Bioreduction in the development of new mineral technology

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Abstract. Reductive dissolution is like “biomining in reverse gear”. Selected sulfur reducing bacteria (SRB) can be used under anaerobic conditions – as in bioloeaching – for metal recovery from oxide minerals and laterite. General assumptions of the BioSulphide® and Ferredox processes for nickel recovery from laterite ores and copper from acid mine drainage or waste water were presented.

1. Introduction
It is natural for bacteria to interact with minerals. This biogeochemical cycle of bioweathering gradually destroys rocks [1]. The intensive interaction of chemolithotrophic bacteria with sulfide minerals results in acid mine drainage The Tinto River (Spain) is an excellent example of this phenomenon [2]. Acid mine drainage (AMD) can be the major source of various heavy metals. Ferric hydroxide precipitation enables selective separation of other metals present in the solution [3, 4]. Such opportunities offer an industry implemented BioSulphide® process [5].

The use of microorganisms for mineral degradation and metal extraction is known as “biomining” [6]. Biological oxidation of sulfide minerals is applied on the industrial scale in biomining. Bioleaching is mainly carried out either as a heap or tank leaching. In the case of the former, low grade sulfide ores are collected in a pile irrigated by acidic liquor containing bacteria which while percolating through the heap come into contact with sulfide grains. As a result, metal ions are extracted. The pregnant leach solution is collected in a special pond and then directed to the top of the heap. Heap bioleaching is used to extract copper from low grade ores [7].

The stirred-tank bioleaching has mainly been applied for gold refractory ores [8]. BIOX®, designed for gold refractory ore treatment, is one of such processes. It consists of the biotreatment of flotation concentrate with a solid content of 20% (w/w). Its duration in the tank is 4 to 6 days. Biopretreatment opens the structure of sulfide minerals for the extraction of gold with the use of cyanide. The biomodification of the mineral surface changes its properties in such a manner that the mineral can be used in selective flotation and flocculation [9].

Bacteria acting on minerals do not only limit biooxidation but under anaerobic conditions can also participate in bioreduction. The main reaction within reductive leaching has been described as “bioloeaching in reverse gear” [10].

Below, we attempt to describe and determine the main mechanism of reductive dissolution of oxide minerals in laterite ores and present the applications of biogenesis of hydrogen sulfide with the metal obtained from acid mine drainage.

2. Sulfate reducing bacteria
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Under anaerobic conditions, many bacteria are able to reduce sulfate, thiosulfate, and elemental sulfur to produce hydrogen sulfide in a process which is defined as biosulfidogenesis [11-13].

SRB is a special group of bacteria which use sulfate as the terminal electron acceptor and reduce sulfates to sulfides. The source of electrons is organic substances accompanying sulfates. Natural SRB can be classified into three main categories:

i. mesophilic proteobacteria – Desulfovibrio, Desulfbacterium, Desulfbacter, and Desulfobulbus;
ii. thermophilic gram-negative bacteria – Thermodesulfovibrio;
iii. gram-positive bacteria – Desulfotomaculum.

SRB convert sulfate into hydrogen sulfide (H$_2$S) at the presence of organic matter. The resultant H$_2$S reacts with some metal cations and forms insoluble metal sulfide precipitates. This process enables metal ions to recovery from waste solutions (BioSulphide® process).

Typical chemolithotrophic bacteria can be used for the anaerobic dissolution of minerals. Acidithiobacillus ferrooxidans growing under anaerobic conditions have been shown to reduce ferric iron in the presence of sulfur [14]. The anaerobic growth of acidophilic bacteria such as mesophiles (Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans) moderate thermophiles (Acidithiobacillus caldus, Sulfobacillus acidiphiles) and thermophiles (Acidianus and Metallosphaera) was induced through the addition of 5 g/dm$^3$ of sulfur and 50 mM of ferric iron, with a pH of 2. The obtained bacterial suspensions were used for metal extraction from mineral material taken from the mound of the Talviaara Mine (Finland). Microbiological reduction of iron under anaerobic conditions takes place in a temperature range of 30-70°C. Iron removal was much greater at 70°C with thermophiles [14].

3. Reductive dissolution of metals

Oxidative dissolution can be carried out by chemoautotrophic bacteria applied to sulfide minerals. Since many metals occur in ore bodies as oxides and silicates, the alternative treatment appears to be reductive dissolution [6]. The presence of goethite is also a positive factor. Biodissolution of goethite was achieved with the transfer of electrons from elemental sulfur to ferric iron present in the mineral. Anaerobic reductive dissolution of iron oxide minerals is referred to as Ferredox [15]. Acidithiobacillus ferrooxidans can grow at anaerobic conditions using ferrous iron as an electron donor. The flowsheet of the Ferredox process enabling the reductive dissolution of limonitic minerals is presented in figure 1.
Acidithiobacillus ferrooxidans were used for the reductive dissolution of limonite. Limonite, an iron ore, is a mixture of a hydrated iron oxide such as goethite, akageneite, schwertmannite, and jarosite.

Iron reducing bacteria utilized ferric iron (Fe$^{3+}$) as an electron acceptor. At the same time, electrons were needed for reduction. Sulfur, hydrogen, or some organic compounds can be electron donors.

The extraction of nickel, cobalt, and manganese from laterite ore was induced by acidophilic Acidithiobacillus ferrooxidans, Sulfobacillus beneficiens, Acidicaldus organivorans, and Acidophilium sp., with the source of Fe$^{3+}$ being the goethite contained in laterite ore. Reductive dissolution of laterite allows for extracting 70-80% of nickel from laterite ore [16].

The reductive dissolution of goethite was connected with the elemental sulfur oxidation. The comparison of aerobic bioleaching with anaerobic reductive dissolution showed greater effectiveness of the latter [16]. Iron reducing bacteria use ferric iron as an electron acceptor. Sulfur, hydrogen or organic compounds are used as an electron donor. The selection of the right electron donor depends on the type of raw material and the used bacteria.

Figure 2 shows the characteristics of the substances most often used as electron donors.
Figure 2. Compounds used as electron donors. Own elaboration based on [15].

The copper laterite ore containing 15.5% of goethite underwent reductive dissolution with the presence of sulfur [17]. The process allows for the recovery of 78% of copper. It turned out that the relatively slow acid dissolution of goethite occurs at the beginning, and can be described as follows:

\[ 2S^0 + 12FeOOH + 21 H^+ = HSO_4^- + SO_4^{2-} + 12Fe^{2+} + 16H_2O \]

More than 60% of the world’s nickel reserves are estimated to occur in the form of laterites. Chemical leaching with the use of organic acids does not yield expected results due to the strong adsorption of nickel ions by the biomass of fungi used for the production of organic acids [18], which has called for studies on the chemolithotrophic bacterial adaptation for laterite ore leaching [19, 20].

Nickel can be leached from limonite ore in the anaerobic bioreactor with adapting chemolithotrophic bacteria. Acidithiobacillus ferrooxidans were first grown aerobically with excess sulfur (50g). When the number of cells reached the level of up to \(5 \cdot 10^8\) cell/ml, the limonite ore was added to the bioreactor. Bioleaching’s Within the course of 30 days This bioleaching yielded an over 75% nickel extraction from limonite ore [21].

The oxidative dissolution of UO\(_2\) entails a serious risk to the environment and people. Microorganisms living within the sulfidogenic environment are capable of reducing U(VI). Desulfovibrio desulfuricans may be included in this group. The enzymatic U(VI) reduction by \(D.\ desulfuricans\) bacteria was carried out at the presence of lactate as electron donors [22]. Three cobalt-bearing oxidized ores were bioleached under the anaerobic condition, at a pH of 1.8 by means of reductive dissolution. Two ores were obtained from Shevchenko, Kazakhstan, and one from the Acoje Mine in the Philippines. The ores contained mainly iron (goethite), manganese, nickel, zinc, and cobalt. The extraction of cobalt from these three ores was far more efficient, with the recovery being close to 90% [23].

Bioreductive treatment of U(VI) species reduces uranium ions mobility. Iron nanoparticles in the form of FeS play a special role during uranium immobilization. With FeS...
present, the dissolution rate of $\text{UO}_2$ is over 1 order of magnitude lower than without nanoparticles [24].

Manganese nodules available from the ocean floor can be an alternative source of metals. Polymetallic manganese nodules are a natural source of Cu, Co, Ni, and Mn [25]. Bioleaching was carried out at 30°C. The bacterial consortium was developed with the bacteria isolated from manganese ore mine. The reduction of $\text{MnO}_2$ phase dissolved Co and about 30% of Mn.

4. **BioSulphide® process**

Sulfate reducing bacteria used for the recovery of metals from minerals have several applications in the mining industry. The development of BioSulphide® technology depends on the thorough understanding of the mechanism of biological sulfate reduction.

The BioSulphide® process consists of (i) the biological conversion of sulfate to hydrogen sulfide and (ii) chemical precipitation of sulfides. This process enables metal ions selective removal from acid mine drainage solutions or wastewater. The same procedure was used for the precipitation of copper ions from industry wastewater [26] where most of the metal occurred as CuS (covellite).

Also, Johnson and Hallberg [27] proposed the recovery of metal from the main wastes containing a variety of soluble metal ions under anaerobic conditions.

The BioSulphide process (figure 3) has been successfully commercialized at the Copper Queen Mine in Bisbee, Arizona, US, which was closed in 1970 after nearly 100 years of exploitation, leaving a large amount of mining waste [28].

![Figure 3. Technological scheme of the BioSulphide® process. Own elaboration based on [29].](image)

5. **Summary**

Sulfidogenesis and bioreduction induced by sulfur reducing bacteria and *Acidithiobacillus ferrooxidans* enable extraction of valuable metals from oxide minerals, mainly laterite ores. The use of typical iron-oxidizing bacteria like *Acidithiobacillus ferrooxidans* for these processes creates new application possibilities. An example of practical use of the biological synthesis of $\text{H}_2\text{S}$ and application is the BioSulphide® process allows the copper recovery from acid mine drainage and wastewater.
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