Lecture 6
Bioleaching Mechanisms

Keywords: Direct Mechanism, Indirect Mechanism, Contact Mechanism

In lectures 6 and 7, mechanisms involved in interaction of *At. ferrooxidans* with sulfide minerals are discussed with respect to direct and indirect attack as well as role of microbial attachment [18-35].

Classical understanding of biooxidation reactions involving *Acidithiobacillus ferrooxidans* involve two possible mechanisms; namely,

Direct and Indirect mechanisms.

In the direct mechanism, bacteria directly oxidize the minerals and solubilise the metal.

\[ MS + H_2SO_4 + \frac{1}{2} O_2 = MSO_4 + S + H_2O \]

\[ S + 1 \frac{1}{2} O_2 + H_2O = H_2SO_4 \]

Bacterial attachment to the mineral surfaces is a prerequisite to the direct attack.

In indirect attack, the bacteria oxidises ferrous to ferric form which is the oxidizing agent for the minerals.

\[ MS + 2Fe^{+++} = M^{++} + 2Fe^{++} + S \]

\[ 2Fe^{++} + \frac{1}{2} O_2 + 2H^+ = 2Fe^{+++} + H_2O \]

Both direct and indirect mechanisms may occur simultaneously along with other physicochemical reactions in real bioleaching systems.
There are several reports on direct cell attachment on several sulfides and the role of ferric ions bound to the cell surface.

Bioleaching of sphalerite by *At. ferrooxidans* was observed to be through an indirect mechanism with the bacterial contribution only to oxidize ferrous ion to ferric.

\[
    \text{Fe}^{2+} = \text{Fe}^{3+} + e \quad \text{(Bacterial oxidation)}
\]

\[
    \text{ZnS} + 2\text{Fe}^{3+} = \text{Zn}^{2+} + 2\text{Fe}^{2+} + \text{S}
\]

The above tests were carried out by maintaining the desired redox potentials through control of ferric to ferrous ion ratio.

However, later studies revealed that when ferrous concentrations were higher, zinc leaching by the bacteria increased, presumably due to removal surface sulfur layers through chemical oxidation by ferric ions.

Sand et al (1995) proposed indirect mechanism promoted by ferric ions. The role of ferric ions bound by extracellular polymeric substances (EPS) for binding of bacterial cells onto pyrite was proposed. [22]

Two ‘indirect’ mechanisms for the sulfur part in the mineral after initial reaction with Fe\(^{3+}\) were also proposed. [22-28]

\[
    \text{FeS}_2 + 6 \text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{S}_2\text{O}_3^{2-} + 7\text{Fe}^{2+} + 6\text{H}^+
\]

\[
    \text{S}_2\text{O}_3^{2-} + 8 \text{Fe}^{3+} + 5\text{H}_2\text{O} = 2\text{SO}_4^{2-} + 8\text{Fe}^{2+} + 10\text{H}^+
\]

The **thiosulfate mechanism** differs from the **polysulfide mechanism** relevant for **acid soluble** sulfides such as ZnS.

For example, ZnS can interact with acid as

\[
    \text{ZnS} + 2\text{H}^+ = \text{Zn} + \text{H}_2\text{S}
\]

\[
    \text{H}_2\text{S} + 2\text{Fe}^{3+} = \text{S} + 2\text{Fe}^{2+} + 2\text{H}^+
\]
On the other hand, pyrite sulfur is mainly oxidized to sulfate (82%), S (16%) and the rest \( \text{SO}_6 \) and \( \text{SO}_6^- \), unlike sulfur in ZnS (mainly elemental S and about 5% as sulfate).

In case of pyrite, bacterial oxidation of ferrous ions and also of sulfur and polythionates to sulfate can occur. All the above contributions are considered \textbf{indirect}.

Tributsch (1999) found the rate of biodissolution of sulfides with \textit{At. ferrooxidans} to be approximately proportional to the solubility products.

\( \text{ZnS}, \text{FeS, PbS} \) are easily dissolved, while \( \text{MoS}_2, \text{FeS}_2 \) are difficult to dissolve.

Biology of leaching bacteria is more complex and recent developments in molecular biology, surface analysis and surface chemistry have enabled better understanding of mechanisms involved in biooxidation processes.

Direct enzymatic oxidation of the sulfur moiety of sulfide minerals as suggested in the direct attack mechanism is questioned. Alternately, nonenzymatic sulfide oxidation by ferric ions in association with reoxidation of ferrous iron enzymatically is a newly proposed mechanism having sub-mechanisms such as \textbf{contact} and \textbf{noncontact} mechanisms. [22-28]

Non-contact mechanism involves ferrous oxidation in solution by planktonic bacteria. However, the oxidized ferric ions come in contact with mineral surfaces where they get reduced (by oxidation of the sulfide mineral).

Recent review by Rohwerder et al. (2003) outlines the current- understanding as follows [23]:

- Two different mechanisms – thiosulfate and polysulfide pathways.
- Reaction pathway determined by mineral species (acid dissolution)
- Reactivity of sulfides with protons is a criterion (acid dissolution)
- Electronic configuration is important in determining solubility criterion.
- Acid insoluble sulfides-\textbf{Thiosulfate pathway} Eg:- Pyrite, Molybdenite
  Free thiosulfate is oxidized to sulfate (via) tetrathionate and other polythionates.
Elemental sulfur also is produced in absence of S-oxidizers. Based on the necessity of an electron transfer reaction, iron oxidising bacteria can leach acid-insoluble sulfide in acid solutions.

- Acid soluble sulfides-**polysulfide pathway**.
  Eg:- sphalerite, galena, chalcopyrite, arsenopyrite etc
  Combination of acid attack and ferric oxidation.

- In both the above mechanisms, the role of bacteria would be generation of ferric ions and ratio between ferric to ferrous ions determines the redox potential. Control of redox potential is needed to promote biooxidation of the mineral.

- Acidophilic sulfur oxidizers can contribute to transformation of intermediate sulfur compounds ultimately to sulfuric acid.

- In the absence of sulfur oxidation (as in abiotic conditions), surface accumulation of sulfur layers would impede mineral dissolution. Thus, sulfur oxidizers can influence dissolution kinetics.

- Electrochemical properties of sulfides can control leaching kinetics-Redox potentials play an important role.