Sulphide Mineral Leaching and Chemistry of Sulphide Oxidation by Bacteria

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Abstract

Bioleaching is a technology which employs extraction of metals from low-grade ores and concentrates by environmental-friendly process. The microorganisms or its metabolites plays crucial role in the dissolution of metals by attacking mineral surface. The extraction of metals from sulphide mineral involves a group of chemolithotrophic bacteria, especially *Thiobacillus ferrooxidans* and *T. thiooxidans*. Whereas, heterotrophic bacteria are used for treating minerals other than sulphides. In these cases, production of organic acids, are produced into the surrounding by the microorganisms for metal solubilization.

Introduction

Metals as mineral are abundant in the earth’s crust. They are present in the form of oxides, carbonates, or sulphides. The sulphide minerals exemplify great potential for metal recovery. Marine sediments, aquifers, or groundwater are some of the anoxic environments where the sulphate reducing bacteria (SRB) reduces sulphates to produce hydrogen sulphide (H2S) and thereby it reacts with iron to form iron sulphides (commonly called pyrite, FeS2). Leaching is being used these days to recover heavy metals. Compared to chemical methods, biological recovery of metals seems to be a natural process and sustainable alternative. The process by which oxidizing microorganisms dissolve metals from its ores is referred to as “biomining”. The natural microorganisms being used in biomining process acts as catalyst. It is divided into two categories, one is bioleaching and other is bio-oxidation. Bioleaching involves conversion of water insoluble metal into its water soluble form by microorganisms and bio-oxidation refers to the decomposition of the mineral by microorganisms, making it available for chemical extraction.

History and Development

The first reported example of ancient mining is that of a Greek naturalist and physician around 166 AD., in several copper mines of Cyprus. Copper heap leaching on a commercial scale started at Rio Tinto Mine, Spain. Bacterial catalysis of iron oxidation and H2SO4 formation in mine waters was demonstrated by Colmer and Hinkle. The zinc sulphide oxidation by unidentified sulphur oxidizing microorganism was reported as early as in 1920, however, involvement of specific microorganisms was not confirmed till 1947.

Bioleaching Processes

The interactions between sulphur oxidising bacteria (SOB) with the pyrite are explained by mechanisms: “direct / contact” and “indirect / non-contact” mechanisms. The recent studies redefined the pathways in terms of acid solubility of minerals. They are thiosulphate and polysulphide.
The factors influencing bioleaching process are nutrients, O₂ and CO₂, pH, temperature, mineral substrate and heavy metals.

Figure 1: Direct leaching

Direct Mechanism

This mechanism entails a physical contact between mineral and the bacteria resulting in pyrite oxidation. In this process the sulphur-oxidizing bacteria gets attach to the surface of minerals, by enzymatic interactions. Particularly, a biofilm formation takes place on the surface of minerals which allows the dissolution of the sulphur moiety. At this stressed contact zone, exopolysaccharides (EPS) are produced by the bacteria serves as protective walls (Figure 1). The pyrite leaching by direct mechanism is expressed in the Eq. (1).

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

A microenvironment is then formed at pH lower than 8, promoting the growth of sulphur-oxidizing bacteria and its metabolism. Perhaps, \textit{A. ferrooxidans} and \textit{T. Denitrificans} produce EPS which plays a protective role as well as provide space for oxidation process of the sulphides to occur. In case of pyrite, the acidic reaction is not capable enough for the dissolution to occur and so then bacteria uses a stronger oxidizing agent such as O₂ as an electron acceptor, particularly for \textit{A. ferrooxidans} (Eq. 2). Thus, sulphate ion is formed along with sulphuric acid which creates acidic environment for further dissolution of iron and optimal bacterial growth.

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

Indirect / Non-contact Mechanism

Compared to the direct mechanism, no such contact is enrolled here. The bacterial “lixiviant” containing acidiorin (III) ions promotes the dissolution. Here, acid and iron (III) are the oxidizing agents and bacteria are recognized as catalyst, with protons or iron (III) at the surface of the minerals. Thus boosting the oxidation process, elemental sulphur, sulphates, thiosulphates, and H₂S are produced along with iron (II) (Figure 2).

For iron (II) to be remained in solution, the oxidation of pyrite must occur with pH < 5, where iron (II) oxidised to iron (III) resulting in a cyclic oxidation process. The acidic conditions are indicated by the presence of either \textit{A. ferrooxidans} or \textit{T. thiooxidans}. Metal sulphides (MS) get oxidized as following Eq. (3).

\[
\text{MS} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{MSO}_4 + 2\text{Fe}(\text{SO}_4)_3 + S^0
\]  

Specifically, indirect oxidation of pyrite can occur with \textit{A. ferrooxidans}, as described in Eqs. (4) and (5) for pyrite.

\[
\text{pyr} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow 3\text{FeSO}_4 + 3S^0
\]  

\[
2S^0 + 2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4
\]

Thiosulfate Mechanism

Thiosulphate pathway occurs when the acid insoluble mineral of sulphide such as pyrite (FeS₂) and molybdenite (MoS₂) are oxidized. The bond between sulphur and iron moiety is very strong to break. The extraction process involves six successive one electron transfer steps from the valance bands to release thiosultates. Further iron (III) ions supplied by \textit{A. ferrooxidans} are reduced to iron (II) ions and thiosulfate intermediate oxidises to sulphate as main product with tetrathionate and polythionates (Figure 3).

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

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

Polysulphides Mechanism

In contrary to the thiosulfates mechanism, the polysulphides mechanism occurs for acid soluble mineral such as sphalerite (ZnS), chalcopyrite (CuFeS₂) or galena (PbS) where an iron (III) ions and proton work together. The proton breaks the bond between the sulphur moiety and iron with consequent formation of hydrogen sulphide. The oxidation of pyrite occurs in a one-step electron transfer in combination with the proton attack. Initially, the free sulphur forms sulphide ions (S²⁻) that impulsively forms hydrogen disulphides by dimerization. Then it oxidizes to form elemental sulphur through polysulphide intermediates.
Conclusion

Sulphide mineral leaching is now more growing field and lot with better understanding of involved oxidation reactions and significant contributions by a variety of microorganisms including bacteria as well as archaea at diverse temperature and pH ranges. In country like India, where for most part of the year the normal temperature is more than 30 °C, thus, the rate of bioleaching process will be more as compared to many cold countries, make the process economically more viable.

References