BIOMINING

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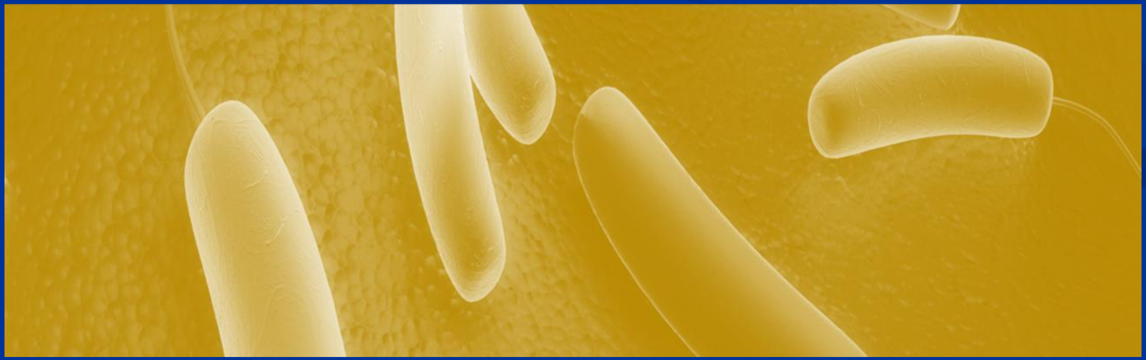


INTRODUCTION

- Continuous depletion of Earth’s high-grade deposits of metals necessitates the need for innovative and economical ways of recovering metals from low-grade deposits.

- Ores with low metal content are not suitable for direct smelting but it is possible to extract metals economically using the activity of microorganisms.

- In the case of some sulfide or sulfide-containing ores, it is possible to extract metal from **low-grade ore** economically using the activity of sulfur-oxidizing bacteria, especially ***T. ferrooxidans.***

- Microbial recovery of metals is sometimes called **"microbial mining" or "biohydrometallurgy"**

- The process is currently applied on a commercial scale to low-grade copper, gold and uranium ores.

- The ability of micro-organisms to solubilize metals from insoluble metals is known as **'bioleaching'**

- Biotechnology can harness and refine these techniques for enhanced recovery of metals

- The process has promise for recovering other metals including; Ni, Zn, Co, Sn, Cd, Mo, Pb, An, As, and Se from low-grade sulfide containing ores.

Biomining

- The extraction of metals using mechanical and chemical methods is **difficult** and **expensive**

- **Biological methods** are;

  - more cost-effective
  - use little energy
  - can function well at low concentration of metals
  - do not usually produce harmful emissions
  - reduce the pollution of metal-containing wastes

- Successful commercial metal-leaching processes include the **extraction of gold, copper, and uranium**.

- The most important mineral-decomposing micro-organisms are the **iron- and sulphur-oxidizing chemolithotrophs**
- **Chemolithothrophs** are represented by **hydrogen-, sulphur-, and iron-reducing Bacteria and Archaea**.
- The most important **metal-leaching** microorganisms use ferrous iron and reduced sulphur compounds as electron donors and fix carbon dioxide.
- Many of these microorganisms produce sulphuric acid (acidophiles).

Organism	**Type**	**Metabolism optimum**	**pH**	**Temperature range (°C)**
Thiobacillus *	*ferrooxidans*	Anaerobe/	2.4 Fe/acid	28-35
T. prosperus		Halotolerant/ Fe/acid	2.5	30
Leptospirillum ferrooxidans		Fe only	2.5-3.0	30
Sulfobacillus acidophilus		Fe/acid	- •-	50
S. thermosulfi- dooxidans		Fe/acid	—	50
L. thermoferro-oxidans		Fe	2.5-3.0	40-50
Acidianus brierleyi		Acid	1.5-3.0	45-75
A. infernus		Acid	1.5-3.0	45-75
A. ambivalens		Acid	1.5-3.0	45-75
Sulfurococcus yellowstonii		Fe/acid	-	60-75
T. thiooxidans		Acid		25-40
T. *acidophilus*		Acid	3.0	25-30
T. *caldus*		Acid		40-60
Sulfolobus	Archaean *solfataricus*	Fe/acid	-	55-85
S. rivotincti	Archaean	Fe/acid	2.0	69
S. yellowstonii	Archaean	Fe/acid	-	55-85

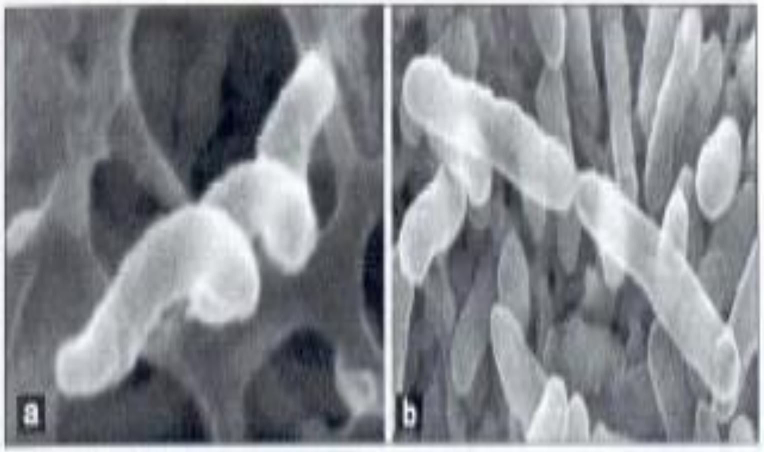


Fig. 11.1. A scanning electron microscope image of (a) *L. ferrooxidans* DSM2705 (magnification =18,000X) and (b) *T. ferrooxidans* ATCC33020 (magnification =15,000X).

Leptospirillum ferooxidans

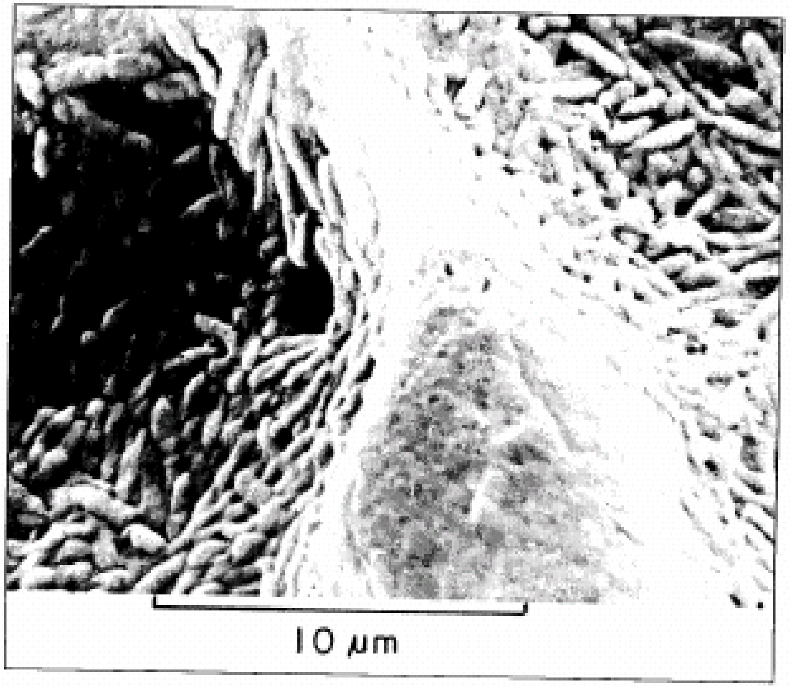


Fig. 14.1. Biofilm of *T. ferrooxidans* on the surface of a sulfur prill. Sulfur prills were colonized by *T. ferrooxidans* for two weeks. After this time, the samples were processed for scanning electron microscopy. The bar indicates 10 µm.

Bioleaching technology

- It has been shown that micro-organisms can extract cobalt, nickel, cadmium, antimony, zinc, lead, gallium, indium, manganese, copper, and tin from sulphur-based ores.
- The basis of microbial extraction is that the metal sulphides, the principal component in many ores, are not soluble but when oxidized to sulphate become soluble so that the metal salt can be extracted.

- The general metal recovery process can be represented by the following equation:

$$MS + 2O_2 \xrightarrow[\textit{\textbf{T. ferrooxidans}}]{} MSO_4$$

- M represents a **bivalent metal** that is **insoluble as a sulfide** but **soluble**, and thus **leachable**, as a **sulfate**
- *T. ferrooxidans* is a **chemolithotrophic** bacterium that derives energy through the oxidation of either a reduced sulfur compound or ferrous iron.
- It exerts its **bioleaching** action **directly** by **oxidizing the metal sulfide** and/or
- **indirectly by oxidizing the ferrous iron content of the ore to ferric iron; the ferric iron, in turn, chemically oxidizes the metal** to be recovered by leaching.

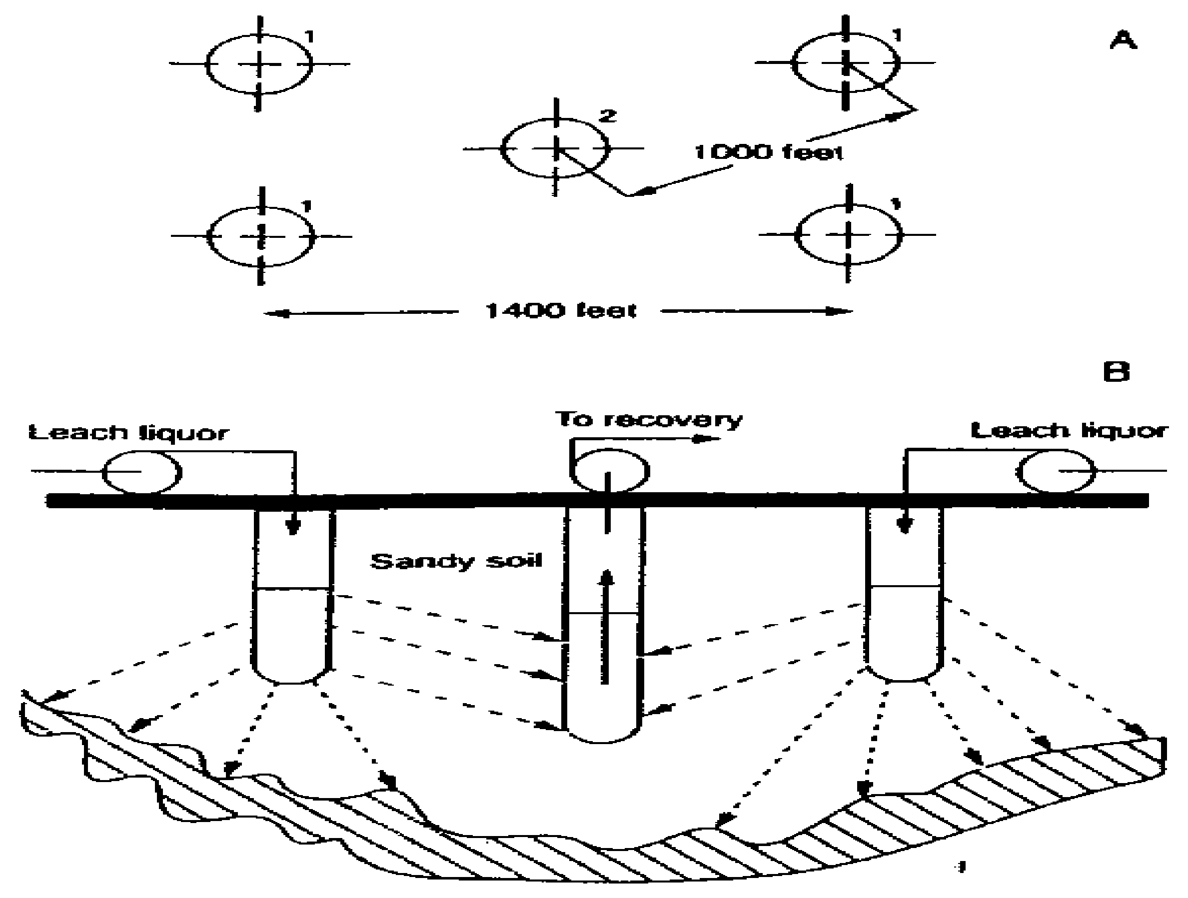
BIOLEACHING METHODS

In situ **bioleaching**

- The leaching solution containing T. *ferrooxidans* is pumped into the mine where it is injected into the ore.
- The leachate is recovered from lower down the mine, pumped to the surface where the metal is recovered.
- The bacterial suspension is aerated before pumping back to the mine.

Hole-to-hole leaching of low-grade ores

– an *in situ* bioleaching method.



The process may be practiced in relatively porous ore overlying impermeable bedrock. Leaching is from injection wells to a collection well.

A – Overhead view of layout of wells. 1 = leach liquor shafts; 2 = recovery shaft

B – Side view of wells

Mine tailings or dumps

- Set on a slope with a depth of 7-20 m of crushed ore or tailings.
- The dump is sprayed with water acidified with sulphuric acid to ensure that the pH is between 1.5 and 3, - encourage the growth of *Thiobacillus*.
- The *Thiobacillus* spp. will leach metals into solution and this can be collected by precipitation from the leachate.
- Anaerobes have also been detected in the anoxic zones of dumps including the sulphate-reducing *Desulfovibrio* sp.
- oxidize sulphides at pH values of 4-7 to give sulphuric acid – the dump represents a **very diverse and dynamic microbial community** of **up to 10^6 cells/g of rock.**

- The ore is usually mined, broken up and heaped in piles on a water-impermeable formation or on a specially constructed apron (**Fig. 15.1**).
- Water is then pumped to the top of the ore heap & allowed to trickle down through the ore to the apron.

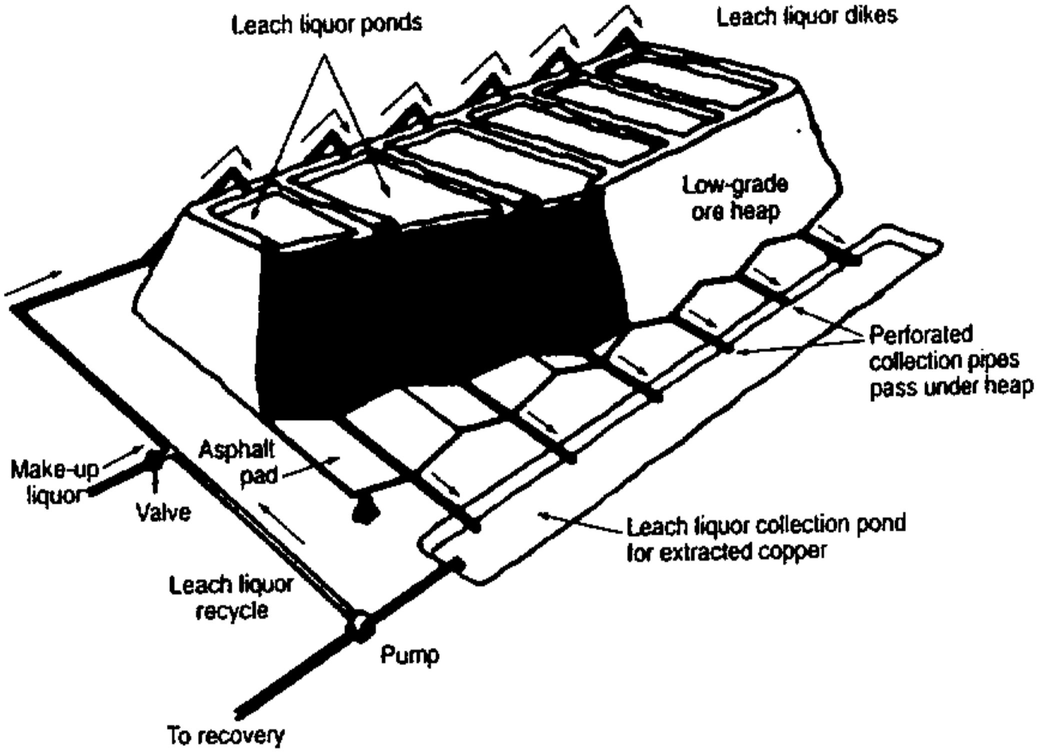


Figure 15.1

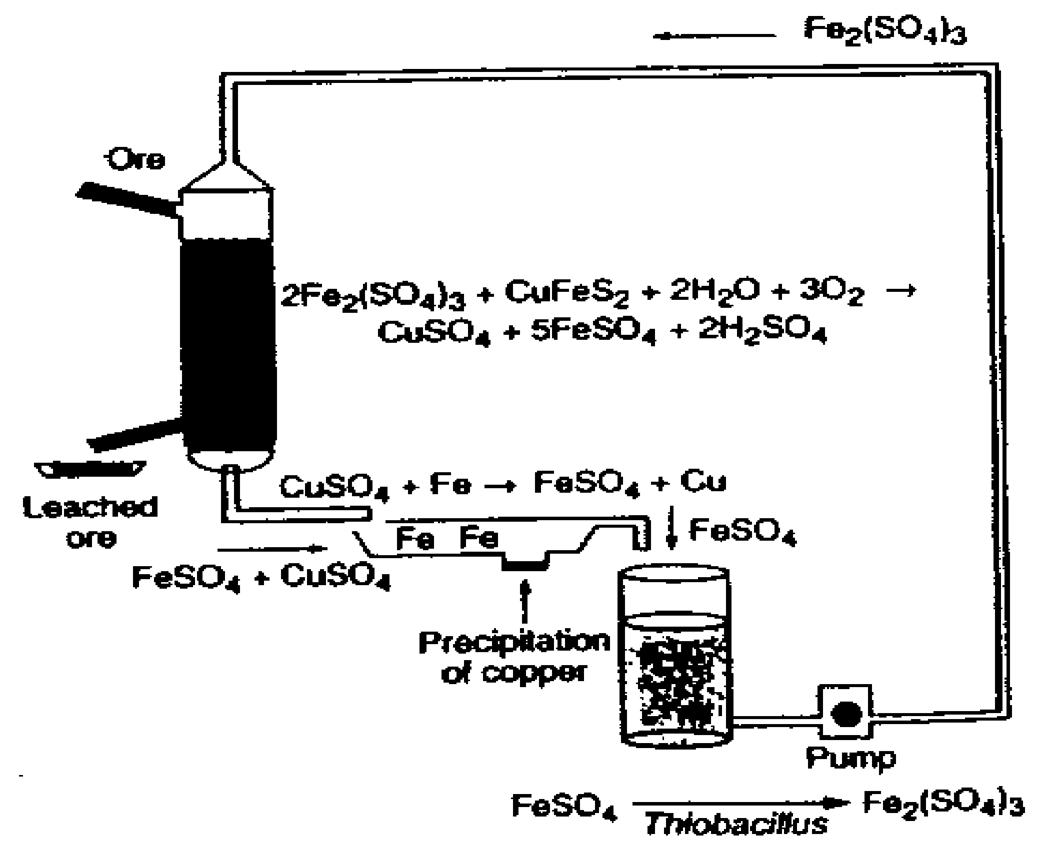
Heap leaching of low-grade ore. The ore is mined, crushed, and heaped in the form of a truncated cone on a suitable asphalt pad. The leaching liquor is pumped to the top of the heap and percolates through the ore. The leachate is collected, processed, and recycled. (Source: Zajic 1969. Reprinted by permission, copyright Academic Press.)

Bioreactors

- The bioreactors used are the **highly aerated stirred-tank designs** where finely ground ore is treated.
- Often nutrients such as ammonia and phosphate are added and the bioreactor operated in a continuous manner.
- The leaching can take days rather than the weeks required with dump extraction as temperatures of 40-50°C are used, although the ore loading is 20% (BIOX®)
- Ores such as chalcopyrite ($CuFeS_2$) and energite (Cu_3AsS_4) require temperatures **as high as 75-80°C** for leaching which cannot be generated in dumps and therefore **can only be carried out in bioreactors**

- A **continuous reactor-type leaching operation** for recovery of copper from low-grade sulfide ore is shown in **Fig. 15.2**.

Copper extraction from low-grade ore by a continuous leaching process



➢Oxidation of sulfide and ferrous iron is carried out by *T. ferroxidans* generating the acid for leaching.

➢Copper is precipitated by exchange, using scrap iron.

- The leached metal is partitioned into an organic solvent and subsequently recovered by "stripping" (evaporating) the solvent (**Fig. 15.3**).

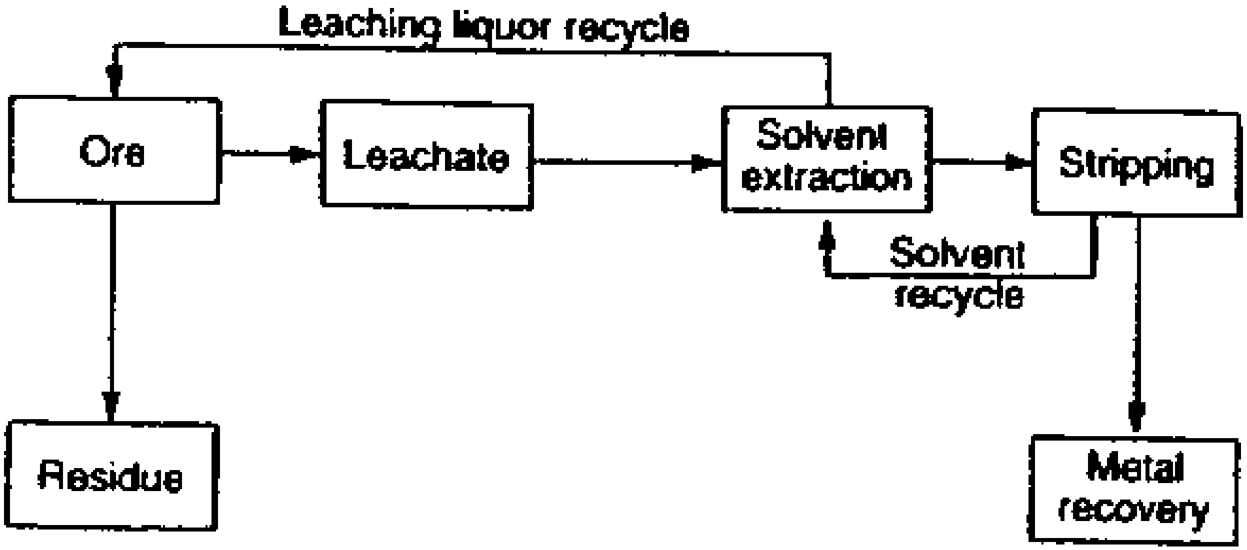


Figure 15.3

Flowchart of metal recovery from low-grade ores by bioleaching using the activity of *Thiobacillus ferrooxidans*. (Source: Torma 1977.)

- **Geological formations** play a key role in determining the **suitability of ore deposits** for recovery by ***in situ* bioleaching**.
  - Porous ore formation that overlies water-impermeable strata allows a suitable pattern of boreholes to be established

- The **mineralogy of the ore** is significant in determining its **susceptibility** to bioleaching.
  - Chemical form of element within the ore may be resistant to microbial attack
  - MOS can attack ores initially but production of toxic products may preclude further bioleaching activities
  - Ore minerals may exist in chemical forms that are readily subject to bioleaching

- The **size of mineral particles to be leached** is critical in determining the **rate of leaching**
  - Increasing the **surface area** (by crushing or grinding) greatly enhances the rate of bioleaching.

Ecological factors affecting the efficiency of bioleaching (factors affecting *T. ferrooxidans*)

- Temperature (optimum: 30 – 50^{o}C)
- pH (optimum: 2.3 – 2.5)
- Iron supply (2-4 g/L of leach liquor oxygen)
- Availability of other nutrients required for growth e.g. NH_4 nitrogen, P, SO_4, & Mg
- Availability of sufficient water
- Light, especially at shorter wavelengths has inhibitory effect on *T. ferroxidans* in open-air leaching operations

- Temperature in some mineral deposits can be significantly increased by the **oxidative activities of the Thiobacilli**
- This may exceed the tolerance limits of a *Thiobacillus* species, leading to **decreased bioleaching** activity.
- **Thermophilic sulfur-oxidizing** microorganisms may play an important role in the bioleaching process.
- Members of the genus ***Sulfolobus***, obligate thermophilic archaebacteria, oxidize ferrous iron and sulfur in a manner similar to the members of the genus ***Thiobacillus***.

- **Thermophilic *Thiobacillus*** species isolated from various hot sulfur-rich environments are likely candidates for use in bioleaching processes.

- ***Sulfolobus*** has been used especially in the **bioleaching of Molybdenite** (molybdenum sulfide), whereas molybdenum is toxic to ***Thiobacillus*** species.

- Microorganisms have also been considered as **accumulators of metals** from dilute solutions through;

- **intracellular uptake and storage via active cation transport systems,**
- **surface binding**, or
- **some undefined mechanisms.**

Copper Bioleaching

- Copper is a metal generally in short supply and is in high demand by the electrical industry and for various metal alloys.

- In the bioleaching of copper, the action of ***Thiobacillus*** involves both **(Table 15.1; Fig. 15.6)**;

- the direct oxidation of CuS
- indirect oxidation of CuS via generation of Ferric (Fe^{3+}) ions from ferrous sulfide

- Ferrous sulfide is present in the economically most important copper ores, such as **chalcopyrite** ($CuFeS_2$)

- Copper is recovered from the leaching solution either by **solvent partitioning** or by the **use of scrap iron**.

- In the latter method, copper replaces iron according to the equation: $CuSO_4 + Fe^0 \longrightarrow Cu^0 + FeSO_4$

- When solvent partitioning is used, unless carefully removed by activated carbon, **residues** in the leaching liquor may **inhibit the activity of *T. ferrooxidans.***

- The **principal disadvantage of bioleaching** is the **relative slowness of the process**.

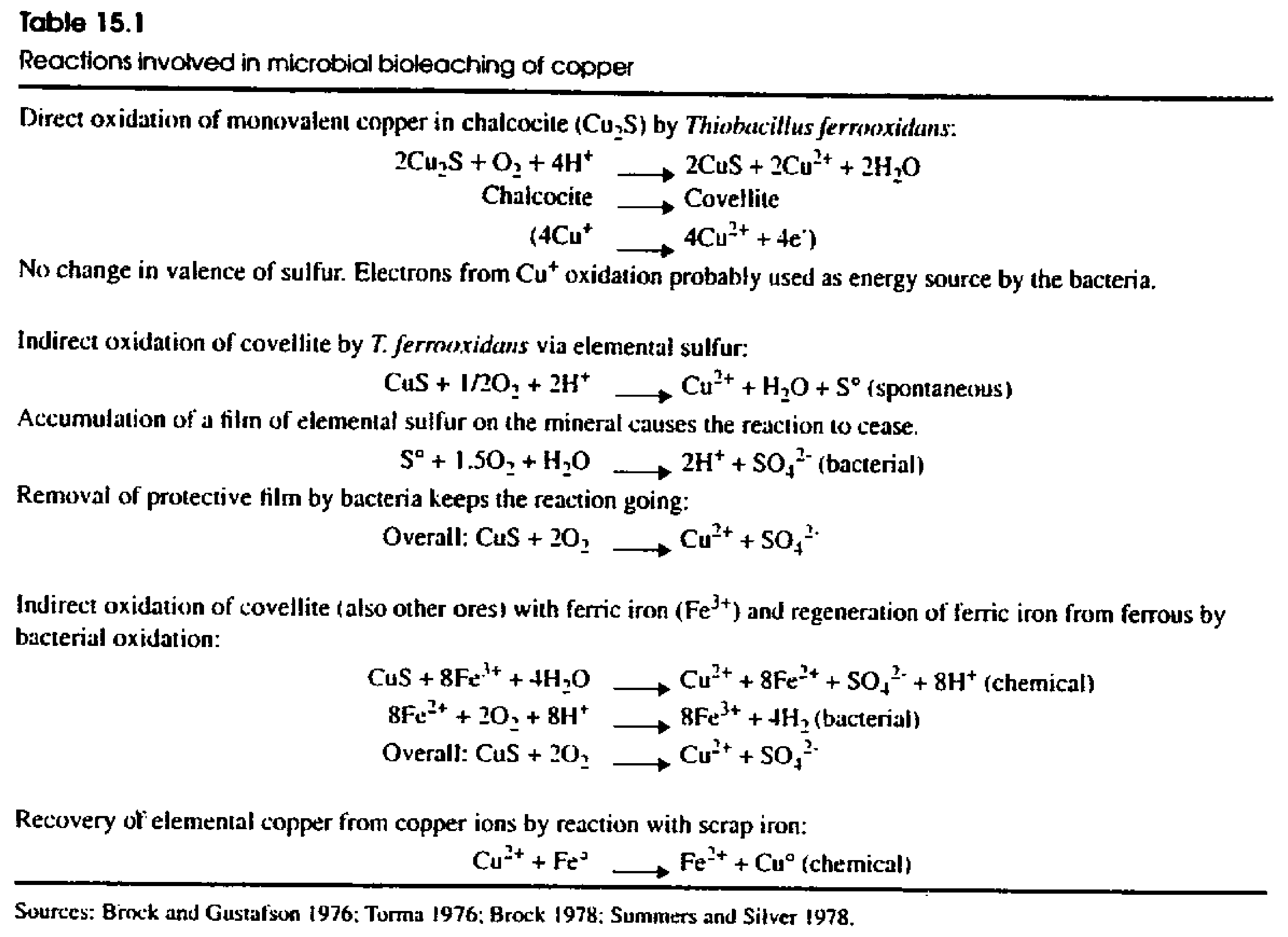


Table 15.1

Reactions involved in microbial bioleaching of copper

Direct oxidation of monovalent copper in chalcocite (Cu_2S) by *Thiobacillus ferrooxidans*:

$$2Cu_2S + O_2 + 4H^+ \longrightarrow 2CuS + 2Cu^{2+} + 2H_2O$$

$$\text{Chalcocite} \longrightarrow \text{Covellite}$$

$$(4Cu^+ \longrightarrow 4Cu^{2+} + 4e^-)$$

No change in valence of sulfur. Electrons from Cu^+ oxidation probably used as energy source by the bacteria.

Indirect oxidation of covellite by *T. ferrooxidans* via elemental sulfur:

$$CuS + 1/2O_2 + 2H^+ \longrightarrow Cu^{2+} + H_2O + S^\circ \text{ (spontaneous)}$$

Accumulation of a film of elemental sulfur on the mineral causes the reaction to cease.

$$S^\circ + 1.5O_2 + H_2O \longrightarrow 2H^+ + SO_4^{2-} \text{ (bacterial)}$$

Removal of protective film by bacteria keeps the reaction going:

$$\text{Overall: } CuS + 2O_2 \longrightarrow Cu^{2+} + SO_4^{2-}$$

Indirect oxidation of covellite (also other ores) with ferric iron (Fe^{3+}) and regeneration of ferric iron from ferrous by bacterial oxidation:

$$CuS + 8Fe^{3+} + 4H_2O \longrightarrow Cu^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+ \text{ (chemical)}$$

$$8Fe^{2+} + 2O_2 + 8H^+ \longrightarrow 8Fe^{3+} + 4H_2 \text{ (bacterial)}$$

$$\text{Overall: } CuS + 2O_2 \longrightarrow Cu^{2+} + SO_4^{2-}$$

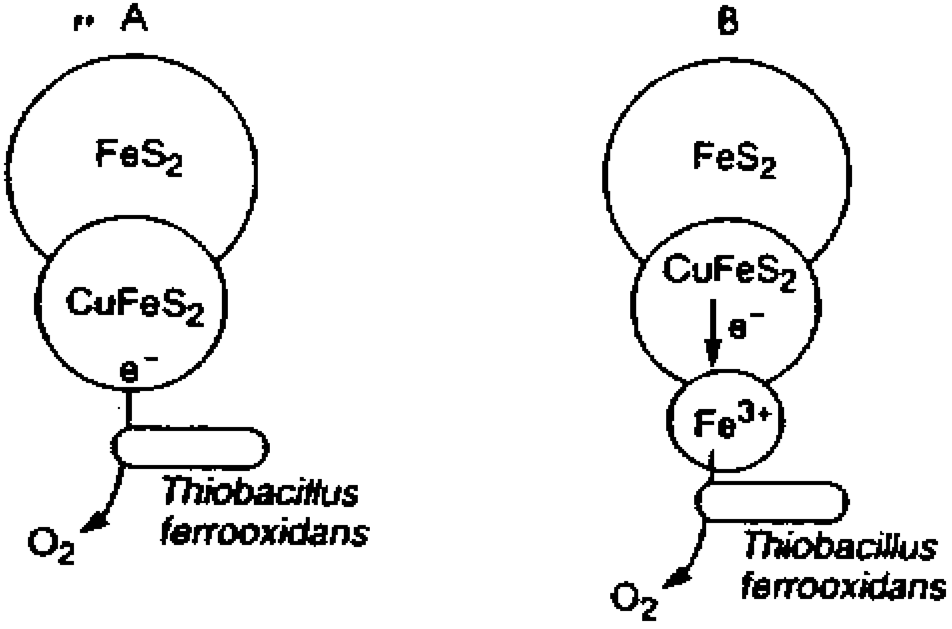
Recovery of elemental copper from copper ions by reaction with scrap iron:

$$Cu^{2+} + Fe^\circ \longrightarrow Fe^{2+} + Cu^\circ \text{ (chemical)}$$

Sources: Brock and Gustafson 1976; Torma 1976; Brock 1978; Summers and Silver 1978.

Figure 15.6

Two biological leaching mechanisms for pyrite (FeS_2)/chalcopyrite ($CuFeS_2$). (A) Direct leaching with transfer of electron (e^-) to molecular oxygen. (B) indirect leaching with Fe^{3+} as the primary electron acceptor. (Source: Tuovinen 1990.)



Uranium Bioleaching

- Uranium is used as a fuel in nuclear power generation.
- Microbial recovery of uranium from otherwise useless low-grade ores can be considered a contribution to energy production.
- Tetravalent uranium oxide (UO_2) occurs in low-grade ores and is insoluble.
- It can be converted to the leachable exhalant form by oxidation with ferric ion (Fe^{3+}).

- **Carbonate-rich uranium** deposits are leached with **alkaline bicarbonate-carbonate solutions**.

- **Pyrite-containing uranium** deposits are leached with **dilute sulfuric acid solutions**.

- The ferrous ions (Fe^{2+}) produced during Uranium oxidation are converted back to Fe^{3+} by chemical oxidants such as chlorate, manganese dioxide or H_2O_2.

- The chemical oxidants add substantial cost to the leaching process.

Extraction of uranium

- There are two possible processes. Direct leaching by T. *ferrooxidans* has been proposed in the following equation.

$$2UO_2 + O_2 + 2H_2SO_4 \longrightarrow 2UO_2SO_4 + 2H_2O$$

- However, in conditions where oxygen is limited this cannot operate, and the indirect bioleaching process operates using pyrite. The ferric (II) ion, which reacts with the uranium ore, and sulphuric acid, which also leaches uranium.

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

$$UO_3 + H_2SO_4 \longrightarrow UO_2SO_4 + H_2O$$

Extraction of gold

- The normal method of extracting gold is to treat it with **cyanide** and then extract the gold from the cyanide extract with carbon.

- The **cyanide waste is a major pollutant** and has to be treated before release into the environment.

- Cyanide can be destroyed by a sulphur dioxide and air mixture or a copper-catalysed hydrogen peroxide mixture.

- However, there are biological methods, both aerobic and anaerobic, for the treatment of cyanide.

- Some of the micro-organisms known to oxidize cyanide include species of the genera *Actinomyces*, *Alcaligenes*, *Arthobacter*, *Bacillus*, *Micrococcus*, *Neisseria*, *Paracoccus*, *Thiobacillus*, and *Pseudomonas*.

- Some ores are resistant to cyanide treatment as the gold is enmeshed in pyrite (FeS_2) and arsenopyrite (FeAsS) and **only 50% of the gold can be extracted**.

- The leaching is carried out in a sequence of bioreactors with the first step bioleaching the FeS_2 and FeAsS so that the gold can subsequently be extracted.

- The processes includes aerobic rotating biological contactors, bioreactors, and stimulated ponds

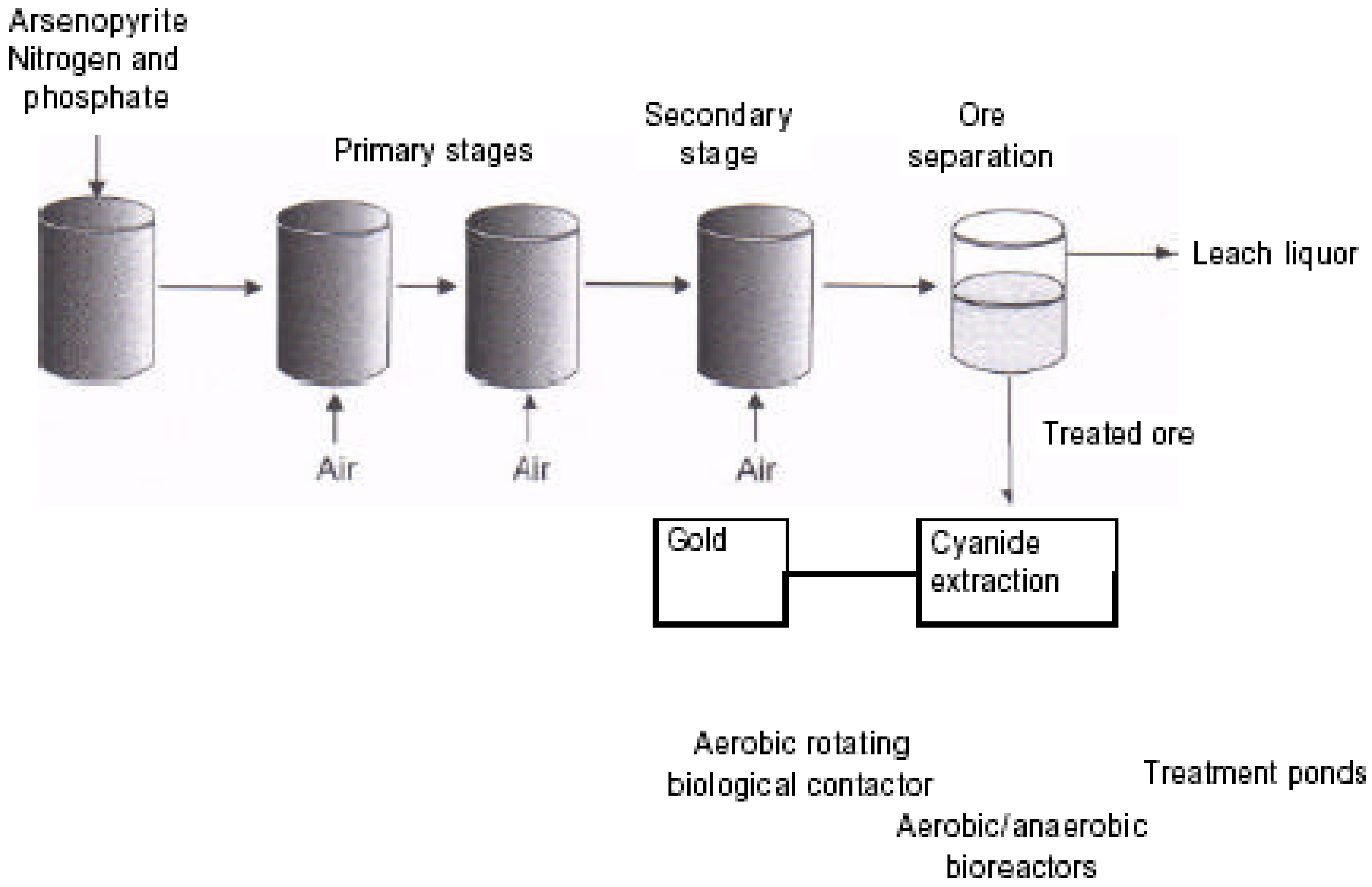


Figure 8.13 The process for the extraction of gold from arsenopyrite-containing ore and the treatment of the cyanide used to extract the gold. The gold is made available for extraction by the removal of arsenopyrite that masks the gold. The gold is removed from the cyanide by the addition of carbon (charcoal) and the waste cyanide can be treated in aerobic rotating biological contactors, aerobic/anaerobic bioreactors, and treatment ponds.

Fig. 1.1. At Youanmi Mine, Western Australia, 120 mt/day of refractory-sulfidic gold concentrate are biooxidized by moderately-thermophilic bacteria to enhance gold recovery.

The future of Bioleaching

- Isolate new bacterial strains from extreme environments, such as mine-drainage sites, hot springs, and waste sites, and use these to seed bioleaching processes.

- Improve isolates by conventional mutation and selection or by genetic engineering. One possibility would be to introduce arsenic resistance into some bioleaching organisms, which could then be used in gold bioleaching.

- Heterotrophic leaching is a solution for wastes and ores of high pH (5.5) where many of the acidophiles would not grow. Fungi like*Trichoderma horzianum* have been shown to solubilize MnO_2, Fe_2O_3, Zn, and calcium phosphate minerals.

- The population dynamics within the bioleaching dumps and the relative importance of various organisms and mechanisms needs to be understood.