BIOMINING ENHANCEMENT METHOD

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ABSTRACT

A biomining enhancement method for metal sulfide ores using sulfurous acid for microbial leaching of heavy metals into solution for subsequent removal via electro winning, ion exchange, or precipitation with alkaline and nutrient reagents for filtration removal.
BIOMINING ENHANCEMENT METHOD

RELATED APPLICATIONS


BACKGROUND OF THE INVENTION

[0002] 1. Field
[0003] This invention pertains to mining of ores. In particular, it relates to a method of enhancing Biomining of Ores.
[0004] 2. Statement of the Art
[0005] According to Wikipedia, Biomining is a new approach to the extraction of desired from ores being explored by the mining industry in the past few years. Microorganisms are used to leach out the minerals, rather than the traditional methods of extreme heat or toxic chemicals, which have a deleterious effect on the environment.
[0006] The development of industrial mineral processing has been established now in several countries including South Africa, Brazil and Australia. Iron and sulfur oxidizing microorganisms are used to release occluded copper, gold and uranium from mineral sulfides. Most industrial plants for biooxidation of gold-bearing concentrates have been operated at 40°C with mixed cultures of mesophilic bacteria of the genera Acidithiobacillus or Leptospirillum ferrooxidans. In subsequent studies the dissimilatory iron-reducing archaea Pyrococcus furiosus and Pyrococcus islandicum were shown to reduce gold chloride to insoluble gold.
[0007] Using bacteria such as Acidithiobacillus ferrooxidans to leach copper from mine tailings has improved recovery rates and reduced operating costs. Moreover, it permits extraction from low grade ores—an important consideration in the face of the depletion of high grade ores.
[0008] The potential applications of biotechnology to mining and processing are countless. Some examples of past projects in biotechnology include a biologically assisted in situ mining program, biodegradation methods, passive bioremediation of acid rock drainage, and bioremediation of ores and concentrates. This research often results in technology implementation for greater efficiency and productivity or novel solutions to complex problems. Additional capabilities include the bioleaching of metals from sulfide materials, phosphate ore bioreprocessing, and the bioconcentration of metals from solutions. One project recently under investigation is the use of biological methods for the reduction of sulfur in coal-cleaning applications. From in situ mining to mineral processing and treatment technology, biotechnology provides innovative and cost-effective industry solutions.
[0009] The potential of thermophile sulfide-oxidizing archaea in copper extraction has attracted interest due to the efficient extraction of metals from sulfide ores that are recalcitrant to dissolution. Microbial leaching is especially useful for copper ores because copper sulfate, formed during the oxidation of copper sulfide ores is very water-soluble. Approximately 25% of all copper mined worldwide is now obtained from leaching processes. The Acidiphilic archaea Sulfolobus metallicus and Metallosphaera sedula tolerate up to 4% of copper and have been exploited for mineral biomining. Between 40 and 60% copper extraction was achieved in primary reactors and more than 90% extraction in secondary reactors with overall residence times of about 6 days.

[0010] The oxidation of the ferrous ion (Fe²⁺) to the ferric ion (Fe³⁺) is an energy producing reaction for some microorganisms. As only a small amount of energy is obtained, large amounts of (Fe²⁺) have to be oxidized. Furthermore, (Fe³⁺) forms the insoluble Fe(OH)₃ precipitate in H₂O. Many Fe²⁺ oxidizing microorganisms also oxidize sulfur and are thus obligate acidophiles that further acidify the environment by the production of H₂SO₄. This is due in part to the fact that at neutral pH Fe³⁺ is rapidly oxidized chemically in contact with the air. In these conditions there is not enough Fe²⁺ to allow significant growth. At low pH, however, Fe²⁺ is much more stable. This explains why most of the Fe²⁺ oxidizing microorganisms are only found in acidic environments and are obligate acidophiles.

[0011] The best studied Fe²⁺ oxidizing bacterium is Acidithiobacillus ferrooxidans, an acidophilic chemolithothroph. The microbiological oxidation of Fe²⁺ is an important aspect of the development of acid pH’s in mines, and constitutes a serious ecological problem. However, this process can also be useful exploited when controlled. The sulfur containing ore pyrite (FeS₂) is at the start of this process. Pyrite is an insoluble crystalline structure that is abundant in coal- and mineral ores. It is produced by the following reaction:

\[ \text{S} + \text{Fe} \rightarrow \text{FeS} \]

[0012] Normally pyrite is shielded from contact with oxygen and not accessible for microorganisms. Upon exploitation of the mine, however, pyrite is brought into contact with air (oxygen) and microorganisms and oxidation will start. This oxidation relies on a combination of chemically and microbiologically catalyzed processes. Two electron acceptors can influence this process: O₂ and Fe³⁺ ions. The latter will only be present in significant amounts in acidic conditions (pH<2.5). First a slow chemical process with O₂ as electron acceptor will initiate the oxidation of pyrite:

\[ \text{FeS}_2 + 7/2 \text{O}_2 + \text{H}_2 \text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2\text{H}^+ \]

[0013] This reaction acidifies the environment and the Fe²⁺ will be formed is rather stable. In such an environment Acidithiobacillus ferrooxidans will be able to grow rapidly. Upon further acidification Ferroplasma will also develop and further acidify. As a consequence of the microbial activity (energy producing reaction):

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

[0014] This Fe³⁺ that remains soluble at low pH reacts spontaneously with the pyrite:

\[ \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \]

[0015] The produced Fe²⁺ can again be used by the microorganisms and thus a cascade reaction will be initiated.

[0016] In the industrial microbial leaching process, low grade ore is dumped in a large pile (the leach dump) and a dilute sulfuric acid solution (pH 2) is percolated down through the pile. The liquid coming out at the bottom of the pile, rich in the mineral is collected and transported to a precipitation plant where the metal is precipitated and purified. The liquid is then pumped back to the top of the pile and the cycle is repeated.

[0017] Acidithiobacillus ferrooxidans is able to oxidize the Cu²⁺ in chalcocite (Cu₉S₈) to Cu³⁺, thus removing some of the copper in the soluble form, Cu²⁺, and forming the mineral
covellite (CuS). This oxidation of Cu⁺ to Cu²⁺ is an energy yielding reaction (such as the oxidation of Fe²⁺ to Fe³⁺). Covellite can then be oxidized, releasing sulfate and soluble Cu²⁺ as products.

[0018] A second mechanism, and probably the most important in most mining operations, involves chemical oxidation of the copper ore with ferric (Fe³⁺) ions formed by the microbial oxidation of ferrous ions (derived from the oxidation of pyrite). Three possible reactions for the oxidation of copper ore are:

\[
\begin{align*}
\text{Cu}_2\text{S}_4 + 17\text{O}_2 + 2\text{H}^+ & \rightarrow \text{Cu}_4\text{S}_4\text{O}_{12} + 4\text{H}_2\text{O} \\
\text{Cu}_2\text{O} + 2\text{O}_2 & \rightarrow \text{Cu}_2\text{O}_2 \quad \text{or} \quad \text{CuO} + \text{O}_2 & \rightarrow \text{CuO}_2 \\
\text{Cu}_2\text{Fe}_4\text{S}_8 + 11\text{H}_2\text{O} & \rightarrow \text{Cu}_4\text{S}_4\text{O}_{12} + 8\text{Fe}^2+ + 8\text{SO}_4^{2-} + 8\text{H}^+ 
\end{align*}
\]

[0019] The copper metal is the recovered by using Fe⁰ from steel cans:

\[\text{Fe}^0 + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu}^{0}\]

[0020] The temperature inside the leach dump often rises spontaneously as a result of microbial activities. Thus, thermophilic iron-oxidizing chemolithophiles such as thermophilic Acidithiobacillus species and Leptospirillum and at even higher temperatures the thermosophilic archaeon Sulfolobus (Metallosphaera sedula) may become important in the leaching process above 40°C. Similarly to copper, Acidithiobacillus ferrooxidans can oxidize U⁴⁺ to U⁶⁺ with O₂ as electron acceptor. However, it is likely that the uranium leaching process depends more on the chemical oxidation of uranium by Fe³⁺, with At. ferrooxidans contributing mainly through the reoxidation of Fe²⁺ to Fe³⁺ as described above.

\[\text{UO}_2\text{Fe}^2\text{(SO}_4\text{)}_2 \rightarrow \text{UO}_2\text{SO}_4 + 2\text{Fe}^3\text{SO}_4\]

[0021] Gold is frequently found in nature associated with minerals containing arsenic and pyrite. In the microbial leaching process At. ferrooxidans and relatives are able to attack and solubilize the arsenopyrite minerals, and in the process, releasing the trapped gold (Au):

\[2\text{FeAsS(Au)} + 7\text{O}_2 + 2\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow 2\text{Fe}^3\text{SO}_4 + 2\text{H}_2\text{O} + \text{Au}
\]

[0022] According to Rawlings, “Heavy Metal Mining Using Microbes,” Annu. Rev. Microbiol. 2002, 56:65-91, at pages 69-71, certain microorganisms, such as Acidithiobacillus and At. Thiobacillus are unable to oxidize ferrous iron and are therefore restricted to using reduced sulfur compounds as an electron donor. At. Thiobacillus is mesophilic and has a limit for growth of about 35°C, but is more acid tolerant than At. Ferrooxidans (pH 0.5-5.5).

[0023] At. Caldis is similar to At. Thiobacillus with an ability to oxidize reduced sulfur compounds, but not ferrous iron, and its ability to grow at very low pH.

[0024] Leptospirillum is similar to Acidithiobacillus in that they are highly acid-tolerant (optimum pH ~1.5-1.8). They are only capable of using ferrous iron as an electron donor. Leptospirillum ferrooxidans are involved in biooxidation processes, usually in combination with a sulfur-oxidizing bacterium such as At. Caldis or At. Thiobacillus.

[0025] According to Briere, “Microbial Mining”, Scientific American, 247, 42-50, 1982, “The bacteria involved in the leaching of metals from ores are among the most remarkable life forms known. The microorganisms are said to be chemolithotrophic (‘rock-eating’); they obtain energy from the oxidation of inorganic substances. Many of them are also autotrophic; that is, they capture carbon for the synthesis of cellular components not from organic nutrients but from carbon dioxide in the atmosphere. The leaching bacteria live in environments that would be quite inhospitable to other organisms; for example, the concentration of sulfuric acid and of soluble metals is often very high. Some thermophilic, or heat-loving, species require temperatures above 50 degrees Celsius (122 degrees Fahrenheit), and a few strains have been found at temperatures near the boiling point of water.

[0026] For many years the only microorganism thought to be important in the leaching of metals from ores was the rod-shaped bacterium Thiobacillus ferrooxidans. This microorganism was discovered in the acidic water draining coal mines. It was not until 1957 that a correlation was realized between the presence of the bacterium and the dissolution of metals in copper-leaching operations. Since then a great deal of information has been amassed on T. ferrooxidans and on its vital role in the leaching of metals.

[0027] T. ferrooxidans is acidophilic, or acid loving; it tends to live in environments such as hot springs, volcanic fissures and sulfide ore deposits that have a high concentration of sulfuric acid. It is also moderately thermophilic, thriving in the temperature range between 20 and 35 degrees C. The bacterium gets energy for growth from the oxidation of either iron or sulfur. The iron must be in the ferrous, or bivalent, form (Fe²⁺), and it is converted by the action of the bacterium into the ferric, or trivalent, form (Fe³⁺). Several forms of sulfur can be attacked. They include both soluble and insoluble sulfides (compounds containing the bivalent sulfur ion S²⁻), elemental sulfur and soluble compounds that incorporate either the thiosulfate ion (S₄O₆²⁻) or the tetrathionate ion (S₈S₇O₂₆⁻). In each case the product of the transformation is a substance in which the sulfur atom has fewer valence electrons, culminating in the formation of the sulfate ion (SO₄²⁻). T. ferrooxidans obtains carbon autotrophically from atmospheric carbon dioxide.

[0028] Although T. ferrooxidans is essential to the bacterial leaching of metals, it is by no means the only microorganism with an important role in the process. Among the other microorganisms taking part is T. thiiodism, a rod-shaped bacterium not unlike T. ferrooxidans that grows on elemental sulfur and some soluble sulfur compounds. Studies by Donovan P. Kelly and his associates at the University of Warwick have confirmed the importance of mixed cultures of bacteria in the extraction of metals from ores. T. ferrooxidans and T. thiiodism combined, for example, are more effective in leaching certain ores than either organism is alone. Similarly, the combination of Leptospirillum ferrooxidans and T. organoporus can degrade pyrite (FeS₂) and chalcocite (CuFeS₂), a feat neither species can accomplish alone.

[0029] In acidic environments supporting leaching bacteria one can often isolate a number of heterotrophic microorganisms: bacteria and fungi that scavenge the small amounts of organic matter present in these environments or that survive on the organic by-products of other organisms’ autotrophic metabolism. The role of the heterotrophic microorganisms in the leaching process is largely undetermined. Thiobacilli that attack some sulfide minerals and certain soluble sulfur compounds under neutral conditions (that is, neither acidic nor alkaline) are often found in sulfide ore deposits and in other habitats where sulfur is available. Thiobacilli of this type may be responsible for the initial increase in acidity that establishes an environment conducive to the growth of the more acidophilic leaching bacteria.
At temperatures between 60 and 75 degrees C. and under neutral conditions the filamentous bacterium *Thermothrix thiopara* oxidizes sulfhydryl ions (HS⁻), sulfite ions (SO₃²⁻), thiosulfate ions and elemental sulfur to form sulfate ions. There is increasing evidence of the widespread existence of *Thermothrix* species and similar filamentous, sulfur-oxidizing bacteria in thermal springs and near volcanic fissures. Few leaching sites have been tested for the presence of these bacteria. Their existence in sulfur-bearing springs, however, suggests they could colonize sulfidic ores and thereby prepare such environments for the more acidophilic species.

Among the most interesting of the leaching microorganisms are the moderately thermophilic and acidophilic bacteria designated TH (for thermophilic and *Thiobacillus*-like). Studies by James A. Brierley of the New Mexico Institute of Mining and Technology and Norman W. Le Roux of the Warren Spring Laboratory in Britain have established that strains of TH bacteria grow on ferrous iron or on minerals such as pyrite, chalcopyrite, covellite (CuS) and pentlandite ([Fe,Ni]₃S₄). An organic supplement to the mineral diet is apparently required by these organisms for growth. Although the TH strains are similar in form to the rod-shaped thiobacilli, their distinctive temperature domain near 50 degrees C., their very different biochemical activities and their inability to metabolize carbon dioxide rule out a close relation with *T. ferrooxidans*. TH strains have been isolated from acidic hot springs and from leaching environments where copper sulfide is present. The role of the organisms in extractive processes has not been fully elucidated; from an industrial point of view, however, they must be considered potentially important to the development of any high-temperature biomining process.

The most robust of the leaching microorganisms are the extremely thermophilic and acidophilic species of the genus *Sulfobulbus*. These bacteria flourish in acidic hot springs and volcanic fissures at temperatures that can exceed 60 degrees C. Some strains of *Sulfobulbus* have been observed in springs at temperatures near the boiling point of water. The cell wall of the *Sulfobulbus* bacteria has a different structure from that of most bacteria. Microorganisms of this type are thought to belong to the Archaeabacteria, a group of unusual bacteria proposed as a separate kingdom of life forms (see "Archaeabacteria," by Carl R. Woese, SCIENTIFIC AMERICAN, June, 1981).

*Sulfobulbus acidocaldarius* and *S. brierleyi* oxidize sulfur and iron for energy, relying on either carbon dioxide or simple organic compounds for carbon. Ordinarily oxygen is required by *Sulfobulbus*, as in other aerobic organisms, the oxygen serves as the ultimate acceptor of the electrons removed in the process of chemical oxidation. *Sulfobulbus* bacteria can also grow anaerobically, however. It has been demonstrated that molybdenum (Mo⁶⁺) and ferric iron can serve as electron acceptors in the absence of air. Minerals that resist most microorganisms, such as chalcopyrite and molybdenite (MoS₂), are readily attacked by *Sulfobulbus*, and the resulting soluble metals are not toxic to the organism. Molybdenum, which is extremely toxic even to the metal-tolerant thiothiobacilli, is readily endured by *S. brierleyi* in concentrations as high as 750 milligrams per liter. *Sulfobulbus* has not been isolated from commercial leaching operations, but laboratory studies confirm the ability of the organism to proliferate in such environments. The potential of *Sulfobulbus* species to leach metals from ores is only now being recognized, because of the extraordinary ability of these organisms to attack resistant mineral structures, however, they are certain to be among the leaching bacteria that will be successfully exploited in the future.

How exactly does the growth of the leaching bacteria result in the extraction of metals from rocks? By conventional bacterial leaching has been divided into two approaches: direct and indirect. Direct bacterial leaching entails an enzymatic attack by the bacteria on components of the mineral that are susceptible to oxidation. In the process of obtaining energy from the inorganic material, the bacteria cause electrons to be transferred from iron or sulfur to oxygen. In many cases the more oxidized product is more soluble. It should be noted that the inorganic ions never enter the bacterial cell; the electrons released by the oxidation reaction are transported through a protein system in the cell membrane and thence (in aerobic organisms) to oxygen atoms, forming water. The transferred electrons give up energy, which is coupled to the formation of adenosine triphosphate (ATP), the energy currency of the cell.

Indirect leaching, in contrast, does not proceed through a frontal attack, by the bacteria on the atomic structure of the mineral. Instead the bacteria generate ferric iron by oxidizing soluble, ferrous iron; ferric iron in turn is a powerful oxidizing agent that reacts with other metals, transforming them into the soluble, oxidized form in a sulfuric acid solution. In this reaction ferrous iron is again produced and is rapidly reoxidized by the bacteria. Indirect leaching is usually referred to as bacterially assisted leaching. In an acidic solution without the bacteria ferrous iron is stable, and leaching mediated by ferric iron would be slow. *T. ferrooxidans* can accelerate such an oxidation reaction by a factor of more than a million.

Direct and indirect leaching by bacteria is difficult to differentiate quantitatively because most minerals include some iron. Even if leaching were to begin with the direct process exclusively, the iron would be released from the mineral and would establish an indirect leaching cycle. Direct leaching by thiothiobacilli has been demonstrated in the laboratory with iron-free synthetic metal sulfides.

In practice the leaching of metals is far more complex than the above analysis might suggest; there are numerous processes in addition to direct enzymatic oxidation and bacterial generation of ferric iron. Some chemical reactions between ferric iron and metal-sulfide minerals result in the formation of secondary minerals and elemental sulfur, which can "blind," or inactivate, the reactive surfaces. When sulfur is formed, *T. ferrooxidans* plays an indispensable role in oxidizing the sulfur to sulfuric acid, thus exposing the metal for further leaching.

The control of acidity is of utmost importance in leaching, because an acidic environment must be maintained in order to keep ferric iron and other metals in solution. Acidity is controlled by the oxidation of iron, sulfur and metal sulfides, by the dissolution of carbonate ions and by the decomposition of ferric iron through reaction with water. The last reaction promotes leaching by generating hydrogen ions (which make the solution more acidic), but it may also be detrimental because precipitates of basic ferric sulfates may inactivate the surfaces of metal-sulfide minerals and in some cases may even prevent the flow of the leaching solution. The chemical and biological processes are part of a complex system whose functioning depends on elements of hydrology, geology, physics and engineering.
The method described below enhances microbial mining by simultaneously controlling acidity, while adding sulfites, bisulfites, and free SO2 to feed microorganisms.

SUMMARY OF THE INVENTION

The method comprises chemically treating drainage and leaching waters with sulfur dioxide to acid leach soluble metals from ores and concentrates into solution, while simultaneously feeding leaching bacteria to break down and dissolve insoluble metal sulfides into solution. The sulfuric acid, (H2SO4), dissociates to produce H+ , bi-sulfite (HSO3-), sulfite (SO32-), and free SO2 species in solution, all hereinafter referred to as sulfuric acid, to provide electron donor sulfur nutrients, while lowering the pH of the leaching waters to that favorable for the growth and leaching bacteria.

The method is employed usually in two main types of processes—the irrigation-type and the stirred tank-type processes. The irrigation processes involve percolation of sulfuric acid leaching solutions through the crushed ore or concentrates that have been stacked in columns, heaps or dumps. In another variation irrigation of an ore body in situ may be employed if porous enough and structure is included to gather the leachate.

In the stirred tank-type process continuously stirred tank reactors are employed, usually with aeration. No attempt is made to maintain sterility of the inoculated ores and concentrates, as the aim of both processes is to foster the growth of those microorganisms most effective to decompose the minerals into solution.

This method is particularly suited for bioleaching of copper. Copper dumps of run-of-mine ore piles are subjected to cycles of preconditioning, irrigation, rest, conditioning, and washing, after extending for over a year. Dump microorganisms catalyze the chemical reactions resulting in insoluble copper sulfides being converted to soluble copper sulfate leachate. The pregnant leach solutions are then recovered via conventional solvent extraction or electro winning. Air or other oxidizing agents, such as Fenton reagent, hydrogen peroxide, or ozone may be added to promote microorganism growth along with inorganic nutrients such as ammonium sulfate, potassium hypophosphates, and other phosphates and nitrogen compounds. Conditioned pre-treated wastewaters containing these supplemental nutrients may be acidified with sufficient SO2 for acid leaching in one preferred embodiment. The sulfur dioxide produces bi-sulfite (HSO3-), and sulfite (SO32-) compounds, which act as a reducing agent to donate electrons to aid in microorganism oxidation.

Sulfur dioxide has lone electron pairs, allowing it to act as a Lewis base. Additionally it can act as a Lewis acid. The dissolved SO3 gaseous content varies with temperature. For example, the maximum grams/liter of dissolved sulfur dioxide in water at 20 degrees C. is 106.4 gm/L. It is 55.4 gm/L at 40 degrees C. It is 32.5 gm/L at 60 degrees, and 21.3 gm/L at 80 degrees C. Consequently, sulfuric acid treated waters with free SO2/sulfuric acid/bi-sulfite/sulfite present in solution at a low pH forms a complex liquid/gas/solid phase chemistry system where reactions are difficult to describe and quantify exactly.

The pH selected for biomining of ores depends upon the nature of the microbe present in the ores and concentrates. Certain microbes eat mining and other waste releasing heavy metals. Nowadays the microbial ore leaching with so-called "lean ores" represents more than 10% of the total production of copper in the USA alone. The biotechnique of extraction for copper from copper ore uses Thiobacillus ferrooxidans bacteria. The bacteria change the copper in the ore into a form that can be readily dissolved by the acid. The dissolved copper is then recovered and subjected to electrolysis to produce unprocessed metal. Bioleaching is one of several applications within bihydrometallurgy and several methods are used to recover copper, zinc, lead, arsenic, antimony, nickel, molybdenum, gold, and cobalt. To encourage the growth of Acidithiobacillus ferrooxidans, the pH is adjusted between 1.5 and 4.5 in basal salt medium so that the bacteria derives its biosynthetic requirements by autotrophy using carbon from atmospheric carbon dioxide.

Most species of Thiobacilli are acid-tolerant, some even extremely acid-tolerant and acidophilic. Some grow best at pH 2 and may grow at pH 1 or even at pH 0.5. Most species are tolerant against heavy metal toxicity. Thiobacilli are chemolithoautotrophs that means CO2 may be the only source of carbon and they derive their energy from a chemical transformation of inorganic matter. All Thiobacilli oxidize sulfur or sulfur compounds to sulfate or sulfuric acid.

Several species of fungi can be used for bioleaching. Fungi can be grown on many different substrates, such as electronic scrap, catalytic converters, and fly ash from municipal waste incineration. Experiments have shown that two fungal strains (Aspergillus niger, Penicillium simplicissimus) were able to mobilize Cu and Sn by 65%, and Al, Ni, Pb, and Zn by more than 95%. Aspergillus niger can produce some organic acids such as citric acid. This form of leaching does not rely on microbial oxidation of metal, but rather uses microbial metabolism as source of acids which directly dissolve the metal.

To promote the growth of these species, the pH of the sulfuric acid containing nutrients is thus set to promote their growth for acid leaching or secondary polishing to further remove arsenic, selenium, mercury, and nitrates.

Biomining then proceeds according to the methods discussed in Rawlings, "Heavy Metal Mining Using Microbes," at pages 76-85, cited above.

Irrigation-Type Processes

The metal recovered in by far the greatest quantities using bioleaching is copper. Recent estimates of the total quantity of copper ore treated by biothermally assisted processes are difficult to obtain. However, in 1999 it was reported that the copper-heap bioleaching plants built since 1991 and remaining in operation produced in excess of 30,000 tonnes of ore per annum (7, 8). All current commercial processes for copper recovery are of the dump, heap, or in situ irrigation type, although stirred tank processes for the extraction of copper from chalcopyrite are in an advanced phase of development.

Dump leaching was initiated in the late 1960s, and one of the best-known dump leaching operations is located at the Kennecott Copper mine in Bingham Canyon, Utah. The largest of the dumps at this site consists of four billion tonnes of low-grade copper ore waste. An example of a smaller, more recent, and deliberately constructed dump operation is the Bala Ley plant of the Chuquicamata division of Codelco in Chile (86). Dumps consist of run-of-mine ore, which may be piled 350 m high. The dumps are subjected to cycles of preconditioning, irrigation, rest, conditioning, and washing, each of which may extend for over a year. Irrigation is carried out with raffinate, an iron- and sulfate-rich recycled wastewater from which the copper has been removed. Microorganisms growing in the dump catalyze the chemical reactions
(see below) that result in insoluble copper sulfides being converted to soluble copper sulfate. The copper sulfate-containing pregnant leach solution is removed from the bottom of the dump, and the modern method for copper metal recovery is by a process of solvent extraction and electro winning.

[0053] Heap leaching of copper is similar to dump leaching except that the process is designed to be more efficient. Ore is crushed, acidified with sulfuric acid, and agglomerated in rolling drums to bind fine particles to coarse particles. The agglomerated ore is stacked 2–10 m high on irrigation pads lined with high-density polyethylene to avoid the loss of solution. Aeration pipes may be included during construction to permit forced aeration and speed up the bioloeaching process. Although inoculation of heaps with bacteria has been considered, bioloeaching bacteria are ubiquitous and it is not clear to what extent inoculation speeds up the process. Inorganic nutrients such as (NH₄)₂SO₄ and KHPo₄ are frequently added to the raffinate prior to irrigation through drip lines placed on the surface of the heap. The increased efficiency that results from the careful construction.

[0054] Mining Using Microbes

[0055] Heap leaching of copper-containing ore. The ore is crushed, agglomerated, and stacked onto plastic-lined pads and irrigated with recycled leach liquor. The bacteria growing on the ore oxidize ferrous iron to ferric iron, which solubilizes the copper, and the pregnant copper-containing solution is recovered from the heap. The copper is concentrated through a solvent extraction process followed by recovery through electro winning, and the spent leach liquor is recycled to the heap.

[0056] . . . and operation of a heap reactor results in the heap bioloeaching processes being completed in a period of months rather than years. An example of a large, modern, heap bioloeaching operation is the plant commissioned in 1994 at Quabraloa Blanca in northern Chile that produces 75,000 tonnes of copper per annum from chalococoe ore containing 1.3% copper (86).

[0057] Heap reactors have also been used for refractory gold-bearing ores. In this case the heap of agglomerated ore is initially irrigated with an acid-ferric iron solution containing bacteria and thereafter with recycled heap reactor effluent. The gold remains in the heap, and after a sufficient amount of ore decomposition has taken place the heap is washed to remove acid and excess cyanide-consuming compounds. The heap is taken up, regglomerated with lime rather than acid, restacked on lined pads, and the gold extracted chemically with a dilute solution of cyanide. Newmont Gold Company has built a demonstration plant using this technology in Carlin, Nev., and the cost of heap bioloeaching and gold extraction is in the range of US$4-6 per tonne of ore processed. This process allows low-grade ore with as little as 1 g Aper tonne to be processed, which would otherwise have been considered as waste. A variation of this process has been developed by GeoBiotics Inc., in which a thin layer of gold-bearing sulfide ore concentrate is coated onto a support rock and stacked in heaps. The thin coating facilitates rapid bioloeoxidation of the ore concentrate, and the heap is used as a cheaper form of reactor than the stirred tanks in which this type of concentrate is usually treated.

[0058] There are several examples of bioloeaching operations that use irrigation-type processes and extract metal in situ. One example is the copper recovery process at San Manuel near Tucson, Ariz., and another, Gunpowder’s Mun moth mine, Queens land, Australia. At San Manuel an array of injection wells is used to introduce acidified leaching solution into the mineral deposit. The leach solution gravitates through the ore and collects in abandoned mine workings or in a centrally placed production well from which it is pumped to the surface. Suitable geology is required for in situ processes to work, and fluid loss at San Manuel is about 13.5%. Although no longer in operation, in situ bioloeaching for the recovery of uranium took place in several mines within the Elliot Lake district of northern Ontario. Typically, underground ore was fractured and a bulkhead built across the opening of a stope. The ore behind the bulkhead was flooded with acid mine drainage liquor and aerated by passing compressed air through perforated pipes. After a period of up to 3 weeks, the liquor was drained and pumped to the surface, where the uranium was extracted. This cycle was repeated until the quantity of uranium fell to a level that was no longer economically viable. In 1988 >>>300 tonnes of uranium were recovered at the Denison mine using in situ bioloeaching, and it was estimated that this process made an additional 4 £ 106 tonnes of ore available that could not have been processed by conventional technologies.

[0059] Microbiology of Irrigation-Type Processes

[0060] Microbes present in copper heap-leach operations have been studied more extensively than most other irrigation-type processes. Espejo and coworkers have used the species-specific sizes of TECR-amplified 16S-23S rRNA intergenic spacer regions to investigate the microbes in heaps or columns in which Chilean chalococoe/covellite ores are leached. L. ferrooxidans and At. thioboxidans were found to dominate the process, and no At. ferrooxidans was detected. If ferrous iron solution (5 g/liter) was added to the leach solution, 16S-23S rRNA spacer regions corresponding to At. ferrooxidans dominated the population, but recovery of copper was enhanced by no more than 5% (68). In a related study agglomerated copper sulfide ore was inoculated and leached by irrigation with recycled leaching solution that contained high concentrations of sulfate ions (120 g/liter). The bacteria were identified by comparing the sizes of 16S-23S 16S rRNA spacer regions and heteroduplex formation with known species. A homogenous population of At. thioboxidans and heterogeneous populations of At. ferrooxidans and L. ferro oxidans were found. In a similar study organisms capable of leaching copper sulfide ores in conditions of high acidity (pH 0.7) had 16S-23S rRNA spacers of a size consistent with those of L. ferrooxidans and At. thioboxidans, but no spacers of a size corresponding to At. ferrooxidans were detected.

[0061] Stirred Tank Processes

[0062] The use of highly aerated, stirred tank bioreactors provides a step up in the rate and efficiency of mineral biooxidation processes. Because these reactors are expensive to construct and operate, their use is restricted to high-value ores and concentrates. The bioreactors are typically arranged in series and are operated in continuous-flow mode, with feed being added to the first tank and overflowing from tank to tank until biooxidation of the mineral concentrate is sufficiently complete.

[0063] Mining Using Microbes

[0064] . . . Finely milled flotation concentrate is added to inorganic nutrients and water in a make-up tank. The mixture is passed through a series of vigorously aerated biooxidation tanks. The microorganisms decompose the arsenopyrite, making the gold accessible to cyanide. Duplication (or doubling in volume) of the number of primary aeration tanks is to
increase the hydraulic retention time above that of the cell doubling time to ensure that microbial cell wash-out does not occur during the mineral treatment process. The concentrate, which after pretreatment still contains the gold, is recovered in a thickening tank and sent to the gold recovery process. The bioreactor tanks in the first stage are usually arranged in parallel to provide sufficient retention time for the microbial cell numbers to reach high steady-state levels without being washed out. The feed is mineral concentrate suspended in water to which small quantities of fertilizer-grade (NH₄)₂SO₄ and KI·I₂PO₄ have been added. Mineral biooxidation is an exothermic process, and the bioreactors have to be cooled to remove excess heat. Large volumes of air are blown through each bioreactor, and a large agitator ensures that the solids remain in even suspension and are carried over into the next tank.

[0066] Most of the commercial operations that use stirred tank bioreactors are pretreatment processes for the recovery of gold from calcitrant arsenopyrite concentrates. Calcitrant ores are those in which the gold is finely divided in a mixture of pyrite/arsenopyrite and cannot easily be solubilized by the usual process of cyanidation. Treatment of the ores to decompose the arsenopyrite is required to allow the cyanide to make contact with the gold. Because the gold is contained in a relatively minor fraction, the ore is crushed and a gold-containing concentrate is prepared by flotation. The finely ground gold-bearing mineral makes up 18%-20% of the feed volume and is fed at a rate that permits a total residence time of about four days in the series of stirred tanks. The microbes that oxidize the mineral release ferric iron and sulphate, which acidifies the environment, and the solution is typically maintained at pH 1.5-1.6.

[0067] The potential for using microbes for the treatment of these minerals was recognized in the 1980s by the late Eric Liversay-Goldblatt. Most of the biooxidation plants were built by Genecor and operate at 40°C, but the plant at the Youanmi mine in Western Australia was designed by Bactech and operated at 50°C. As may be expected, the consortia of microbes present in the two processes differ substantially, but both mixtures of organisms have proved to be robust and have successfully treated gold-bearing concentrate for extended periods of time. Once the required amount of mineral biooxidation has taken place, the recovered mineral is washed, separated from the liquid fraction in thickeners, neutralized, and the gold extracted with cyanide. The first commercial operation to use stirred tank biooxidation of gold-containing concentrates was commissioned in 1986 at the Fairview mine in Barberton, South Africa. Since then at least six similar plants have been built in other countries, including Australia, Brazil, Ghana, and Peru.

[0068] . . . The plant at Sansu, Ghana, was commissioned in 1994, expanded in 1995, and is probably the largest fermentation process in the world. It consists of 24 tanks of 1,000,000 liters each, processes 1000 tonnes of gold concentrate per day, and earns about half of Ghana’s foreign exchange.

[0069] Stirred tank processes for other ores and concentrates have also been developed. These include the full-scale cobalt biotreatment plant initiated by BRGM of France at Kasese, Uganda, and the pilot-scale BioNIC process for leaching of nickel by Billiton Process Research in South Africa. New stirred tank processes to recover copper from chalcopyrite ore that operate at temperatures in excess of 75°C are undergoing trials. These high temperatures are required because chalcopyrite is more stable than ores like chalcocite, and decomposition of chalcopyrite is too slow at 40°C or 50°C.

[0070] Microbiology of Stirred Tank Processes

[0071] Organisms present in continuous-flow, high-rate, stirred biooxidation tanks used to pretreat gold-bearing arsenopyrite concentrates have been studied in most detail. In a study of the bacteria in the biooxidation plant at the Fairview mine, restriction enzyme patterns of 16S rDNA that were amplified from known cultures of At. ferrooxidans, At. thiooxidans, and Leptospirillum were compared with those from total DNA isolated from the biooxidation tanks. There was no restriction pattern corresponding to At. ferrooxidans, and the population was reported to be dominated by Leptospirillum and At. thiooxidans. Subsequent studies have shown that the restriction enzyme patterns of At. thiooxidans and At. caldus are similar and that the bacteria were almost certainly At. caldus.

[0072] An examination of the bacteria in commercial biooxidation tanks operating at 40°C, using an immunofluorescent-antibody microscope count detection technique, differed from the PCR-based work in that At. ferrooxidans cells were detected in most samples. At. ferrooxidans cells were, however, in the minority. The proportions of bacterial types in continuous-flow biooxidation tanks from Sao Bento (Brazil) and Fairview were 48%-57% L. ferrooxidans, 26%-34% At. thiooxidans, and 10%-17% At. ferrooxidans. The proportions varied within the ranges given, depending on whether the sample had been treated with Triton X to release attached bacteria and from which tank in the series of biooxidation tanks the sample was derived. Using the immunofluorescent technique, a slightly different distribution of bacteria was found in pilot-scale bioreactors treating a nickel pentlandite-pyrrhotite ore. In this case numbers of At. ferrooxidans were higher, although they never exceeded about 33% of the total population.

[0073] Published information on the dominant bacteria in processes operating at 50°C is limited. The fatty acid methyl ester composition was used in an attempt to identify the attached and unattached microbes in a commercial continuous-flow, stirred tank process used to treat an arsenopyrite concentrate operating at 50°C. Although the species of bacteria could not be identified, bacteria with a fatty acid profile related to Thiobacillus species were found to dominate the culture. A small quantity of fatty acids with a profile related to Sh. thermaosulfidooxidans was identified in a batch reactor inoculated with the commercial culture. No evidence of Leptospirillum ferrooxidans was found using fatty acid composition or by visualization using a microscope.

[0074] Mechanism of Biooxidation

[0075] In 1970 it was reported that At. ferrooxidans increased the rate of ferrous iron oxidation by half a million to a million times, compared with the abiotic chemical oxidation of ferrous iron by dissolved oxygen. The ferric iron produced as a result was able to chemically oxidize sulfide minerals. There has been a long-standing debate concerning whether the microbially assisted biooxidation of minerals is by a so-called direct or indirect mechanism. Some of the disagreement appears to have been caused by a lack of clarity as to what is meant by direct and indirect. There is general agreement as to what is meant by the indirect mechanism, namely the chemical attack by ferric iron or protons on a mineral sulfide that results in the dissolution of the mineral and the formation of ferrous iron and various forms of sulfur.
oxidizing microbes use the ferrous iron as an electron donor, reoxidizing it to ferric iron, thereby regenerating the reactant. If the role of the microbes is nothing more than their ability to regenerate ferric iron and protons . . ., then the efficiency of biooxidation should be independent of whether the microbes are in contact with the mineral or not. What is understood by the direct mechanism is not always unequivocal. In a loose sense it has meant that attachment of the microbes to the ore enhances the rate of mineral dissolution. In a more strict sense, direct attack is viewed as a process by which components within the bacterial membrane interact directly with the metal and sulfide moieties of the mineral by using an enzymatic type of mechanism.

**[0076]** A number of scientists from a variety of disciplines have addressed this problem in recent years. It is not possible to cover fully the points made by each contributor. Schematic diagram illustrating the proposed mechanisms of pyrite biooxidation, to this debate. However, there is a growing consensus view on many aspects of the mechanism of bioleaching. An understanding of metal sulfide dissolution is complicated because different metal sulfides have different types of crystal structure, and it has been observed that the oxidation of different metal sulfides proceeds via different intermediates. In addition, as is discussed below, different iron-oxidizing bacteria may use different bond-breaking strategies. For example, the ability of *At. ferroxidans* to oxidize iron is subject to ferric iron inhibition and is inhibited at high-redox potentials, whereas the ability of *L. ferroxidans* to oxidize iron is far less inhibited by ferric iron and continues at high-redox potentials. Among the most helpful contributions to an understanding of the mechanism of mineral biooxidation are those from the laboratories of Wolfgang Sand, Frank Grundwell, and Helmut Tributsch. Bacteria like *At. ferroxidans*, or *L. ferroxidans* have a strong affinity for mineral surfaces like pyrite, to which they rapidly attach. In the case of *At. ferroxidans* arpinocystatin appears to play an important role, especially during the early stages of attachment. Sand and Tributsch and their coworkers have stressed the role played by the exopolysaccharide (EPS) layer produced by *At. ferroxidans* and *L. ferroxidans* when attached to a mineral. The EPS layer attaches the bacteria to a mineral surface and forms the matrix in which the cells divide and eventually form a biofilm. Iron species within the EPS layer have been estimated to be >53 g/liter, a concentration that can be maintained only by the formation of complexes, possibly with gluconic acid. The iron-impregnated EPS layer serves as a reaction space in which the high concentration of ferric iron mounts chemical attack on the valence bonds of the mineral. In the process the ferric iron is reduced to ferrous, which is reoxidized to ferric by the iron-oxidizing microbes:

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

**[0077]** This microbially mediated reoxidation of ferrous iron can result in a localized increase in pH within the EPS near the surface of the mineral. Researchers from the Grundwell laboratory have evidence to suggest that it is this local rise in pH that assists in mineral dissolution.

**[0078]** Sand and coworkers have observed that the oxidation of different metal sulfides proceeds via different intermediates. Therefore, the dissolution reaction is not identical for all metal sulfides. They have proposed a thiosulfate mechanism for the oxidation of acid-insoluble metal sulfides such as pyrite (*FeS_2*), molybdenite (*MoS_2*), and tungstenite (*WS_2*), and a polysulfide mechanism for acid-soluble metal sulfides such as sphalerite (*ZnS*), chalcopyrite (*CuFeS_2*), and galena (*PbS*).

**[0079]** In the thiosulfate mechanism, solubilization is through a ferric iron attack on the acid-insoluble metal sulfides, with thiosulfate being the main intermediate and sulfate the main end product. Using pyrite as an example, the reactions proposed by Schippers & Sand are:

\[ \text{FeS}_2 + 5\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow 7\text{Fe}^{2+} + 2\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ \]

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

**[0080]** In the case of the polysulfide mechanism, solubilization of the acid-soluble metal sulfide is through a combination of ferric ions and protons, with elemental sulfur as the main intermediate. This elemental sulfur is relatively stable but may be oxidized to sulfate by sulfur-oxidizing bacteria. *ZnS* is an example of an acid soluble mineral:

\[ \text{MS} + \text{Fe}^{3+} + \text{H}^+ \rightarrow \text{M}^{2+} + \text{H}_2\text{S} + \text{Fe}^{2+} (\text{n} = 2) \]

\[ 0.5\text{H}_2\text{S}_4 + \text{Fe}^{3+} + 4 + 0.125\text{S}_8 \rightarrow \text{Fe}^{2+} + 2\text{H}^+ \]

\[ 0.125\text{S}_8 + 1.5\text{O}_2 + \text{H}_2\text{O} \rightarrow 0.8\text{SO}_4^{2-} + 2\text{H}^+ \]

**[0081]** As Schippers & Sand point out, this explains why strictly sulfur-oxidizing bacteria such as *A. thiocomanis* are able to leach some metal sulfides but not others.\(^2\) The role of the microorganisms in the solubilization of metal sulfides is, therefore, to provide sulfuric acid for a proton hydrolysis attack and to keep the iron in the oxidized ferric state for an oxidative attack on the mineral.

**[0082]** Tributsch has argued that the break-up of the pyrite crystal structure can be the result of one of five mechanisms: (a) reaction of protons with a sulfide to give S\(^{-}\) ions; (b) extraction of electrons from the sulfide valence band resulting in the release of metal ions and sulfur compounds (in the case of *At. ferroxidans*); (c) broken chemical bonds already present in the sulfide (p-type conduction), which leads to higher interfacial dissolution; (d) reaction with a polysulfide or metal complex-forming agent; or (e) electrochemical dissolution resulting from multiple electron extraction and depolarization of the pyrite, which occurs at high concentrations of ferric ions (in the case of iron-oxidizing bacteria like *L. ferroxidans*). Mechanisms (a), (b), and (c) are clearly equivalent to the indirect mechanism. However, Tributsch has argued that mechanisms in which a sulfur carrier may be involved (d) or those for which a high concentration of ferric iron is necessary (e) require contact (or close proximity) between the cell and the mineral surface. These mechanisms would not be as effective if they relied on carriers or chemicals in the bulk liquid. Holmes et al. have argued that the idea that an increase in ferric iron concentration at the surface of a mineral results in an increase in the rate of pyrite dissolution is not consistent with their observations of changes in the mixed potential of bacterial and chemically leached pyrite.

**[0083]** Tributsch and coworkers have shown that during the oxidation of pyrite the EPS layer of *At. ferroxidans* becomes loaded with colloidal sulfur and that much of this is released into the environment. The sulfur particles and globules released in this apparently wasteful process feed other sulfur-oxidizing bacteria in a cooperative leaching interaction. Undefined carrier molecules that contain reactive thiol groups provided by the amino acid cysteine greatly assist in pyrite dissolution. Indeed, these workers have shown that on its own cysteine rapidly oxidizes pyrite in the absence of oxygen or...
bacteria (80). Free-SH groups from the pyrite react with the sulphydryl group of cysteine. This thiol-disulphide reaction results in cysteine being consumed by the pyrite with the release of iron-sulfur species. The thiol-dependent mechanism alone is probably insufficient to oxidize pyrite at the rates observed. In the case of a strictly iron-oxidizing bacterium like L. ferrooxidans, electrochemical dissolution of pyrite owing to high concentrations of ferric iron results in small fragments of pyrite becoming visibly entrapped in the EPS layer. However, there appears to be much less, if any, colloidal sulfur present. The observation that the oxidation of ferrous iron is not inhibited by ferric iron in the case of L. ferrooxidans, as it is with At. ferrooxidans, is consistent with this proposed mechanism. Because what many understand by “direct leaching” implied direct contact of cell membrane components with the mineral, as opposed to only close proximity (in this model), the term “contact leaching” is preferred to direct leaching. Taking into account the views of most of the important contributors to the direct versus indirect leaching debate, regarding reaction kinetics, stoichiometry, and several other considerations and including a recent scanning electron microscope study of mineral surface leaching, a consensus view is that the mechanism of mineral solubilization is strictly sensu indirect (physicochemical). Tributsch and colleagues have presented a strong case that a close proximity between the cell and the mineral surface is required for a certain types of metal solubilization reactions to proceed efficiently. Bacterial attachment may speed up the rate of leaching owing to the proximity to the mineral surface of a high concentration of ferric iron complexed in the EPS, a localized rise in pH, or the proximity of thiol groups of cysteine-containing molecules produced by sulfur-oxidizing bacteria. However, in none of these processes is direct contact between the cell surface (membrane) and the mineral essential. In this sense they are not strictly direct mechanisms. In the absence of firm evidence for the need for direct mineral-cell membrane contact, the term contact leaching should be used to replace direct leaching because of the confusion around this latter term.

[0084] Mining Using Microbes

[0085] Heavy metals are acid leached from the ores via sulfuric acid addition into an aqueous fraction, which also provides sulfites, bisulfites, and SO₂ as promoters to promote bacterial growth for reducing metal sulfides into metal ions in a liquid fraction for metal recovery using any of the methods described above. The exact pH selected is dependent upon the type of microbes present. For example, if required by certain microbes, ferric ions may be added to promote the growth of iron-oxidizing bacterium Thiobacillus ferrooxidans, which uses ferric ions as electron acceptors for oxidation of sulfide. As these ore reducing bacterial communities are complex and vary based on the metals present, the sulfuric acid concentrations are adjusted to provide the pH required to encourage growth and speed the reactions producing metal ions in solution. These metal ions are then recovered and processed into metals.

[0086] For example, with pH adjustment forming metal hydroxides for filtration separation, different metals behave differently.

[0087] Generally, the oxides of metals are basic and the oxides of non-metals are acidic because of the following reaction:

\[
\text{Metal Oxide: } \text{Na}_2\text{O}(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{Na}^+(aq) + \text{OH}^-(aq)
\]

\[
\text{Non-metal Oxide: } \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{CO}_3(aq)
\]

\[
\rightarrow \text{HCO}_3^-(aq) + \text{H}^+(aq)
\]

[0088] However, some metals are amphoteric and can act as either acids or bases and include metals such as Al, Cr, and Zn. These amphoteric metals, as shown below, form different complexes at differing pHs, depending on the hydrogen and hydroxide concentrations.

[0089] With acid Al, Cr, Zn dissolve forming salts and releasing hydrogen gas

\[
2\text{Al}(s) + 6\text{H}^+(aq) \rightarrow 2\text{Al}^{3+}(aq) + 3\text{H}_2(g)
\]

\[
2\text{Cr}(s) + 6\text{H}^+(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 3\text{H}_2(g)
\]

\[
\text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)
\]

[0090] With bases they dissolve forming complex ions and hydrogen gas

\[
2\text{Al}(s) + 2\text{OH}^-(aq) + 6\text{H}_2\text{O}(l) \rightarrow 2[\text{Al(OH)}_3]^-(aq) + 3\text{H}_2(g)
\]

\[
2\text{Cr}(s) + 2\text{OH}^-(aq) + 6\text{H}_2\text{O}(l) \rightarrow 2[\text{Cr(OH)}_3]^-(aq) + 3\text{H}_2(g)
\]

\[
\text{Zn}(s) + 2\text{OH}^-(aq) + 2\text{H}_2\text{O}(l) \rightarrow [\text{Zn(OH)}_2]^2-(aq) + \text{H}_2(g)
\]

[0091] Their amphoteric metal hydroxides dissolve with acid forming a salt and water.

\[
\text{Al(OH)}_2(s) + 6\text{H}^+(aq) \rightarrow \text{Al}^{3+}(aq) + 3\text{H}_2\text{O}(l)
\]

\[
\text{Cr(OH)}_2(s) + 6\text{H}^+(aq) \rightarrow \text{Cr}^{3+}(aq) + 3\text{H}_2\text{O}(l)
\]

\[
\text{Zn(OH)}_2(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + 2\text{H}_2\text{O}(l)
\]

[0092] Their amphoteric metal hydroxides dissolve with a base forming complex ions

\[
\text{Al(OH)}_2(s) + \text{OH}^-(aq) \rightarrow [\text{Al(OH)}_3]^-(aq)
\]

\[
\text{Cr(OH)}_2(s) + \text{OH}^-(aq) \rightarrow [\text{Cr(OH)}_3]^-(aq)
\]

\[
\text{Zn(OH)}_2(s) + 2\text{OH}^-(aq) \rightarrow [\text{Zn(OH)}_2]^2-(aq)
\]

[0093] Their amphoteric metal oxides found in soils dissolve with sulfuric acid forming salts and water:

\[
\text{Al}_2\text{O}_3(s) + 6\text{H}^+(aq) \rightarrow 2\text{Al}^{3+}(aq) + 3\text{H}_2\text{O}(l)
\]

\[
\text{Cr}_2\text{O}_3(s) + 6\text{H}^+(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 3\text{H}_2\text{O}(l)
\]

\[
\text{ZnO}(s) + \text{2H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2\text{O}(l)
\]

[0094] At elevated pH, these amphoteric metal oxides dissolve forming complex ions:

\[
\text{Al}_2\text{O}_3(s) + 2\text{OH}^-(aq) + 3\text{H}_2\text{O}(l) \rightarrow 2[\text{Al(OH)}_2]^-(aq)
\]

\[
\text{Cr}_2\text{O}_3(s) + 2\text{OH}^-(aq) + 3\text{H}_2\text{O}(l) \rightarrow 2[\text{Cr(OH)}_2]^-(aq)
\]

\[
\text{ZnO}(s) + 2\text{OH}^-(aq) + \text{H}_2\text{O}(l) \rightarrow [\text{Zn(OH)}_2]^2-(aq)
\]

[0095] Thus, the heavy metals present in the SO₂ treated liquid fraction can be removed as metal hydroxides precipitates for filtration removal as the pH is elevated. The pH required is dependent upon the metals to be removed.

[0096] Most metal hydroxides are insoluble. Some such as Ca(OH)₂, Mg(OH)₂, Fe(OH)₃, Al(OH)₃ etc are sparingly soluble. However, alkali metal hydroxides Ca(OH)₂, KOH, and NaOH are very soluble, making them strong bases. When dissolved, these hydroxides are completely ionized. Since the
hydroxide concentration, [OH⁻], is an integrated property of the solution, the solubility of metal hydroxide depends on pH, pOH or [OH⁻].

[0097] Alkali metal hydroxides LiOH, NaOH, KOH, CsOH are soluble, and their solutions are basic. Hydroxides of alkali earth metals are much less soluble. For example, quicklime (CaO) reacts with water to give slaked lime, which is slightly soluble.

[0098] For the amphoteric metal hydroxides dissolving as the pH is raised above their optimal insolubility pH, the pH required may vary from the theoretical based on the presence of other compounds present in the soil so field testing is usually required to determine the optimal solubility for precipitating a given metal from different soils. For example, the following are amphoteric:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Optimal theoretical pH</th>
<th>Amphoteric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td>8.2</td>
<td>yes pH 8-12</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>10</td>
<td>yes pH 10-12</td>
</tr>
<tr>
<td>Pd⁺</td>
<td>8.9</td>
<td>yes pH 8-10.6</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>10.5</td>
<td>yes pH 10.5-12</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>8.5</td>
<td>yes pH 8.5-12</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>8.5</td>
<td>yes pH 8.5-11.8</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

[0099] Thus most metal hydroxides are removed by raising the pH from 6.8 to 8.6. For those heavy metals requiring a higher pH, the pH may be sequentially raised in different precipitation steps resulting in metal-free filtrate. For example, at higher pH levels, chromium and possibly iron and aluminum become more soluble as Fe(OH)₃⁺ or Al(OH)₃⁺ or Cr(OH)₄⁻ ions. They therefore are removed at the pH at which they precipitate before the pH is then raised higher to remove other heavy metal hydroxides.

[0100] After sulfur dioxide biological ore reduction treatment, the resultant liquid fraction is then neutralized with an alkaline reagent, such as ammonium hydroxide, lime or calcium carbonate to raise the pH to that suitable for precipitating out the heavy metals for filtration removal. The heavy metal contents of wastewaters can be effectively removed to acceptable levels by precipitating the metal in an insoluble form. Heavy metals are typically precipitated from wastewater as: hydroxides, sulfides or sometime sulfates, and carbonates. Metal co-precipitation during flocculation with iron or aluminum salts is also possible for some metals (e.g., arsenic). Arsenic is removed by co-precipitation with FeCl₃ when a Fe(OH)₃ floc is formed. The effluent concentration is 0.005 ppm. Cadmium is removed by co-precipitation at pH 6.5 with FeCl₃ when a Fe(OH)₃ floc is formed. The effluent concentration is 0.008 ppm. Mercury can also be removed by co-precipitation with FeCl₃ when a Fe(OH)₃ floc is formed. The effluent concentration is 0.0005 to 0.005 ppm. Alternatively, mercury can be removed by co-precipitation with alum. The effluent concentration is 0.001 to 0.01 ppm.

[0101] If high levels of bicarbonates are present in the water fraction, some metals (lead, cadmium, nickel) form insoluble carbonates that can be used in carbonate precipitation and filtration removal before hydroxide precipitation. These insoluble metal bicarbonates are thus removed before sulfuric acid treatment. The pH required for lead carbonate removal is between 7.5 and 8.5, providing an effluent concentration comparable to that obtained through hydroxide precipitation at high pH.

[0102] Sulphurous acid leaching also has the advantage of adding sulfates (after reduction) to the treated water fraction aiding in heavy metals precipitation. Barium can be removed by precipitation as sulfate, by adding any sulfate ion source. The solubility of barium sulfate is 1.4 ppm. Even lower residual barium concentrations (0.5 ppm) can be obtained using an excess of sulfate ions.

[0103] Precipitation by hydroxide formation is the most common heavy metal precipitation method. The precipitation typically follows the reaction:

\[ \text{M}^{\text{n+}} + \text{nOH}^- \rightarrow \text{M(OH)}_\text{n} \]

[0104] Many heavy metals are amphoteric. Therefore, their solubility reaches a minimum at a specific pH (different for each metal).

[0105] The addition of caustic materials is used to raise the pH. The most common caustics are:

[0106] sodium hydroxide (NaOH)

[0107] calcium hydroxide (Ca(OH)₂; lime)

[0108] Sodium hydroxide is more expensive than lime, and lime has the advantage of also acting as a coagulant during the precipitation/settling process, whereas NaOH does not. Lime also precipitates excess sulfides forming gypsum to assist in plant growth where sulfate levels are too elevated.

[0109] Many transition metals (e.g., Cd, Co, Cu, Fe, Hg, Ni, Zn) can form complexes with a number of different ligands such as hydroxides, sulfides, chlorides, cyanides, EDTA (ethylenediaminetetraacetic acid). If hydroxide precipitation is not adequate for heavy metal removal, other different ligands may be employed.

[0110] After neutralizing the sulfur dioxide/sulphites/bisulfites, and removing the heavy metal precipitates, the filtrate final high pH may then be adjusted for phytoremediation, phytoextraction, or phytostabilization by plants, bacteria, and other organisms—usually at a pH range of approximately 6 to approximately 8 for land application if it is not to be acidified and applied for ore extraction. Other factors in the selection of this pH are the soil alkalinity in a region, and whether the treated wastewater will be land applied or discharged to an aqueous environment.

[0111] The reagents selected for heavy metals precipitation are thus selected not only for their effects on pH, but for their nutrient compositions to raise plants, bacteria, algae and photo biomass, all hereinafter referred to as “biomass”. For example, where addition ammonia is required for fertilizer stimulation, ammonium hydroxide may be used to elevate pH for heavy metals precipitation, provided heavy metals precipitates, such as copper, have been previously removed. Phosphates may be added not only to precipitate heavy metals, such as lead, but also to add additional fertilizer to the filtrate treated waters. Thus, the type of heavy metal also determines what type of microbial nutrient is used for bio-mining.

[0112] Alternatively, dissolved heavy metals may be removed from solution using electrolytic and ion exchange media methods.

[0113] The invention thus provides a method for sulfurous acid bio-mining of heavy metals from sulfide ores into a metal ion water fraction for subsequent removal via electro-winning, ion exchange, or precipitation with alkaline and other suitable reagents for filtration removal.

I claim:

1. A bio-mining enhancement method for metal sulfide ores comprising:
a. applying sufficient sulfuric acid, bisulfites/sulfites, and free SO₂ to the metal sulfide ores to provide electron donors and adjust the pH to that required for microbial leaching of the metal sulfide ores to release metal ions into solution, and
b. removing the metal ions from solution using electrolysis, ion exchange, and electro winning methods to produce metals.

2. A biomining enhancement method for metal sulfide ores according to claim 1, including adding oxidizing agents to expedite microbial leaching.

3. A biomining enhancement method for metal sulfide ores according to claim 1, including adding ferric ions to the sulfuric acid solution to feed iron-oxidizing bacterium *Thiobacillus ferroxidans*.

4. A biomining method for metal sulfide ores according to claim 1, including adding microorganisms to the sulfuric acid solution, which reduce metal sulfide ores to release metal ions into solution.

5. A biomining enhancement method for metal sulfide ores comprising:
   a. applying sufficient sulfuric acid, bisulfites/sulfites, and free SO₂ to the metal sulfide ores to provide electron donors and adjust the pH required for microbial leaching of metal sulfide ores to release metal ions into solution,
   c. adding sufficient complexing agents to the water to precipitate heavy metals for separation, and
d. removing the metal ions from solution using electrolysis to produce metals.

6. A biomining enhancement method for metal sulfide ores according to claim 5, including filtering the heavy metal precipitates from the water, leaving metal free filtrate with nutrients to aid plants, bacteria, and other photo biomass in phytoremediation, phytoextraction, and phytostabilization.

7. A biomining enhancement method for metal sulfide ores according to claim 5, including re-acidifying the metal free filtrate with more sulfuric acid to re-apply to the metal sulfide ores to provide electron donors and adjust the pH required for microbial reduction of the metal sulfide ores to release metal ions into solution.

8. A biomining enhancement method for metal sulfide ores according to claim 5, wherein the complexing agent is lime.

9. A biomining enhancement method for metal sulfide ores according to claim 5, wherein the complexing agents are ammonium hydroxide and phosphate solutions.

10. A biomining enhancement method for metal sulfide ores according to claim 5, wherein the pH for precipitating heavy metal hydroxides is sequentially adjusted for sequential precipitation and filtration of different heavy metal hydroxides.

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