
galvanic interactions  
formation of secondary minerals  |
| Microbiological parameters of a bioleaching environment | leaching mode (*in situ*, heap, dump, or tank leaching)  
pulp density  
stirring rate (in case of tank leaching operations)  
heap geometry (in case of heap leaching)  |
| Properties of the minerals to be leached |                                                                           |
| Processing                                |                                                                           |
• **ADVANTAGES**
  - **Economical:** bioleaching is generally simpler and therefore cheaper to operate and maintain than traditional processes.
  
  - **Environmental:** The process is more environmentally friendly than traditional extraction methods. Liquid effluent generated can be neutralized and no sulphur dioxide emission.
  
  - Less landscape damage occurs, since the bacteria involved grow naturally, and the mine and surrounding area can be left relatively untouched.
  
  - Bacteria are easily cultivated and recycled.

• **DISADVANTAGES**
  - The bacterial leaching process is very slow compared to smelting.
  
  - Toxic chemicals are sometimes produced in the process. **Sulfuric acid** and H\(^+\) ions formed can leak into the ground and surface water turning it acidic, causing environmental damage.
Bioleaching of Copper
Bioleaching of copper

- Copper has been one of mankind's most important metal resources since the beginning of civilization, and to this day it holds an important role in the functioning of modern society.

- Copper is necessary in the electrical industry, piping, coinage.

- Copper compounds are used as bacteriostatic substances, fungicides, and wood preservatives.

- In 2009, global copper consumption topped 21 billion tons (Copper Development Association).
• Copper is rarely found in its native form; most often it exists as ores made up of various copper sulfides and oxides that have little practical value of their own.
• The most efficient copper minerals are chalcocite (Cu2S), chalcopyrite (CuFeS2), covellite (CuS).

<table>
<thead>
<tr>
<th>Table 1. Common copper ores (Gaines et al. 1997).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mineral</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td><strong>Oxides</strong></td>
</tr>
<tr>
<td>Cuprite</td>
</tr>
<tr>
<td>Tenorite</td>
</tr>
<tr>
<td>Malachite</td>
</tr>
<tr>
<td>Chrysocolla</td>
</tr>
<tr>
<td>Atacamite</td>
</tr>
<tr>
<td><strong>Sulfides</strong></td>
</tr>
<tr>
<td>Chalcocite</td>
</tr>
<tr>
<td>Covellite</td>
</tr>
<tr>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>Bornite</td>
</tr>
<tr>
<td>Enargite</td>
</tr>
<tr>
<td>Tennantite</td>
</tr>
</tbody>
</table>
Chalcopyrite

(1) \( \text{CuFeS}_2 + 4 \text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 5 \text{Fe}^{2+} + 2 \text{S}_0 \) (spontaneous)

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

(3) \( 2 \text{S}^0 + 3 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{SO}_4^{2-} + 4 \text{H}^+ \) (sulfur oxidizers)

**Net reaction**

(4) \( \text{CuFeS}_2 + 4 \text{O}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{SO}_4^{2-} \)
A. Sulfide oxidation

\[ S^{2-} \rightarrow S^0 \rightarrow SO_3^{2-} \rightarrow SO_4^{2-} \]

(A) Metal leaching

\[ MS \rightarrow M^{2+} + SO_4^{2-} \]

\[ ZnS \rightarrow Zn^{2+} + SO_4^{2-} \]

B. Ferrous iron oxidation

\[ Fe^{2+} \rightarrow Fe^{3+} \]

(A+B) Metal leaching

\[ FeS_2 \rightarrow Fe^{3+} + 2SO_4^{2-} \]

\[ CuFeS_2 \rightarrow Cu^{2+} + Fe^{3+} + 2SO_4^{2-} \]

C. Ferric iron as oxidizing agent

\[ Fe^{2+} \rightarrow Fe^{3+} \]

Indirect leaching

\[ MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^0 \]

\[ FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S^0 \]

\[ UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+} \]

Fig. 1. Classical understanding of reactions carried out by *T. ferrooxidans* and metal leaching.
The following equations describe the “direct” and “indirect” mechanism for the oxidation of pyrite (Murr, 1980; Sand et al., 1999):

**direct:**

\[
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{thiobacilli}} 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4
\]  

(1)

**indirect:**

\[
4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \xrightarrow{T. \text{ferrooxidans, L. ferrooxidans}} 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}
\]  

(2)

\[
\text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{chemical oxidation}} 3\text{FeSO}_4 + 2\text{S}
\]  

(3)

\[
2\text{S} + 3\text{O}_2 + \text{H}_2\text{O} \xrightarrow{T. \text{thiooxidans}} 2\text{H}_2\text{SO}_4
\]  

(4)
The following equations summarize the oxidation mechanisms (SAND et al., 1999):

Thiosulfate mechanism (found for FeS$_2$, MoS$_2$, WS$_2$):

$$\text{FeS}_2 + 6\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^{2-} - 7\text{Fe}^{2+} + 6\text{H}^+$$  \hspace{1cm} (5)

$$\text{S}_2\text{O}_3^{2-} + 8\text{Fe}^{3+} + 5\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 8\text{Fe}^{2+} + 10\text{H}^+$$ \hspace{1cm} (6)

Polysulfide mechanism (found for PbS, CuFeS$_2$, ZnS, MnS$_2$, As$_2$S$_3$, As$_3$S$_4$):

$$2\text{MS} + 2\text{Fe}^{3+} + 2\text{H}^+ \rightarrow 2\text{M}^{2+} + \text{H}_2\text{S}_n + 2\text{Fe}^{2+}$$ \hspace{1cm} (7)

$$\text{H}_2\text{S}_n + 2\text{Fe}^{3+} \rightarrow 0.25\text{S}_8 + 2\text{Fe}^{2+} + 2\text{H}^+$$ \hspace{1cm} (8)

$$0.25\text{S}_8 + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+$$ \hspace{1cm} (9)
• Copper is recovered from leaching solution by:

1. Solvent partitioning
2. Scrap iron

1. **Ligand exchange solvent extraction:** The copper is removed by bonding to a ligand, which is a large molecule consisting of a number of smaller possessing a lone electron pair groups, each. The ligand-copper complex is extracted from the solution using an organic solvent:

   \[ \text{Cu}^2+ (\text{aq}) + 2\text{LH(organic)} \rightarrow \text{CuL}_2(\text{organic}) + \text{H}^+(\text{aq}) \]

• Then the copper is passed through an **electro-winning process** to increase its purity:

   An electric current is passed through the resulting solution of copper ions. Because copper ions have a 2+ charge, they are attracted to the negative cathodes and collect there.

2. **Scrap iron:**

   • CuSO$_4$ + Fe$^0$ → Cu$^0$ + FeSO$_4$
   • Solvent partitioning may lead to presence of residues, which if not removed, may inhibit the activity of *A. ferrooxidans*
Fig. 13.1 General scheme showing how an acidophilic chemolithoautotroph such as *A. ferrooxidans* oxidizes ferrous iron and sulfur and reduced sulfur compounds to generate sulfuric acid. Surface proteins from *A. ferrooxidans*, most of which are periplasmic proteins involved in energetic metabolism, are shown. The proteins shaded in gray were identified experimentally by proteomic analysis of the periplasmic fraction. The unknown periplasmic proteins indicated are most likely unique of *A. ferrooxidans*, and may have several different unknown functions (Chi et al. 2007). Adapted from Rawlings 2005; Chi et al. 2007 and Jerez 2008.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Period of operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lo Aguirre, Chile</td>
<td>1982-2001</td>
</tr>
<tr>
<td>Cerro Colorado, Chile</td>
<td>1993-present</td>
</tr>
<tr>
<td>Quebrada Blanca, Chile</td>
<td>1994-present</td>
</tr>
<tr>
<td>La Escondida, Chile</td>
<td>2006-present</td>
</tr>
<tr>
<td>Andacollo, Chile</td>
<td>1996-present</td>
</tr>
<tr>
<td>Dos Amigos, Chile</td>
<td>1996-present</td>
</tr>
<tr>
<td>Ivan-Zar, Chile</td>
<td>1994-present</td>
</tr>
<tr>
<td>Zaldivar, Chile</td>
<td>1998-present</td>
</tr>
<tr>
<td>Cerro Verde, Peru</td>
<td>1998-present</td>
</tr>
<tr>
<td>Gunpowder’s Mammoth, Australia</td>
<td>1991-present</td>
</tr>
<tr>
<td>Mt. Leyson, Australia</td>
<td>1992-1997</td>
</tr>
<tr>
<td>Girilambone, Australia</td>
<td>1993-2004</td>
</tr>
<tr>
<td>Equatorial Tonopah, USA</td>
<td>2001-2002</td>
</tr>
<tr>
<td>S&amp;K Copper, Myanmar</td>
<td>1998-present</td>
</tr>
<tr>
<td>Plant and location/owner</td>
<td>Cathode copper production (t/year)</td>
</tr>
<tr>
<td>----------------------------------------------------------------------------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Lo Aguirre, Chile/Sociedad Minera Pudahel</td>
<td>15,000</td>
</tr>
<tr>
<td>Mount Gordon (formerly Gunpowder), Australia/Aditya Birla</td>
<td>33,000</td>
</tr>
<tr>
<td>Lince II, Chile/Antofagasta plc</td>
<td>27,000</td>
</tr>
<tr>
<td>Mt. Leyshon, Australia/(formerly Normandy Poseidon)</td>
<td>750</td>
</tr>
<tr>
<td>Cerrro Colorado, Chile/BHP-Billiton</td>
<td>115,000</td>
</tr>
<tr>
<td>Girilambone, Australia/Strait Resources and Nord Pacific</td>
<td>14,000</td>
</tr>
<tr>
<td>Ivan-Zar, Chile/Compañía Minera Milpro</td>
<td>10,000–12,000</td>
</tr>
<tr>
<td>Punta del Cobre, Chile/Sociedad Punta del Cobre</td>
<td>7,000–8,000</td>
</tr>
<tr>
<td>Quebrada Blanca, Chile/Teck Resources</td>
<td>75,000</td>
</tr>
<tr>
<td>Andacollo Cobre, Chile/Teck Resources</td>
<td>21,000</td>
</tr>
<tr>
<td>Dos Amigos, Chile/CEMIN</td>
<td>10,000</td>
</tr>
<tr>
<td>Skouriotissa Copper, Cyprus/Hellenic Copper</td>
<td>8,000</td>
</tr>
<tr>
<td>Cerrro Verde, Peru/Freeport McMoran</td>
<td>54,200</td>
</tr>
<tr>
<td>Zaldivar, Chile/Barrick Gold</td>
<td>150,000</td>
</tr>
<tr>
<td>Lomas Bayas, Chile/Xstrata</td>
<td>60,000</td>
</tr>
<tr>
<td>Monywa, Myanmar/Myanmar No. 1 Mining Enterprise</td>
<td>40,000</td>
</tr>
<tr>
<td>Nifty Copper, Australia/Aditya Birla</td>
<td>16,000</td>
</tr>
<tr>
<td>Equatorial Tonopah, Nevada/Equatorial Tonopah, Inc.</td>
<td>25,000 (projected)</td>
</tr>
<tr>
<td>Morenci, Arizona/Freeport McMoran</td>
<td>380,000</td>
</tr>
<tr>
<td>Zijinshan Copper, China/Zijin Mining Group</td>
<td>20,000</td>
</tr>
<tr>
<td>Lisbon Valley Mining Company, Utah</td>
<td>10,000</td>
</tr>
<tr>
<td>Jinchuan Copper, China/Zijin Mining Group</td>
<td>10,000</td>
</tr>
<tr>
<td>Whim Creek and Mons Cupri, Australia/Strait Resources</td>
<td>17,000</td>
</tr>
<tr>
<td>Spence, Chile/BHP Billiton</td>
<td>200,000</td>
</tr>
<tr>
<td>Tres Valles, Chile/Vale SA</td>
<td>18,500</td>
</tr>
</tbody>
</table>
Theory diagram for the electrolysis of COPPER(II) SULFATE SOLUTION with a COPPER ANODE and a COPPER CATHODE.

Deposit of copper metal on electrode surface

Positive ions are attracted to the negative electrode, gain electrons, so are reduced REDUCTION

Net ion movement

Method of collecting electrode products ignored in this diagram

copper anode dissolving eaten away by oxidation!

electrolyte of dilute copper sulfate solution

Negative ions are attracted to the positive electrode, BUT they do not change, instead copper atoms lose electrons, oxidised to copper 2+ ions still OXIDATION
As the atoms of the impurities are not transported, the copper that builds up on the anode is extremely pure.
BIOLEACHING OF GOLD
Chemolithotrophs: organisms able to use reduced inorganic compounds (e.g., H2, sulfide) as a source of energy and CO2 as carbon source for growth. These organisms are also termed chemoautotrophs.

Chitosan: a derivative of chitin (poly b(1–4)-N-acetyl-D-glucosamine), the second most abundant natural polymer worldwide after cellulose. Chitin can be solubilized in acidic medium by increasing deacetylation to 50%. The acid-soluble form of chitin is termed chitosan.

Critical metals: elements which are essential for economic development but are associated with scarce availability and a supply security risk. The scarcity of critical metals is perceived as an increased supply risk faced by the industry and is made evident by price volatility. These elements are essential in electronic and green energy technologies, but are only available at low abundance and/or are produced in only a few countries. The list often includes platinum group metals, REEs, cobalt, and tellurium.

Cyanogenic bacteria: bacteria that produce the secondary metabolite hydrogen cyanide (HCN) from glycine. Cyanide is used as a lixiviant for selective leaching of Au from ores and waste materials. Bioleaching of Au cyanogenic bacteria is attractive for recovering precious Au from e-waste.

Methylicotrophic bacteria: are able to thrive by using single-carbon compounds such as formate, formaldehyde, or methanol as the sole carbon and energy source. Methanol dehydrogenase mediates methanol oxidation, which requires small amounts of lanthanides as a cofactor. Thus, growth medium is often supplemented with small quantities of lanthanides during isolation and for improving the growth of methylotrophs.

Ore beneficiation: a pretreatment process used for removing gangue minerals in the form of tailings and to produce higher-grade ore. For example, beneficiation processes separate iron minerals (e.g., Fe2O3 or Fe3O4) from other impurities (e.g., alumina, silica) in the iron ore.

Strategic metals: elements required for national defense applications but which face supply risk due to limited domestic production. Urban biomining
1. Biooxidation of refractory gold bearing sites by chemolithotrophic bacteria to liberate encapsulated gold before cyanidation.

2. Direct gold solublization by heterotrophic bacteria.

3. Recovery of gold from leachets & effluent solutions through biosorption.

4. Biodegradation of cyanide waste (bioenvironmental control)
Leaching of gold from sulfidic ores

- *T. ferroxidans* attach themselves to pyrite & chalcopyrite minerals in gold ores.

- Bacteria dissolve the sulphide away, liberating the gold particles.

- Sulfidic ores need to be pre-treated by roasting or by pressure-oxidation to free the gold from the sulfides.

- After this pre treatment, 70%-95% of gold can be recovered by the usual cyanide leaching process.

- This process was introduced in south africa on a pilot scale in 1986 but became a full scale commercial operation in 1990.

- Such plants for sulfidic gold ores are being constructed in Ghana & Australia.
LATERITIC & QUARTZITIC GOLD ORES

- Different heterotrophic bacteria are used, directly solublising gold.
- *Aeromonas* can solublise gold at an alkaline pH 8-8.5.
- Other organisms are *B.subtilis*, *B.mesentricus*, & *Bacillus sp.*
- These organisms secrete gold solublising peroxides and amino acids.
The solubility of gold in a water and cyanide solution was discovered in 1783 by Carl Wilhelm Scheele, but it was not until the late 19th century, that an industrial process was developed.

The expansion of gold mining in the Rand of South Africa began to slow down in the 1880s, as the new deposits being found tended to be pyritic ore. The gold could not be extracted from this compound with any of the then available chemical processes or technologies.

In 1887, John Stewart MacArthur, working in collaboration with brothers Dr Robert and Dr William Forrest for the Tennant Company in Glasgow, Scotland, developed the MacArthur-Forrest Process for the extraction of gold ores. By suspending the crushed ore in a cyanide solution, a separation of up to 96 percent pure gold was achieved.

The process was first used on a large scale at the Witwatersrand in 1890, leading to a boom of investment as larger gold mines were opened up.

In 1896, Bodländer confirmed that oxygen was necessary for the process, something that had been doubted by MacArthur, and discovered that hydrogen peroxide was formed as an intermediate.
Gold Ores

- Gold occurs principally as a **native metal**, usually **alloyed** to a greater or lesser extent with **silver** (as **electrum**), or sometimes with **mercury** (as an **amalgam**).

- Native gold can occur as sizeable nuggets, as fine grains or flakes in **alluvial deposits**, or as grains or microscopic particles embedded in other rocks.

- Ores in which gold occurs in chemical composition with other elements are comparatively rare. They include **calaverite**, **sylvanite**, **nagyagite**, **petzite** and **krennerite**.
**Refractory gold processes**

A "refractory" gold ore is an ore that is naturally resistant to recovery by standard cyanidation and carbon adsorption processes.

These refractory ores require pre-treatment in order for cyanidation to be effective in recovery of the gold.

A refractory ore generally contains sulfide minerals, organic carbon, or both.

Sulfide minerals often trap or occlude gold particles, making it difficult for the leach solution to complex with the gold.

Organic carbon present in gold ore may adsorb dissolved gold-cyanide complexes in much the same way as activated carbon.
Pre-treatment options for refractory ores:

- **Roasting**
- Bio-oxidation or **Bacterial oxidation**
- **Pressure oxidation**

The refractory ore treatment processes may be preceded by concentration (usually sulfide flotation).

Roasting is used to oxidize both the sulfur and organic carbon at high temperatures using air and/or oxygen.

Bio-oxidation involves the use of bacteria that promote oxidation reactions in an aqueous environment.

Pressure oxidation is an aqueous process for sulfur removal carried out in a continuous autoclave, operating at high pressures and somewhat elevated temperatures.
BIOLEACHING OF GOLD

- **Au + 8 NaCN + O2 + 2H2O → 4NaAu(CN)2 + 4NaOH**

Iron and sulphur oxidising bacteria are able to break down the gold bearing sulfides (pyrites and arsenopyrite) and leave behind the exposed gold for cyanide leaching.

\[
\begin{align*}
4FeS_2 + 14O_2 + 4H_2O & \rightarrow 4FeSO_4 + 4H_2SO_4 \\
4FeSO_4 + O_2 + 2H_2SO_4 & \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \\
FeS_2 + Fe_2(SO_4)_3 & \rightarrow 3FeSO_4 + 2S^0 \\
2S^0 + 2H_2O + 3O_2 & \rightarrow 2H_2SO_4
\end{align*}
\]

- Heap bioleaching
- Stirred tank bioreactor
Chemical reactions

The chemical reaction for the dissolution of gold, the "Elsner Equation", follows:

\[ 4 \text{Au} + 8 \text{NaCN} + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{Na[Au(CN)\textsubscript{2}]} + 4 \text{NaOH} \]

In this redox process, oxygen removes, via a two step reaction, one electron from each gold atom to form the complex \( \text{Au(CN)\textsubscript{2}^-} \) ion. [6]
Cyanide in the beneficiation of gold

- 0.05% NaCN solution is used to extract Au and Ag from ore
- Au dissolves by two processes occurring simultaneously on its surface.
  
  **Cathode**
  
  - At one end of the metal, the cathodic zone, oxygen takes up electrons and undergoes a reduction reaction.
    \[ \text{O}_2 + 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2 + 2 \text{OH}^- \]
  
  **Anode**
  
  - At the other end, the anodic zone, the metal gives up electrons and undergoes an oxidation reaction.
    \[ \text{Au} \rightarrow \text{Au}^+ + \text{e}^- \]
    \[ \text{Au}^+ + 2\text{CN}^- \rightarrow \text{Au(CN)}_2^- \]

- And then form strong complexes by Elsener’s/Adamson’s 1st reaction:
  \[ 4\text{Au} + 8\text{NaCN} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{NaAu(CN)}_2 + 4\text{NaOH} \]
  Or Adamson’s 2nd reaction
  \[ 2\text{Au} + 4\text{NaCN} + 2\text{H}_2\text{O} = 2\text{NaAu(CN)}_2 + \text{H}_2\text{O}_2 + 2\text{NaOH} \]
### Table 1. Sources of cyanide.

#### A. Natural sources

Cyanogenic bacteria (Castric 1975, 1981)
- *Chromobacterium violaceum*
- *Pseudomonas aeruginosa*
- *Pseudomonas chloraphis*
- *Pseudomonas fluorescens*

Cyanogenic algae (Vennesland et al. 1981)
- *Chlorella vulgaris*
- *Nostoc muscorum*
- *Pleococcus boryanum*
- *Anacystis nidulans*

Pathogenic fungi generating cyanide (Ward 1964; Millar & Higgins 1970)
- *Marasmius oreades*
- *Stemphylium loti*
- *Gloeocercosporea sorghii*
- *Snow moulds*

Cyanogenic crops (Gyorgy et al. 1969; Esquivel & Maravalhas 1973)
- Almonds
- Cassava
- Apple
- Loquat
- Lima Beans

#### B. Anthropogenic sources of cyanide (Mooney & Quin 1965; Towill et al. 1978)

- Electroplating industries
- Coal-gasification plants
- Coal-coking plants
- Manufactured gas plants
- Synthetic-fibre-producing plants
- Metallurgy and metal-cleaning operations
- Recovery of precious metals
- Processing of cyanogenic crops
- Pharmaceutical industries
- Paint-manufacturing industries
Biooxidation pretreatment of refractory gold concentrates and ores

- Biooxidation of concentrates in stirred tanks

- Gencor pioneered research and development of stirred-tank reactors for biooxidation of sulfidic-refractory gold concentrates for enhanced recovery of gold

- This technology later became known as the BIOX® process. The first engineered bioreactor system for commercial biooxidation pretreatment of a refractory sulfidic-gold concentrate was implemented by Gold Fields in 1986 at the Fairview Mine in South Africa.

- The success of the BIOX® technology is reflected in the number of plants built and those in operation listed in Table 2

- In addition to plants using the BIOX® technology, other stirred-tank reactor plants have been built using mineral biooxidation technology other than BIOX® (Table 2).

- Stirred tank biooxidation technology for sulfidic-refractory gold concentrates has advanced since its 1986 inception. In the early commercial BIOX® reactors, the bacterial populations were dominated by A. ferrooxidans, A. thiooxidans, and L. ferrooxidans
Operating temperatures of the reactors were increased to 42–45 °C in the mid-1990s to improve process performance, and this change resulted in a shift of the predominant microbial population to A. caldus and L. ferriphilum.

More recent examination of some of the operating BIOX® plants using the qPCR technique has shown L. ferriphilum to be absent with the dominant iron-oxidizing organisms being species of Acidiplasma and Ferroplasma.

Whether this change in dominant organisms is a reflection of mineralogical differences in the concentrates being treated in the plants or whether changes in other operating parameters have been made that would result in selection is unknown.

Sulfobacillus species were found to dominate in several bioreactors at the BIOX® plant in Ghana (Table 2), where temperature control had been compromised and reactors had operated at 45 °C (van Hille et al. 2011).

Advances in both aeration and agitation have also been instituted in more recently built BIOX® plants. The numbers of stirred-tank reactor plants built and those in operation demonstrate the acceptance by industry of biohydrometallurgy. Not only are the numbers of plants increasing but the amount of sulfide concentrate processed in these plants is also increasing.
Biooxidation of ores in heaps

- In December of 1999, Newmont Mining Corporation commissioned the first industrial-scale biooxidation heap facility for pretreatment of refractory sulfide-locked gold ore.

- The Newmont BIOPRO® commercial process was initiated after 10 years of development from laboratory-scale column testing, pilot plant testing at the mine site, and process demonstration using a 708,000 t heap–biooxidation facility.

- From commissioning in 1999 through 2005, more than 8.8 Mt of sulfidic ore was biooxidized with recovery of approximately 12.2 t of gold.

- Biooxidation of the sulfide was designed to achieve 30% in the commercial heap.

- In practice, the measured sulfide oxidation averaged about 22%. Biooxidation improved gold recovery from a baseline range of 30–39 to 50–63% after pretreatment.

- Regardless of the compromises made due to economic conditions at the time, the robustness of the biooxidation–heap process was confirmed and efficacy of the technology was demonstrated.
<table>
<thead>
<tr>
<th>Plant and location</th>
<th>Process</th>
<th>Treatment capacity (t/day)</th>
<th>Operational status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fairview, South Africa</td>
<td>BIOX®</td>
<td>62</td>
<td>1986–present</td>
</tr>
<tr>
<td>Sao Bento, Brazil</td>
<td>BIOX®</td>
<td>150</td>
<td>1990–1994 (currently under care and maintenance)</td>
</tr>
<tr>
<td>Tamboraque, Peru</td>
<td>BIOX®</td>
<td>60</td>
<td>1990–present</td>
</tr>
<tr>
<td>Harbour Lights, Australia</td>
<td>BIOX®</td>
<td>40</td>
<td>1991–1994 (mine depleted)</td>
</tr>
<tr>
<td>Wiluna, Australia</td>
<td>BIOX®</td>
<td>128</td>
<td>1993–present</td>
</tr>
<tr>
<td>Sansu, Ghana</td>
<td>BIOX®</td>
<td>960</td>
<td>1994–present</td>
</tr>
<tr>
<td>Youanmi, Australia</td>
<td>BacTech</td>
<td>120</td>
<td>1994–1998 (mine depleted)</td>
</tr>
<tr>
<td>Coriancha, Peru</td>
<td>BIOX®</td>
<td>60</td>
<td>1998–2008</td>
</tr>
<tr>
<td>Beaconsfield, Australia</td>
<td>BacTech</td>
<td>70</td>
<td>2000–present</td>
</tr>
<tr>
<td>Laizhou, China</td>
<td>BacTech</td>
<td>100</td>
<td>2001–present</td>
</tr>
<tr>
<td>Olimpiada, Russia</td>
<td>Tank reactors</td>
<td>8220</td>
<td>2003–present</td>
</tr>
<tr>
<td>Fosterville, Australia</td>
<td>BIOX®</td>
<td>211</td>
<td>2005–present</td>
</tr>
<tr>
<td>Suzdal, Kazakhstan</td>
<td>BIOX®</td>
<td>196</td>
<td>2005–present</td>
</tr>
<tr>
<td>Bogoso, Ghana</td>
<td>BIOX®</td>
<td>820</td>
<td>2007–present</td>
</tr>
<tr>
<td>Jinfeng, China</td>
<td>BIOX®</td>
<td>790</td>
<td>2007–present</td>
</tr>
<tr>
<td>Kokpatas, Uzbekistan</td>
<td>BIOX®</td>
<td>1069</td>
<td>2008–present</td>
</tr>
<tr>
<td>Agnes, South Africa</td>
<td>BIOX®</td>
<td>20</td>
<td>2010–present</td>
</tr>
</tbody>
</table>
BIOLEACHING OF URANIUM
Uranium

- Uranium is a silvery-white metallic chemical element in the actinide series of the periodic table, with symbol U and atomic number 92.

- Uranium is an important natural resource used for the generation of nuclear energy.
Conventional Process

- Employs use of **strong acids as reagents**

- Include sulphuric, nitric and hydrochloric acids, sodium carbonate and bicarbonate, ammonium carbonate and bicarbonate, as well as potassium carbonate compounds. As oxidizers, materials such as oxygen, hydrogen peroxide, ferric iron, nitrate, hypochlorite and some others may be employed.

- Process often create environmental problems, requires **large amounts of energy**, and involves a **complex operational plant**.

- Not economical because the content of uranium is very low by weight.

- Hence it is necessary to use an alternative process to facilitate the efficient and economic recovery of the uranium.
Bioleaching Process

- **Organism involved**: *Acidithiobacillus ferrooxidans*

- In the leaching of uranium, the bacteria do not directly attack the uranium mineral. They generate Fe(III) from pyrite(FeS$_2$) which is often associated with the uranium ore

- Ferric iron is an oxidizing agent

  e.g., metal sulfides and is chemically reduced to ferrous iron which, in turn, can be oxidized microbial again

\[
\begin{align*}
\text{FeS}_2 + \text{H}_2\text{SO}_4 &\rightarrow 2 \text{FeSO}_4 + \text{H}_2\text{O} + 2\text{S}^0 \\
\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O}_2 &\rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\end{align*}
\]
• The ferric ion gets reduced to ferrous ion and in return causing oxidation of the metal and converts it to $U^{+4}$ to $U^{+6}$ state which is soluble in water, hence the metal is leached out to the liquor solution

$$UO_2 + Fe_2 (SO_4)_3 \rightarrow UO_2SO_4 + 2FeSO_4$$

• *A. ferrooxidans* can accelerate such an oxidation reaction by a factor of about $10^5$-$10^6$ times faster than the chemical oxidation
1.2. Microbial uranium solubilization

Aerobically, microorganisms can directly (enzymatically) or indirectly (chemically) oxidize U. Indirect, microbially assisted oxidation of U(IV) to U(VI) is used for the recovery of U from low-grade ores worldwide (Choi et al., 2005; Pal et al., 2010; Tuovinen and Kelly, 1974). During this process iron and/or sulfur oxidizing microorganisms metabolize the iron and/or sulfur in the ore, producing Fe(III) and sulfuric acid, which act as effective oxidants for the insoluble U(IV) within the ore (Guay et al., 1977; Hamidian et al., 2009; Munoz et al., 1995a; Soljanto and Tuovinen, 1980; Tuovinen and Kelly, 1974).

\[
4 \text{Fe}^{2+} + \text{O}_2(\text{aq}) + 4\text{H}^+ \rightarrow 4 \text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (1)
\]

[microbial, aerobic]

\[
\text{UO}_2(\text{s}) + 2\text{Fe}^{3+} \rightarrow \text{UO}_2^{2+} + 2\text{Fe}^{2+} \quad (2)
\]

[inorganic - with Fe\textsuperscript{3+} from Eq. (1)]

\[
\text{UO}_2^{2+} + \text{SO}_4^{2-} \rightarrow \text{UO}_2\text{SO}_4(\text{aq}) \quad (3)
\]

[complexation with sulfate, enhances uranyl mobility]

\[
\text{UO}_2(\text{s}) + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{UO}_2^{2+} + \text{H}_2\text{O} \quad (4)
\]

[inorganic and microbial]

\[
5 \text{UO}_2(\text{s}) + 2\text{NO}^{3-} + 12\text{H}^+ \rightarrow 5 \text{UO}_2^{2+} + 2\text{N}_2 + 6\text{H}_2\text{O} \quad (5)
\]

[microbial, anaerobic]
BIOLEACHING OF URANIUM

- Proceeds by the indirect mechanism
- $\text{UO}_2 + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{UO}_2\text{SO}_4 + 2\text{FeSO}_4$
  $(\text{U}^{4+} + 2\text{Fe}^{3+} \rightarrow \text{U}^{6+} + 2\text{Fe}^{2+})$
- $\text{Fe}^{2+}$ is reoxidised by *A. ferrooxidans*
In uranium biomining, the ferric iron generated by the microbial oxidation of ferrous iron (Equation 5), acts as the electron donor and reduces insoluble uranium (IV) to soluble uranium (VI) species, which is released from the ore mineral to the liquor solution [13,14]. Bioleaching of Au by cyanide (CN) produced by cyanogenic bacteria (e.g., Chromobacterium violaceum) is seriously considered for recovering Au.

\[
\begin{align*}
\text{FeS}_2 + 6\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{S}_2\text{O}_3^{2-} + 7\text{Fe}^{2+} + 6\text{H}^+ \\
\text{S}_2\text{O}_3^{2-} + 2\text{O}_2 + \text{H}_2\text{O} & \rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\text{S}_2\text{O}_3^{2-} + 4\text{Fe}^{3+} + 5\text{H}_2\text{O} & \rightarrow 2\text{SO}_4^{2-} + 4\text{Fe}^{2+} + 10\text{H}^+ \\
2\text{Fe}^{2+} + 2\text{H}^+ + 0.5\text{O}_2 & \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} \\
\text{UO}_2 + 2\text{Fe}^{3+} & \rightarrow \text{UO}_2^{2+} + 2\text{Fe}^{2+} \\
4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{Au(CN)}_2^- + 4\text{OH}^- 
\end{align*}
\]
Figure 1 Flowchart for Uranium bioprocessing.
<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Chemical formula</th>
<th>% Uranium extractability</th>
<th>Locality found</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autunite</td>
<td>Ca(UO_{2})<em>2 (PO</em>{4})_2·12H_2O</td>
<td>62.39</td>
<td>Many worldwide</td>
<td>Casas et al. 1998; Ohnuki et al. 2005</td>
</tr>
<tr>
<td>Becquerelite</td>
<td>Ca_{2}UO_{9}·7H_{2}O</td>
<td>72.47</td>
<td>Kasolo, Belgian Congo</td>
<td>Rakotoson, Raelina, and Pai 1983</td>
</tr>
<tr>
<td>Batafit (Samiresite)</td>
<td>(Ca,Na,U)<em>{2}(Ti, Nb,Ta)</em>{2}O_{6}(OH)</td>
<td>16.04</td>
<td>Betafo, Malgasy Republic, Ontario (Many worldwide)</td>
<td>Rakotoson et al. 1983</td>
</tr>
<tr>
<td>Brannerite</td>
<td>(U, Ca, Ce) (Ti, Fe) O_6</td>
<td>33.54</td>
<td>Witwatersrand field, South Africa (many world wide)</td>
<td>John et al. 1999</td>
</tr>
<tr>
<td>Carnotite</td>
<td>K_{2} (UO_{2})<em>2 (VO</em>{4})<em>2·3H</em>{2}O</td>
<td>52.77</td>
<td>Southwestern USA</td>
<td>Maozhong, Changquan, and Mostafa 2005a</td>
</tr>
<tr>
<td>Chadwickite</td>
<td>UO_{2} HA_{3}O_{3}</td>
<td>60.42</td>
<td>Wittichen in Black forest, Aufschluss, Germany</td>
<td>Amme et al. 2005</td>
</tr>
<tr>
<td>Coffinite</td>
<td>U(SiO_{4})<em>{1-x} (OH)</em>{4x}</td>
<td>72.63</td>
<td>Temple Mountain, USA</td>
<td>Currier 2002; Maozhong et al. 2005b</td>
</tr>
<tr>
<td>Cuproskladowskite</td>
<td>Cu[UO_{2}SiO_{2}OH]<em>2·6H</em>{2}O</td>
<td>55.24</td>
<td>Congo</td>
<td>Frondel 1958</td>
</tr>
<tr>
<td>Curienite</td>
<td>Pb_{2}U_{2}O_{17}·4H_{2}O</td>
<td>61.08</td>
<td>Congo</td>
<td>Amme et al. 2005</td>
</tr>
<tr>
<td>Davidite</td>
<td>(Fe, Ce, U)<em>{2} (Ti, Fe, V, Cr)</em>{3} O_{12}</td>
<td>3.18</td>
<td>Tufane, Norway</td>
<td>Mostafa and Janecek 1997</td>
</tr>
<tr>
<td>Franceville</td>
<td>(Ba,Pb) UO_{2} 2 V_{2}O_{5}·8H_{2}O</td>
<td>48.66</td>
<td>France</td>
<td>Peter et al. 1983</td>
</tr>
<tr>
<td>Lanthinite</td>
<td>UO_{3}·5UO_{2}·10 H_{2}O</td>
<td>78.29</td>
<td>Kasolo, Belgian Congo</td>
<td>Currier 2002</td>
</tr>
<tr>
<td>Jacchamovite</td>
<td>(UO_{2})<em>{3}SO</em>{4} (OH)<em>{14}·13H</em>{2}O</td>
<td>69.76</td>
<td>Jacchamov, Czech Republic.</td>
<td>Chadwick 1997</td>
</tr>
<tr>
<td>Johannite</td>
<td>Cu(UO_{2})<em>{2} (SO</em>{4})<em>2(OH)</em>{2}·12H_{2}O</td>
<td>48.88</td>
<td>Jacchamov, Bohemia, Czech Republic</td>
<td>Polikarpova 1957</td>
</tr>
<tr>
<td>Joliotite</td>
<td>UO_{2} CO_{3}·2H_{2}O</td>
<td>65.03</td>
<td>Menzeenscheid, Schwarzwald, Germany</td>
<td>Shoep 1923</td>
</tr>
<tr>
<td>Nenadkevite</td>
<td>H K(UO_{2} SiO_{4})·1/5H_{2}O</td>
<td>55.44</td>
<td>Rossing U-mine, Nambia.</td>
<td>Leonardos et al. 1987</td>
</tr>
<tr>
<td>Parsonite</td>
<td>Pb_{2}UO_{2} (PO_{4})<em>2·2H</em>{2}O</td>
<td>26.14</td>
<td>Grury, Saone-et-Loire, Iachaux, Puy-de-Dome, France</td>
<td>Defeyes and MacGregor 1980; Williams et al. 1985</td>
</tr>
<tr>
<td>Pitchblende</td>
<td>UO_{2}</td>
<td>88.11</td>
<td>Many world wide</td>
<td>Mostafa and Janecek 1997; Maozhong et al. 2005b</td>
</tr>
<tr>
<td>Renardite</td>
<td>Pb(UO_{2})<em>4 PO</em>{4} (OH)<em>{4}·7H</em>{2}O</td>
<td>56.97</td>
<td>Kaslo mine, Shinkolobre, Shaba, Zaire and France</td>
<td>Williams et al. 1985</td>
</tr>
<tr>
<td>Rutherfordine</td>
<td>UO_{2} CO_{3}</td>
<td>72.03</td>
<td>Uruguru Mountains, Tanganyika, East Africa</td>
<td>Williams et al. 1985</td>
</tr>
<tr>
<td>Sabugalite</td>
<td>H Al(UO_{2})<em>4 (PO</em>{4})<em>4·16H</em>{2}O</td>
<td>53.62</td>
<td>Sabugal in Portugal, and France.</td>
<td>Shoep 1923</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Chemical formula</th>
<th>% Uranium extractability</th>
<th>Locality found</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabugalate</td>
<td>H Al(UO₂)₄ (PO₄)₄·16H₂O</td>
<td>55.45</td>
<td>Subugal in Portugal, and France</td>
<td>Shoep 1923</td>
</tr>
<tr>
<td>Sklodowskite</td>
<td>Mg(UO₂)₂ Si₂O₇·6H₂O</td>
<td>63.47</td>
<td>Congo</td>
<td>John and Andrew 1997; Currier 2002</td>
</tr>
<tr>
<td>Tobernite</td>
<td>Cu(UO₂)(PO₄)₂·8H₂O</td>
<td>51.86</td>
<td>Tura-Kavak, Issyk-Kul’skaya Oblast, Kyrgyzstan</td>
<td>Chadwick 1997; John and Andrew 1997</td>
</tr>
<tr>
<td>Tyuyamunite</td>
<td>Ca (UO₂)₂ (VO₄)₂·8H₂O</td>
<td>61.91</td>
<td>Tyuya-Muyun hill, Ferghana, Tukestan</td>
<td>Deffeyes and MacGregor 1980</td>
</tr>
<tr>
<td>Uranphite</td>
<td>NH₄ UO₂·(PO₄)·3H₂O</td>
<td>54.46</td>
<td>Many worldwide</td>
<td>Chi and Yun 2006</td>
</tr>
<tr>
<td>Uraninite (bragerite)</td>
<td>UO₂</td>
<td>40.60</td>
<td>Oberpfalz, Bavaria</td>
<td>Saraswat 1988; Rao, Nagabhushana, and Jeyagopal 1989</td>
</tr>
<tr>
<td>Uranophane (Uranotile)</td>
<td>Ca UO₂SiO₃ (OH)₂·5H₂O</td>
<td>63.91</td>
<td>Krunkelbach Valley, Germany</td>
<td>Saraswat 1988</td>
</tr>
<tr>
<td>Uranopilite</td>
<td>(UO₂)₆ SO₄ (OH)₂·4H₂O</td>
<td>44.84</td>
<td>Schneeburg, Saxony, Germany</td>
<td>Dawn et al. 2004</td>
</tr>
<tr>
<td>Zeunerite</td>
<td>Cu (UO₂)₂ (AsO₄)₂·12H₂O</td>
<td>61.91</td>
<td>Jackpile Mine, Laguna, New Mexico, USA</td>
<td>Dawn et al. 2004</td>
</tr>
<tr>
<td>Zippeite</td>
<td>(UO₂)₂ (SO₄) (OH)₂·4H₂O</td>
<td>54.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid leaching</td>
<td>Alkali leaching</td>
<td>Bioleaching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>It is not simple and hence sophisticated training is needed.</td>
<td>It is also not simple and hence sophisticated training is needed.</td>
<td>It is simple and no sophisticated training is needed.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>It is applied to large operations.</td>
<td>It is also applied to large operations.</td>
<td>It may be applied to small and large operations.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid leaching achieves a high uranium extraction, typically 70–90%.</td>
<td>Extraction from alkaline leaching is low, typically 60–70%.</td>
<td>Bioleaching using micro-organisms achieves moderately high uranium extraction, typically 50–98%.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid leaching yields faster dissolution of uranium, requiring 40–70 pore volume.</td>
<td>Slower kinetics of uranium dissolution; requires typically more pore volumes than acid leaching</td>
<td>Bioleaching yields very slower dissolution of uranium, requires more pore volumes.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No elevated concentration of leaching agents.</td>
<td>No elevated concentration of leaching agents.</td>
<td>The formation of a microclimate around the ore particle with elevated concentration of leaching agents.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High acid consumption of carbonate bearing ores.</td>
<td>Potential to treat ores containing high levels of carbonates.</td>
<td>Potential to treat all minerals including silicates.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mandatory use of anti-corrosive material for carbonate-bearing ores.</td>
<td>Common material and equipment can be used.</td>
<td>Common material and simple equipments can be used.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Addition of oxidant not always required because of presence of iron in recycled solution, with accurate amounts of acid is necessary.</td>
<td>Addition of oxidant always required and accurate amounts of alkali is necessary.</td>
<td>Addition of oxidant not required as it is generated in situ. The excess acid generated must be neutralized.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Possibility of recovering by-products. Leaching efficiency is high.</td>
<td>Leaching chemistry is very selective. Leaching efficiency is lower than acid leaching.</td>
<td>Leaching chemistry is highly selective. Leaching efficiency is generally high.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additional processing on surface may be required to produce contaminant free product.</td>
<td>Product dissolution from ion-exchange should produce product of required quality.</td>
<td>Additional processing is not required.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid leaching causes the emission of gaseous pollutants. The air pollution by sulfur oxides cannot be eliminated but sulfur byproducts can be recovered.</td>
<td>Alkali leaching causes the emission of gaseous pollutants. The air pollution by sulfur oxides cannot be eliminated but sulfur byproducts can be recovered.</td>
<td>No emission of gaseous pollutants (eco-friendly). The air pollution by sulfur oxides can be eliminated but sulfur byproducts cannot be recovered.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid leaching</td>
<td>Alkali leaching</td>
<td>Bioleaching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>--------------------------------------</td>
<td>-----------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ore cannot be upgraded at mining site.</td>
<td>Ore cannot be upgraded at mining site.</td>
<td>Ore can be upgraded at mining site.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leaching agents are to be transported.</td>
<td>Leaching agents are transported.</td>
<td>Leaching agents are produced <em>in situ</em> (no need for the transportation).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>It is not dependent on the climate.</td>
<td>It is also not dependent on the climate.</td>
<td>Dependence on the climate.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital costs are high.</td>
<td>Capital costs are low compared to acid leaching.</td>
<td>Capital costs are low.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High energy demand.</td>
<td>High energy demand.</td>
<td>Low energy intensive.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro-organism</td>
<td>Characteristics</td>
<td>Leaching agent</td>
<td>Carbon Req.</td>
<td>Oxygen (Optimum)</td>
</tr>
<tr>
<td>---------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Acidithiobacillus ferrooxidans</td>
<td>Oxidize: Fe²⁺, S⁰, U⁴⁺, Cu⁺, Se²⁻, thiosulphate, tetrathionate, S⁺</td>
<td>Fe³⁺, H₂SO₄</td>
<td>OC</td>
<td>A</td>
</tr>
<tr>
<td>Consortia of Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans</td>
<td>Oxidize: S⁰, thiosulphate, tetrathionate</td>
<td>H₂SO₄</td>
<td>OC</td>
<td>SA</td>
</tr>
<tr>
<td>Acidithiobacillus acidophilus</td>
<td>Oxidize: S⁰, organic compounds</td>
<td>H₂SO₄</td>
<td>OC</td>
<td>A</td>
</tr>
<tr>
<td>Leptospirillum ferrooxidans</td>
<td>Oxidize: Fe²⁺, pyrite</td>
<td>Fe³⁺</td>
<td>OC</td>
<td>A</td>
</tr>
<tr>
<td>Pseudomonas fluorescens</td>
<td>Accumulation by siderophores</td>
<td>Fe³⁺</td>
<td>H</td>
<td>A</td>
</tr>
<tr>
<td>Aspergillus niger</td>
<td>Metabolite-mediated leaching, with accumulation on surface</td>
<td>Oxalate</td>
<td>H</td>
<td>SA</td>
</tr>
<tr>
<td>Aspergillus terreus</td>
<td>Oxalate</td>
<td>H</td>
<td>SA</td>
<td>3.0–6.3</td>
</tr>
<tr>
<td>Penicillium spiriculosum</td>
<td></td>
<td>Fumarate</td>
<td>H</td>
<td>SA</td>
</tr>
<tr>
<td>Cladosporium oxysporum</td>
<td></td>
<td>Unknown</td>
<td>H</td>
<td>SA</td>
</tr>
<tr>
<td>Aspergillus flavus and Curvularia clavata</td>
<td>Unknown</td>
<td>H</td>
<td>SA</td>
<td>3.0</td>
</tr>
</tbody>
</table>

OC = Obligate Chemolithotroph; H = Heterotroph; A = Aerobic; SA = Strict Aerobic.
The above reactions can be summarized as:

\[ 4 \text{FeS}_2 + 15 \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4 \] \hspace{1cm} (3)

Therefore, the direct bioleaching can be described according to the following reaction:

\[ 2\text{UO}_2 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{UO}_2\text{SO}_4 + 2\text{H}_2\text{O}, \Delta G_{303} = -130.4 \text{kJ} \cdot \text{mol}^{-1} \] \hspace{1cm} (4)
\[ \text{FeS}_2 + \text{H}_2\text{SO}_4 \rightarrow 2 \text{FeSO}_4 + \text{H}_2\text{O} + 2 \text{S}^\circ \] (5)

\[ \text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \] (6)

The Fe(II) can be oxidized by microbes to Fe(III) which takes part in the oxidation process again. Sulfur formed is simultaneously oxidized depending on the species to \( \text{H}_2\text{SO}_4 \) which aids (oxidizing agent) the dissolution of uranium as follows:

\[ 2\text{S}^\circ + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2 \text{H}_2\text{SO}_4 \] (7)

The insoluble uranium (IV) is oxidized to the water soluble uranium (VI) sulphate as:

\[ \text{UO}_2 + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{UO}_2 \text{SO}_4 + 2 \text{FeSO}_4 \] (8)
<table>
<thead>
<tr>
<th>Mine name</th>
<th>Micro-organism</th>
<th>Type of operation</th>
<th>Acid Consumption (kg/t)</th>
<th>% U recovery/day(s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Figueria mine</td>
<td><em>A. ferrooxidans</em></td>
<td>Heap</td>
<td>30</td>
<td>51.3/83 days</td>
<td>Garcia Jr. 1993</td>
</tr>
<tr>
<td>Canada</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rio Algom Mine</td>
<td><em>A. ferrooxidans</em></td>
<td>Heap</td>
<td>1-6</td>
<td>47/210 days</td>
<td>McCready and Gould 1990</td>
</tr>
<tr>
<td>Dension Mine</td>
<td><em>A. ferrooxidans</em></td>
<td>Stope</td>
<td>1-4</td>
<td>50/200 days</td>
<td></td>
</tr>
<tr>
<td>Angew Lake Mine</td>
<td><em>A. ferrooxidans</em></td>
<td>Stope</td>
<td>1-4</td>
<td>57/210 days</td>
<td></td>
</tr>
<tr>
<td>Australia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ranger Mine</td>
<td><em>A. ferrooxidans</em> or natural</td>
<td>Heap &amp; Dump</td>
<td>1-3</td>
<td>78/150 days</td>
<td>Kawatra and Natarajan 2001</td>
</tr>
<tr>
<td>Olympic Dam Mine</td>
<td><em>Mixed Culture</em></td>
<td>In-situ</td>
<td>1-3</td>
<td>70/year</td>
<td></td>
</tr>
<tr>
<td>Beverley Mine</td>
<td><em>Mixed Culture</em></td>
<td>In-situ</td>
<td>1-3</td>
<td>70/year</td>
<td></td>
</tr>
<tr>
<td>Kazakhstan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Stepnogorsk Mine</td>
<td><em>A. ferrooxidans</em></td>
<td>Heap</td>
<td>1-5</td>
<td>82/year</td>
<td>Fyodorov 1999</td>
</tr>
<tr>
<td>Southern ISL Mines</td>
<td><em>A. ferrooxidans</em></td>
<td>In-situ</td>
<td>1-10</td>
<td>51/year</td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ENUSA Mine</td>
<td><em>A. ferrooxidans and A. thiooxidans</em></td>
<td>Heap</td>
<td>1-2</td>
<td>75/150 days</td>
<td>Muñoz et al. 1995a</td>
</tr>
<tr>
<td>France</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Saint Pierre Mine</td>
<td><em>A. ferrooxidans</em></td>
<td>Heap</td>
<td>1-3</td>
<td>90/year</td>
<td>Rossi 1990</td>
</tr>
<tr>
<td>India</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turamdiff Mines</td>
<td><em>A. ferrooxidans</em></td>
<td>Column</td>
<td>1.26</td>
<td>70/60 days</td>
<td>Abhilash et al. 2007</td>
</tr>
<tr>
<td>Sl. no.</td>
<td>Type of ore</td>
<td>References</td>
<td>Conditions</td>
<td>Remarks</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------------</td>
<td>------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Keruadungri ore</td>
<td>Mathur and Dwivedi 1994</td>
<td>Bench Ferric sulphate leaching</td>
<td>92.8% extraction</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Mosabani plant tailings with uranium oxide</td>
<td>Murali Krishna and Bhurat 1993</td>
<td>Percolation bioleaching using ferric sulphate (0.5 t)</td>
<td>64% extraction</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Uraninite ore of Chhinjra, Himachal Pradesh</td>
<td>Sankaran et al. 1988</td>
<td>Heap leaching (sulphuric acid as leachant and manganese dioxide as oxidant)</td>
<td>84% extraction</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Quartz chlorite-sericite (Jaduguda mine)</td>
<td>Mathur et al. 1989</td>
<td>Bench scale Biogenically generated ferric sulfate as an oxidative leachant using A. ferrooxidans by Bacfox process</td>
<td>95% extraction</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Uraninite ore of Turamdih, Jharkhand</td>
<td>Abhilash et al. 2009</td>
<td>Bench scale leaching by mine isolate of bacteria (A. ferrooxidans)</td>
<td>98% extraction</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Abhilash et al. 2007</td>
<td>80 kg and 2.0 T column leaching by mine isolate of bacteria (A. ferrooxidans)</td>
<td>68–70% extraction</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>Mishra et al. 2009</td>
<td>Bench scale leaching by mine isolate of fungus (Cladosporium oxysporum)</td>
<td>71% extraction</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Pal et al. 2010</td>
<td>Bench scale leaching by mine isolate of bacteria (A. ferrooxidans)</td>
<td>49% extraction</td>
<td></td>
</tr>
<tr>
<td>Uranium oxide</td>
<td>Valence</td>
<td>Natural form</td>
<td>Solution ability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>---------</td>
<td>----------------</td>
<td>------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO$_2$</td>
<td>IV</td>
<td>Uraninite</td>
<td>Insoluble</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$_2$O$_5$</td>
<td>IV</td>
<td>-</td>
<td>Little soluble</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$_3$O$_8$</td>
<td>IV,VI</td>
<td>Pitchblende</td>
<td>Little soluble</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO$_3$</td>
<td>VI</td>
<td>Carnotite</td>
<td>Soluble</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. The type of uranium oxides in nature [40]
<table>
<thead>
<tr>
<th>Uranium ores</th>
<th>Chemical composition</th>
<th>Degree of bioleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uraninite</td>
<td>UO₂</td>
<td>+</td>
</tr>
<tr>
<td>Gummite</td>
<td>UO₃·nH₂O</td>
<td>+</td>
</tr>
<tr>
<td>Becquerelite</td>
<td>CaU₆O₁₉·11H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Brannerite</td>
<td>(U,Ca,Ce)(Ti,Fe)O₆</td>
<td>+</td>
</tr>
<tr>
<td>Davidite</td>
<td>(Fe,Ce,U)₂(Ti,Fe,V,Cr)₅O₁₂</td>
<td>+</td>
</tr>
<tr>
<td>Coffinite</td>
<td>U(SiO₄)₁·x(OH)₄ₓ</td>
<td>-</td>
</tr>
<tr>
<td>Uranophane</td>
<td>Ca(UO₂)₂Si₂O₇·6H₂O</td>
<td>+ -</td>
</tr>
<tr>
<td>Sklodowskite</td>
<td>Mg(UO₂)₂Si₂O₇·6H₂O</td>
<td>+ -</td>
</tr>
<tr>
<td>Autunite</td>
<td>Ca(UO₂)₂(PO₄)₂·12H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Torbernite</td>
<td>Cu(UO₂)₂(PO₄)₂·8H₂O</td>
<td>+</td>
</tr>
<tr>
<td>uramphite</td>
<td>NH₄·UO₂·PO₄·3H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Zeunerite</td>
<td>Cu(UO₂)₂(AsO₄)₂·12H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Carnotite</td>
<td>K₂(UO₂)₂(VO₄)₂·3H₂O</td>
<td>+ -</td>
</tr>
<tr>
<td>Tyuyamunite</td>
<td>Ca(UO₂)₂(VO₄)₂·8H₂O</td>
<td>+ -</td>
</tr>
<tr>
<td>Zippeite</td>
<td>(UO₂)₂(SO₄)(OH)₂·4H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Uranopilite</td>
<td>(UO₂)₆SO₄(OH)₁₀·12H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Johannite</td>
<td>Cu(UO₂)₂(SO₄)₂(OH)₂·H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Schroeckingerite</td>
<td>NaCa₃UO₂SO₄(CO₃)₃F·10H₂O</td>
<td>+</td>
</tr>
<tr>
<td><strong>Urano-oranic Compounds</strong></td>
<td></td>
<td>+</td>
</tr>
</tbody>
</table>

+: easy, -: hard, + -: variable

Table 2. Uranium mineralization and bioleaching.
<table>
<thead>
<tr>
<th>Bacterial class</th>
<th>Optimum temp. range /°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryophiles</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>Mesophiles</td>
<td>20-40</td>
</tr>
<tr>
<td>Moderate thermophiles</td>
<td>40-55</td>
</tr>
<tr>
<td>Extreme thermophiles</td>
<td>&gt; 55</td>
</tr>
</tbody>
</table>

Table 3. Classification of chemolithotrophic bacteria in terms of their optimum temperature ranges.
<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Optimum pH</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidithiobacillus albertensis</td>
<td>3.5-4</td>
<td>2-4.5</td>
</tr>
<tr>
<td>Acidithiobacillus ferrooxidans</td>
<td>2.0-2.5</td>
<td>1.3-4.5</td>
</tr>
<tr>
<td>Acidithiobacillus thiooxidans</td>
<td>2.0-3.0</td>
<td>0.5-5.5</td>
</tr>
<tr>
<td>Acidithiobacillus caldus</td>
<td>2.0-2.5</td>
<td>1.0-3.5</td>
</tr>
</tbody>
</table>

Table 4. pH range for Acidithiobacillus culture
Fig. 3. In situ leaching operation. Adapted from Pannier (2009).
Fig. 5. Model of uranium roll-front deposit.