METHOD OF LEACHING COPPER SULFIDE ORES CONTAINING CHALCOPYRITE

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ABSTRACT
An object of the present invention is to provide a method of recovering copper from primary copper sulfide ores containing chalcopyrite as a main constituent under versatile conditions for real operation in all efficient and cost-effective manner.

A method of leaching copper sulfide ores, wherein the growth of microorganisms present on ore surfaces and in a leaching solution is inhibited and the pH of the leaching solution is adjusted to 1.5 or less upon leaching of copper from copper sulfide ores containing chalcopyrite, is provided.
METHOD OF LEACHING COPPER SULFIDE ORES CONTAINING CHALCOPYRITE

TECHNICAL FIELD

[0001] The present invention relates to a method of efficiently recovering copper from copper sulfide ores and particularly from primary copper sulfide ores such as chalcopyrite.

BACKGROUND ART

[0002] The SX-EW (SX-EW: solvent extraction-electrowinning) method, which is known as a method of recovering copper from copper ores, involves hydrometallurgy. In the method, copper is leached from copper ores with the use of sulfurous acid or the like, copper is concentrated in the leaching solution with the use of an organic solvent, and electrolytic copper is obtained via electrowinning. A typical solvent used for copper hydrometallurgy is sulfurous acid. Thus, target ores treated with hydrometallurgical processes have been limited to copper oxide ores that are readily dissolved in sulfurous acid or the like. However, in general, there are fewer copper oxide ore reserves than copper sulfide ore reserves. Thus, applicability of hydrometallurgical processes for extraction of copper from copper sulfide ores with large ore reserves has been investigated.

[0003] Examples of known leaching methods for copper sulfide ores via hydrometallurgy include agitation leaching method of performing an agitated batch reaction with the use of sulfurous acid or hydrochloric acid and a heap leaching method of forming ore heaps, supplying sulfurous acid or hydrochloric acid to the tops of the ore heaps, and recovering liquid dripping therefrom due to the gravity. However, operation with such heap leaching method takes several years with low copper recovery, resulting in poor efficiency. Further, a bacterial leaching method of leaching copper with the help of activity of microorganisms has also been used. The bacterial leaching method has been applied in practice for the extraction of copper from secondary copper sulfide ores containing chalcocite (Cu₉S₅), covellite (CuS), or the like, which have been found in secondary enriched zones of porphyry copper deposits. Recently, research and development of such leaching technology has been focused into the extraction of copper from primary copper sulfide ores containing chalcopyrite (CuFeS₂), which most abundantly exist as copper resources.

[0004] However, chalcopyrite is so refractory that the copper leaching rate of chalcopyrite is extremely slow in sulfurous acid. Therefore, a variety of attempts have been made in order to improve the leaching rate. For instance, high temperature-pressure treatments (JP Patent No. 3046986, JP Patent Publication (Kokai) No. 2001-515145 A, and JP Patent Publication (Kokai) No. 2003-328050 A), the maintenance of a certain oxidation-reduction potential by adjusting iron content and the ratio of trivalent iron to divalent iron (JP Patent Publication (Kokai) No. 10-265864 A (1998)), the maintenance of a certain oxidation-reduction potential by adding activated carbon and iron to a leaching solution (JP Patent Publication (Kokai) No. 2005-15684 A), and other techniques have been reported. Although aforementioned methods show some effect on improvement of rate of chalcopyrite leaching, these methods are too costly to apply them to industrial operation, due to requirement of high energy consumption, reagents, and so on.

[0005] Meanwhile, it is also problematic that, as leaching progresses, the leaching rate is significantly lowered due to passivation phenomenon caused by a coat formed on the ore surface with residual sulfur and/or an iron-derived substance from the ore. In addition, divalent iron, which is reported to be effective for promoting chalcopyrite leaching, is oxidized to trivalent iron with iron-oxidizing bacteria existing in nature, resulting in inhibition of copper leaching. In order to avoid this inhibition, there was a suggestion that an inhibitor for an iron-oxidizing bacterium, such as, sodium lauryl sulfate or tannic acid, be added to a leaching solution. However, contrary to their expectation, it has been reported that addition of such an inhibitor for an iron-oxidizing bacterium inhibits copper leaching (“Shigen to Sozai” (Journal of the Mining and Materials Processing Institute of Japan) vol. 115, 1999, pp. 172-176). Therefore, in practice, there is no viable technology involving hydrometallurgy with the use of primary copper sulfide ores containing chalcopyrite.

DISCLOSURE OF THE INVENTION

[0006] In view of the aforementioned reasons, it is an objective of the present invention to provide a method of recovering copper from primary copper sulfide ores containing chalcopyrite as a main constituent under versatile conditions for real operation in an efficient and cost-effective manner.

[0007] As a result of intensive studies to achieve above objectives, the inventors of the present invention have found that leaching of copper from chalcopyrite can be significantly improved in a manner such that the growth of microorganisms present on ore surfaces and in a leaching solution is inhibited and the pH of the leaching solution is adjusted to 1.5 or less upon leaching of copper from primary copper sulfide ores containing chalcopyrite. This has led to the completion of the present invention.

[0008] Specifically, the present invention encompasses the following inventions:

[0009] (1) A method of leaching copper sulfide ores, wherein the growth of microorganisms present on ore surfaces and in leaching solution is inhibited and the pH of the leaching solution is adjusted to 1.5 or less upon leaching of copper from copper sulfide ores containing chalcopyrite.

[0010] (2) The method of leaching copper sulfide ores according to (1), wherein the growth of microorganisms is inhibited by heating ores to 100°C or more prior to leaching.

[0011] (3) The method of leaching copper sulfide ores according to (1), wherein the growth of microorganisms is inhibited by treating ores with an agent capable of inhibiting the growth of microorganisms prior to leaching.

[0012] (4) The method of leaching copper sulfide ores according to (1), wherein the growth of microorganisms is inhibited by adding an agent capable of inhibiting the growth of microorganisms to a leaching solution.

[0013] (5) The method of leaching copper sulfide ores according to any one of (1) to (4), wherein the microorganisms are chemolithotrophic bacteria.

[0014] Hereinafter the present invention will be described in detail. The present application claims the priority of Japanese Patent Application No. 2008-076405 filed on Mar. 25, 2008 and encompasses contents described in the specification and/or drawings of the patent application.
The method of leaching copper sulfide ores of the present invention is characterized in that the growth of microorganisms present on ore surfaces and in a leaching solution is inhibited and the pH of the leaching solution is adjusted to 1.5 or less upon leaching of copper from copper sulfide ores containing chalcopryte.

The method of the present invention may be copper sulfide ores containing chalcopryte as a main constituent or copper sulfide ores that partially contain chalcocite, for example. The chalcocite content is not particularly limited. However, in the case of ores mainly comprising so-called secondary copper sulfide ores containing chalcocite and covellite, the growth of microorganisms promotes copper leaching, which is contrary to the conditions of the method of the present invention. Thus, it is preferable to use ores containing moderate or low amounts of such secondary copper sulfide ores, to use ores (residues) after the leaching treatment targeted to the copper from secondary copper sulfide ores accompanied with the growth of microorganisms, or to subject secondary copper sulfide ores to a leaching treatment accompanied by the growth of microorganisms following the leaching step of the present invention.

The method of the present invention can be applied in any types of copper-leaching operations using a sulfuric acid solution as a leaching solution, for example, not only agitated batch leaching but also heap or dump leaching where copper is leached into sulfuric acid by irrigating sulfuric acid over ores. In addition, leaching can be carried out at ambient temperatures and does not particularly require heating or the like. However, it is also possible to promote the leaching rate by heating.

According to the method of the present invention, methods for inhibiting the growth of microorganisms and methods for sterilizing microorganisms that are generally and widely used can be applied to the inhibition of the growth of microorganisms. Of these, the following methods are preferably used as convenient and economical methods: a method wherein ores are heat-treated prior to leaching; a method wherein ores are treated with an agent capable of inhibiting the growth of microorganisms; and a method wherein an agent capable of inhibiting the growth of microorganisms is added to a leaching solution.

In a case in which ores are heated before leaching, the heating temperature is not particularly limited, but it is preferably 100°C or more for efficient sterilization. In addition, as a heating method, a variety of means involving steam heating, heating with pressurization, and the like can be used in view of convenience, economic efficiency, sterilization efficiency, and the like. In addition, the upper limit of heating temperature differs depending on heating methods to be used, but it is preferably 125°C or less in a case of, for example, high-pressure steam sterilization.

Further, in a case in which ores are treated with an agent capable of inhibiting the growth of microorganisms prior to leaching or an agent capable of inhibiting the growth of microorganisms is added to a leaching solution, the type of agent to be used is not particularly limited as long as the agent has the action of inhibiting the growth or proliferation of microorganisms. However, examples of such an agent include: compounds containing halogens such as fluorine, chlorine, bromine, and iodine, and salts thereof; compounds containing metals such as silver, molybdenum, and cobalt, and salts thereof; alcohols such as ethyl alcohol and methyl alcohol; phenols such as ethylphenol, xylenol, and chlorphenol; organic solvents such as acetone; invert soaps such as benzalkonium chloride and benzethonium chloride; and organic acids such as acetic acid. These agents are used at concentrations exceeding the limiting concentration thereof at which the growth of microorganisms is inhibited.

In a case in which ores are treated with an agent capable of inhibiting the growth of microorganisms prior to leaching, any method wherein an agent comes into contact with ores can be used. An example thereof is a method involving dispersion of an agent. In such cases, an agent is preferably in a particle form in order to prevent it from being splashed upon dispersion, to allow it to be handled with ease, and to avoid it from being washed away by rain.

In addition, examples of a microorganism the growth of which is inhibited by one of the above methods include chemoautotrophic bacteria that obtain energy by oxidizing inorganic compounds (e.g., hydrogen sulfide, ammonia, and divalent iron ions), mainly including iron-oxidizing bacteria, sulfur-oxidizing bacteria, denitrifying bacteria, hydrogen bacteria, ammonia-oxidizing bacteria, and nitrite-oxidizing bacteria. Further, heterotrophic bacteria that obtain energy by oxidizing organic compounds, nucleated microorganisms such as yeast and mold, and archaeabacteria may also be included.

According to the method of the present invention, in addition to a means for inhibiting the growth of the above microorganisms, the pH of a sulfuric acid solution serving as a leaching solution is adjusted to 1.5 or less and preferably to between 1.0 and 1.5.

BEST MODES FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention is more specifically described by way of examples and comparative examples. However, the present invention is not limited thereto.

**EXAMPLE 1**

A concentrate (mined in Chile) containing chalcocypyte as a main constituent was used as a target. The quality of the concentrate was as follows: Cu=28% by mass; Fe=28% by mass; and S=32% by mass.

Three grams of the above concentrate was mixed with 300 mL of a leaching solution (containing: ammonium sulfate=3 g/L; potassium hydrogen phosphate=0.5 g/L; magnesium sulfate heptahydrate=0.5 g/L; and potassium chloride=0.1 g/L) that had been adjusted to a pH of 1.2 with sulfuric acid and poured into a 500 mL Sakaguchi flask. The flask was sterilized by heating at 121°C for 15 minutes, followed by shaking leaching at 30°C for 49 days. Then, the number of microorganisms (counted by microscopic observation with a counting chamber) and the copper concentration in the leaching solution were determined.

**COMPARATIVE EXAMPLE 1**

Shaking leaching was performed at 30°C as in Example 1, except that, prior to shaking leaching, a sulfur-oxidizing bacterium *Acidithiobacillus* sp. TTH-19A strain (NITE BP-164) and an iron-oxidizing bacterium *Acidithiobacillus ferrooxidans* DSM 14882 strain (1.0x10⁷ cells/mL.
each) were added, as autotrophic bacteria, to the flask subjected to heat sterilization described in Example 1 and the bacteria were allowed to grow simultaneously upon leaching. Then, the number of microorganisms and the copper concentration in the leaching solution were determined.

**COMPARATIVE EXAMPLE 2**

[0029] Shaking leaching was performed at 30°C as in Example 1, except that the pH of the leaching solution described in Example 1 was adjusted to 1.8. Then, the number of microorganisms and the copper concentration in the leaching solution were determined.

[0030] Table 1 lists the test results obtained in Example 1 and Comparative Examples 1 and 2. Each result represents the average value obtained by carrying out each experiment 2 or 3 times under the relevant conditions. In addition, oxidation-reduction potentials (ORPs) are values measured with the use of a silver/silver chloride reference electrode.

<table>
<thead>
<tr>
<th></th>
<th>ORP at the beginning of leaching (mV)</th>
<th>ORP on day 49 (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH at the beginning of leaching</strong></td>
<td><strong>Cell number on day 49 (cells/mL)</strong></td>
<td><strong>Copper concentration on day 49 (g/L)</strong></td>
</tr>
<tr>
<td>Example 1</td>
<td>1.21</td>
<td>356</td>
</tr>
<tr>
<td>Comparative</td>
<td>1.21</td>
<td>356</td>
</tr>
<tr>
<td>Example 1</td>
<td>1.85</td>
<td>340</td>
</tr>
</tbody>
</table>

[0031] As shown by the above results, in a case in which the growth of microorganisms present on ore surfaces and in a leaching solution was inhibited and the pH of the leaching solution was adjusted to 1.5 or less (Example 1), the leaching rate of copper was significantly improved compared with a case accompanied by the growth of microorganisms (Comparative Example 1). Thus, the efficacy of the present invention was confirmed. In addition, in a case in which the pH of a leaching solution exceeded 1.5 (Comparative Example 2), effects of improving the leaching rate of copper were not obtained, although the growth of microorganisms present on ore surfaces or in the leaching solution was inhibited.

[0032] In Comparative Example 1, a decrease in the leaching rate of copper was observed, although a significant increase in the oxidation-reduction potential (ORP) was not observed. Therefore, a decrease in the leaching rate of copper in a case in which the growth of microorganisms is observed at a pH of 1.5 or less is mainly caused by microorganisms adhering to ores or those derived from the external environment, especially autotrophic microorganisms using sulfur compounds/iron compounds as energy sources to grow, but not as a result of oxidation of divalent iron to trivalent iron caused by iron-oxidizing bacteria as previously reported in "Mining and Materials Processing Institute of Japan" vol. 115, 1999, pp. 172-176.

[0033] All publications, patents, and patent applications cited herein are incorporated herein by reference in their entirety.

**INDUSTRIAL APPLICABILITY**

[0034] According to the present invention, efficient leaching of copper from copper sulfide ores containing chalcopyrite can be achieved at ambient temperature. With the method of the present invention, it is possible to promote a copper leaching rate by merely inhibiting the growth of microorganisms and adjusting the pH of a leaching solution. Therefore, the method of the present invention is simple and highly cost-effective.

What is claimed is:

1. A method of leaching copper sulfide ores, wherein the growth of microorganisms present on ore surfaces and in a leaching solution is inhibited and the pH of the leaching solution is adjusted to 1.5 or less upon leaching of copper from copper sulfide ores containing chalcopyrite.

2. The method of leaching copper sulfide ores according to claim 1, wherein the growth of microorganisms is inhibited by heating ores to 100°C or more prior to leaching.

3. The method of leaching copper sulfide ores according to claim 1, wherein the growth of microorganisms is inhibited by treating ores with an agent capable of inhibiting the growth of microorganisms prior to leaching.

4. The method of leaching copper sulfide ores according to claim 1, wherein the growth of microorganisms is inhibited by adding an agent capable of inhibiting the growth of microorganisms to a leaching solution.

5. The method of leaching copper sulfide ores according to any one of claims 1 to 4, wherein the microorganisms are chemotrophic bacteria.