Lecture 13
Bioleaching Of Nickel From Sulfides And Laterites

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In lectures 13, bioleaching of nickel from sulfide ores and concentrates as well as from lateritic ores is discussed. Heap bioleaching of nickel along with other metals such as zinc and copper from a schist belt as practised in Talvivaara, Finland is illustrated in lecture 14 [64 – 86].

Bioleaching of nickel ores and concentrates

Nickel occurs in nature mainly as its sulfides such as pentlandite, \((\text{Ni Fe})_9 \text{S}_8\) along with pyrite and pyrrhotite or interlocked with chalcopyrite-cubanite and pyrrhotite. Another form of nickel is as its oxide in laterites. Both the above forms are amenable for nickel biodissolution; either through heap bioleaching or reactor leaching of bulk concentrates. [64 – 80].

Several microorganisms inhabiting nickel ore deposits develop natural tolerance to nickel. Nickel – tolerance is important in judging bacterial nickel dissolution. Nickel tolerance can also be imparted to mine-isolated organisms through serial subculturing in the presence of increasing nickel ion concentrations. Bioleaching of nickel sulfides is temperature sensitive and use of thermophiles in place of mesophiles significantly enhances leaching kinetics.

Typical bioleaching reactions involving nickel sulfides are illustrated below:

\[(\text{Ni Fe})_9 \text{S}_8 = 9\text{Ni}^{++} + 9\text{Fe}^{++} + 8\text{S} + 18\text{e}\]

Pentlandite

\[\text{Fe}^{++} = \text{Fe}^{+++} + \text{e}\]

\[2\text{S} + 2\text{H}_2\text{O} + 3\text{O}_2 = 2\text{H}_2\text{SO}_4\]

\[\text{NiS} + 2\text{H}_2\text{SO}_4 = \text{NiSO}_4 + \text{H}_2\text{S}\]

Millerite

\[\text{NiS} + 2\text{Fe}^{+++} = \text{Ni}^{++} + 2\text{Fe}^{++} + \text{S}\]
Pyrite or pyrrhotite present in the nickel sulfide ores also get biodissolved similarly. Pyrrhotite \((\text{Fe}_{(1-x)} \text{S})\) is commonly associated with nickel sulfide ores. It is easily dissociated and oxidized under acidic conditions.

\[
\text{FeS} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2\text{S}
\]

On the other hand, pyrite is a nobler mineral compared to electrochemically active pentlandite or millerite. Presence of pyrite can galvanically enhance anodic dissolution of pentlandite, so also the presence of chalcopyrite.

The role of galvanic interactions in the bioleaching of pentlandite containing complex sulfides has been studied.

Rest potential measurements in a bioleaching medium at pH-2.5 in the absence of iron, indicated the following values.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Eh, mV</th>
</tr>
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<tbody>
<tr>
<td>Chalcopyrite</td>
<td>+500mV</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>+350 – 420 mV</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>+350 – 370 mV</td>
</tr>
</tbody>
</table>

In a pyrite-chalcopyrite-pentlandite-pyrrhotite combination, galvanic dissolution of pentlandite and pyrrhotite will be promoted. In a pentlandite-pyrrhotite combination, higher dissolution of pyrrhotite can be expected. Similarly, in a chalcopyrite-pentlandite galvanic contact, enhanced selective dissolution of pentlandite can be expected. (fig. 13.1).
In laboratory bioleaching tests using a copper-nickel-iron sulfide ore in the presence of *At.ferrooxidans*, nickel dissolution was found to be faster and in all cases, occurred before copper extraction was initiated. Nickel dissolution (from pentlandite) was almost 2-3 times higher than that of copper (from chalcopyrite).

Thermophiles such as *Sulfobacillus* isolated from nickel ore deposits and tailings can develop nickel tolerance. General observations with regard to nickel tolerance, especially in *At.ferrooxidans* are given below:

- Strains isolated from nickel-rich zones exhibit higher tolerance compared to other normal strains.
- Mesophiles exhibit relatively higher nickel tolerance compared to thermophilic organisms.
- Higher nickel tolerance to normal strains can be imparted through serial subculturing in the medium containing successively increasing metal concentrations.
- It is also essential to maintain nickel-tolerant strains under the developed **nickel stress** to retain the acquired metal tolerance.
Several laboratory research studies have been carried out on the bioleaching of pentlandite ores and concentrates.

- Nickel-copper-iron sulfide concentrate grown adapted *At.ferrooxidans*, could extract about 55% nickel after 18 weeks of adaptation.
- Selective bioleaching of a pentlandite-chalcopyrite concentrate in the presence of *At.ferrooxidans* in a bioreactor established preferential nickel extraction (55%).
- Bioleaching of a nickel-rich pyrrhotite concentrate in the presence of unadapted and adapted strains of *At.ferrooxidans* yielded 87% and 91% recovery in 16 days, respectively.
- Bioleaching of a pentlandite-pyrrhotite-chalcopyrite concentrate resulted in about 60% nickel recovery after about a month.
- Thermophiles (*Acidimicrobium, Sulfobacillus, At.caldus*) at higher temperatures of about 50-80°C were found to be more efficient in nickel extraction. For example, at about 70°C, 98% nickel could be extracted with a retention period of four days using adapted cultures from nickel-copper concentrates.

In the presence of *Acidianus brierleyi*, a nickel-copper concentrate was bioleached at 68°C and pH 1.6 to recover 99.8% if nickel and about 86% of copper in about 4 days.

- Several studies have been made using pentlandite ores in different countries such as Finland and China. The black schist ore of Talvivaara in Finland has been studied in detail for the bioextraction of nickel, zinc, copper and cobalt. Based on laboratory results, pilot trials on heap bioleaching were carried out and ultimately commercial scale heap bioleaching is being attempted.
- Nickel-copper ores in the Jinchuan mines of China were also studied using *Acidithiobacillus* bacteria. Role of adapted bacteria was assessed. In an airlift reactor at 15% pulp density, more than 95% of nickel and 48% of copper and 82% of cobalt could be bioleached after 20 days.

Bioheap™ technology for nickel-copper sulfides uses moderate thermophiles and tested on an W.Australian ore. Two 5000 tonnes heaps were erected at Radio Hill and inoculated at 50-55°C
at pH 1.8 with mixed cultures of *Sulfobacillus* and *Thermoplasma*. 90% nickel recovery was achieved in less than an year with 50% copper.

Heap leaching trials for nickel-copper sulfide ores of Jinchuan in China have been reported. Pilot tests were also undertaken at a nickel mine in Mojiang county of S.China. Six test heaps were arranged (6-8 meters high) having 10,000 tonnes of crushed ore in each heap and inoculated with a mixed mesophilic culture and aerated. In an year, nickel and cobalt recoveries higher than 60% were achieved.

A salt-tolerant mixed culture has also been developed for application in Bioheap™ technology in W.Australia.

The BioNic® is a bioleaching process conceived in early 1990s in stages form batch tests to demonstration level for 300 Kg/day of pentlandite concentrate. Mixed cultures including *At.ferrooxidans*, *At.thiooxidans* and *L.ferrooxidans* were adapted to the concentrate. In the temperature range of 30-40°C, higher than 90% nickel recoveries in 8 days were achieved. Validity of the BioNic® process for commercial applications has been confirmed. Modification of the above process using thermophiles at 65-80°C has also been reported.

**Bioleaching of nickel from laterites**

Recently, renewed interest has been generated to establish nickel bioleaching processes not only from nickel sulfide ores and concentrates, but also for nickel laterites.[81 – 84].

Applicability of bioleaching has also been tested to extraction of nickel from the more abundant lateritic ore reserves. Almost 72% of world’s cobalt and nickel is contained in lateritic ores. Unlike in sulfide mineralization, the nickel and cobalt in the laterites are not discrete and separate, but are invariably interlocked with other oxides such as those of iron. Such interlocking of nickel and cobalt in laterites makes their recovery more difficult due to poor liberation even in smaller sizes. Prior reduction of iron oxides (hematite, magnetite, goethite, limonite) becomes essential to liberate the encapsulated nickel and cobalt to facilitate their easy dissolution in a lixiviant. Reductive dissolution can be brought about either by bacterial
reduction or through use of reducing agents secreted by microorganisms. The following biological approaches are possible:

- Use of biologically-derived reducing and metal-complexing organic acids.
- Use of fungi and their metabolites (organic acids)
- Use of *Acidithiobacillus* type bacteria which produces sulfite and thiosulfate reducers, and also mineral acids.
- Use of acidophilic organisms capable of dissimilatory ferric iron reduction-iron reducing bacteria and bacterially-catalyzed reductive dissolution.

Bioprocessing of laterite ores has been studied using fungi such as *Aspergillus* and *Penicillium*.

Bacteria of the genus *Acidithiobacillus* have been shown to solubilise nickel through production of sulfuric acid and reducing thiosulphate and thionate species.

A mixed culture containing *At.ferrooxidans*, *At.caldus* and *L.ferrooxidans* was used to extract nickel from laterites.

In oxidative dissolution, the mineral substrate provides the energy (as reduced sulfur compounds or ferrous iron) to the microbes, while in reductive dissolution, an external electron donor becomes necessary.

\[ \alpha \text{-FeO.OH} \rightleftharpoons \text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+} \]

Reductive dissolution of goethite coupled to sulfur oxidation is given below

\[ 6 \alpha \text{- Fe O.OH} + \text{S} + 10\text{H}^+ = 6 \text{ Fe}^{3+} + \text{SO}_4^{2-} + 8\text{H}_2\text{O} \]

Acidophiles such as *At.ferrooxidans* and *Acd.organivorans* were found to catalyse reductive dissolution of nickel laterite, demonstrating nickel release under atmospheric conditions in acid pH (1.5 – 2).
A new process, titled, *Ferredox* process is reported recently to extract nickel and cobalt from limonitic (goethite) laterites through reductive dissolution. Iron dissolution and precipitation occur separately.