Method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme.

**Abstract**

Disclosed is a method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme. The method includes dipping the sulfide mineral containing the molybdenum (Mo) and the copper (Cu) into a solution having chloride dissolved therein, loading an electrode into the solution, and then applying a current to the solution.

**Flowchart Description**

1. **Start**
2. Dip sulfide mineral containing Mo and Cu into solution having chloride dissolved therein (S100)
3. Load electrode and apply current (S200)
4. **End**
dip sulfide mineral containing Mo and Cu into solution having chloride dissolved therein

load electrode and apply current

End
Fig. 4

[Diagram showing leaching yield (%) at different pH levels: pH0 = 55.2%, pH0+Al = 69.3%, pH9 = 91.3%, pH14 = 8.4%]
[Fig. 6]

Leaching yield (%) vs. Time (min.)

- MO
- Cu
- Fe

Points:
- 24.5 at 30 min.
- 37.9 at 60 min.
- 48 at 90 min.
- 57.7 at 120 min.
- 67.9 at 150 min.
[Fig. 7]

- Leaching yield (%) vs. Time (min.)
- Three conditions: No ultrasound, 15W, 85W
- Points representing leaching yield at different times:
  - No ultrasound: 48.0, 57.7, 77.6, 91.7
  - 15W: 52.4, 67.9, 85.0, 101.0
  - 85W: 65.3, 72.5, 89.1, 91.7
METHOD OF LEACHING MOLYBDENUM FROM SULFIDE MINERAL CONTAINING MOLYBDENUM AND COPPER THROUGH ELECTROLYTIC OXIDATION SCHEME

BACKGROUND OF THE INVENTION

1) Field of the Invention

The present invention relates to a method of leaching molybdenum (Mo) from a sulfide mineral containing molybdenum (Mo) and copper (Cu) through an electrolytic oxidation scheme.

2) Background of Related Art

Since molybdenum (Mo) has a superior thermal conductivity and a low thermal expansion coefficient, the Mo has a significant extensive application field including a tank, a vehicle, machine, paint, a reagent, a semiconductor, and an electric furnace from a military industry to electric and electronic part fields. As the demand for Mo is rapidly increased in China since 2003 and the demand for iron ore are increased all around the world, the price of the Mo has been sharply raised.

Currently, in our country, low-quality molybdenum (Mo) has been produced and mined from the Geum-um mine located at Hapop, Uljin-gun, Gyeongsangbuk-do, the Shinyemi mine located at Sin-dong, Jeongseon, Gangwon-do, and the Donwon mine located at Jecheon, Chungcheongbuk-do. In the case of the Geum-um mine, ore concentrate facilities have been constructed, and current ore production to operate 670 ton of concentrates by processing 900 ton of gemstones a day. In most domestic molybdenite (MoS₂) mines, chalcopyrite (CuFeS₂), which is sulfide mineral, and pyrite (FeS₂) are produced together to degrade the quality of the concentrate as the above minerals are contained in the concentrate. Accordingly, currently, low-quality concentrates have been produced. Therefore, after the content of Mo is increased through a physical flotation step to refine Mo, a calcinations step is performed to make molybdenum oxide (MoO₃) for use. In addition, Mo has been produced through a chemical leaching scheme and a chemical processing scheme having various process steps.

Further, in order to lower the content of copper (Cu) to 0.5% or less, after performing a calcinations process for molybdenite (MoS₂), Mo may be leached using sulfuric acid. According to the leaching scheme using the sulfuric acid, only copper (Cu) is not selectively leached, but a great amount of Mo is eluted together. Due to the lack of domestic technologies, all leached wastewater containing a great amount of Mo has been wasted.

There is a related art which is Korea Unexamined Patent Publication No. 10-2011-0046024 (published on May 4, 2011) titled “method of leaching impurities contained in molybdenum oxide concentrate”.

SUMMARY OF THE INVENTION

The present invention provides a method of selectively leaching only molybdenum from sulfide mineral through an electrolytic oxidation scheme. The objects of the present invention are not limited to the above-mentioned objects, and other objects will be clearly understood by those skilled in the art.

In order to accomplish the above object, there is provided a method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme. The method includes dipping the sulfide mineral containing the molybdenum (Mo) and the copper (Cu) into a solution having chloride dissolved therein, loading an electrode into the solution, and then applying a current to the solution.

In this case, the sulfide mineral containing the molybdenum (Mo) and the copper (Cu) is a molybdenum disulfide (MoS₂).

The chloride comprises at least one selected from the group consisting of NaCl, KCl, and NH₄Cl.

The chloride has a concentration in a range of 1 M to 6 M.

An anode of the electrode comprises one selected from the group consisting of platinum (Pt), iridium dioxide (IrO₂), stainless steel, gold (Au), silver (Ag), titanium (Ti), zirconium (Zr), iron (Fe), cobalt (Co), and nickel (Ni). A cathode of the electrode comprises one selected from the group consisting of glassy carbon, platinum (Pt), gold (Au), iridium dioxide (IrO₂), and graphite.

The current is in a range of 10 mA/cm² to 100 mA/cm². The solution has a temperature in a range of 25°C to 80°C, when the current is applied. In addition, the solution has pH of 9 when the current is applied.

In addition, according to the embodiment, there is provided a method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme, which includes dipping the sulfide mineral containing the molybdenum (Mo) and the copper (Cu) into a solution having chloride dissolved therein, loading an electrode into the solution, and then applying a current to the solution, in which an ultrasonic wave is irradiated when the current is applied.

In this case, the ultrasonic wave is irradiated while supplying power in a range of 15 W to 65 W at a frequency of 20 kHz.

As described above, the present invention is suggested by solving the problem of the related art in which a great amount of Cu is contained in Mo when Mo is leached from a sulfide mineral, so that the quality of the Mo is degraded. Therefore, according to the present invention, only Mo not only can be selectively leached from the sulfide mineral, but also high-quality Mo (less than 0.5% of Cu and 50% or more of Mo) can be retrieved.

In addition, the sulfide mineral can be decomposed and leached by electrochemically producing an oxidation agent without separately adding an oxidation agent through an electrolytic oxidation scheme, which is eco-friendly. The process is simple and cost is reduced. A process of irradiating an ultraviolet wave is applied to the leaching process of the Mo, so that the leaching yield of the Mo can be improved to 90% or more.
BRIEF DESCRIPTION OF DRAWINGS

[0021] FIG. 1 is a flowchart showing a method of leaching Mo from a sulfide mineral containing Mo and Cu through an electrolytic oxidation scheme according to the present invention.

[0022] FIG. 2 is a schematic view showing an electrolytic oxidation device in the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention.

[0023] FIG. 3 is a graph showing a leaching yield of Mo as a function of reaction time in the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention.

[0024] FIG. 4 is a graph showing a leaching yield of Mo as a function of the pH of a solution in the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention.

[0025] FIG. 5 is a graph showing a leaching yield of Mo as a function of reaction temperature in the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention.

[0026] FIG. 6 is a graph showing a leaching yield of Mo, Cu, and Fe in the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention.

[0027] FIG. 7 is a graph showing leaching yields according to the irradiation of an ultrasonic wave in the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0028] Hereinafter, an example embodiment of the present invention will be described in detail with reference to accompanying drawings.

[0029] The advantages, the features, and the schemes of achieving the advantages and features of the present invention will be apparently comprehended by those skilled in the art based on the embodiments, which are detailed later in detail, together with accompanying drawings.

[0030] The present invention is not limited to the following embodiments but includes various applications and modifications. The embodiments will make the disclosure of the present invention complete, and allow those skilled in the art to completely comprehend the scope of the present invention. The present invention is only defined within the scope of accompanying claims.

[0031] In addition, the details of the generally-known technology that makes the subject matter of the present invention unclear will be omitted in the following description.

[0032] The present invention provides a method of leaching molybdenum (Mo) from a sulfide mineral containing molybdenum (Mo) and copper (Cu) through an electrolytic oxidation scheme, characterized in that the sulfide mineral containing molybdenum (Mo) and copper (Cu) is dipped into a solution having chloride dissolved therein and an electrode is inserted into the solution to apply a current to the solution.

[0033] The method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme of the present invention is made in order to solve the problem of the related art in which a great amount of Cu is contained in Mo when Mo is leached from a sulfide mineral, so that the quality of the Mo is degraded. Therefore, according to the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme of the present invention, only Mo not only can be selectively leached from the sulfide mineral, but also high-quality Mo (less than 0.5% of Cu and 50% or more of Mo) can be retrieved. In addition, the sulfide mineral is decomposed and leached by electrochemically producing an oxidation agent without separately adding an oxidation agent through an electrolytic oxidation scheme, which is eco-friendly. The process is simple and cost is reduced. A process of irradiating an ultraviolet wave is applied to the leaching process of the Mo, so that the leaching yield of the Mo can be improved to 90% or more.

[0034] FIG. 1 is a flowchart showing the method of leaching Mo from a sulfide mineral containing Mo and Cu through an electrolytic oxidation scheme according to the present invention. Hereinafter, the present invention will be described in detail with reference to FIG. 1.

[0035] The method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention includes step S100 of dipping the sulfide mineral containing Mo and Cu into a solution having chloride dissolved therein.

[0036] According to the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention, the sulfide mineral, which is the mixture of metal or non-metal and sulfur, occupies 0.15% of a land. However, since important metal is extracted from the sulfide mineral, the sulfide mineral is economically advantageous. The sulfide mineral containing Mo and Cu according to the present invention is ore mined from the Geum-um mine located at Hupou, Uijin-gun, Gyeonsangbuk-do, Republic of Korea. In most domestic molybdenite (MoS₂) mines, chalcopyrite (CuFeS₂), which is sulfide mineral, and pyrite (FeS₂) are produced together to degrade the quality of the concentrate as the above ores are contained in the concentrate. Therefore, the present invention provides a method of leaching only Mo without an additional process to remove Cu from the low-quality concentrate and retrieve high-quality Mo.

[0037] In the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention, the chloride may include at least one selected from the group consisting of NaCl, KCl, and NH₄Cl, and preferably has the concentration of 1 M to 6M. If the concentration of the chloride is less than 1 M, the leaching yield may be degraded. If the concentration of the chloride exceeds 6M, the leaching yield is not increased any more. Accordingly, the concentration of the chloride is preferably 6 M or less in terms of energy saving.

[0038] The method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention includes step S200 of loading an electrode into the solution and applying the current.

[0039] FIG. 2 is a schematic view showing an electrolytic oxidation device in the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention. Referring to FIG. 2, after the sulfide mineral containing Mo and Cu has been dipped into the solution having the chloride dissolved therein, the electrode is loaded and the current is
applied. In this case, Cl₂ gas is generated, and the generated Cl₂ reacts with the solution to produce ClO⁻. The ClO⁻ ion has a high oxidizing power to oxidize molybdenum disulfide (MoS₂), so that the molybdenum disulfide (MoS₂) is decomposed. Accordingly, Mo ions are leached. In this case, the anode of the electrode may include platinum (Pt), iridium dioxide (IrO₂), stainless steel, gold (Au), silver (Ag), titanium (Ti), zirconium (Zr), iron (Fe), cobalt (Co), or nickel (Ni). The cathode of the electrode may include glassy carbon, platinum (Pt), gold (Au), iridium dioxide (IrO₂), and graphite. The electrolytic oxidation reaction and the chemical reaction occurring in the anode and the cathode are expressed in reaction formula 1 and reaction formula 2.

Anode: 2Cl₂ → 2Cl⁻ + 2²⁺ + 2e⁻ (standard hydrogen electrode)

Cathode: 2H₂O + 2e⁻ → 2OH⁻ + H₂, E₀ = 0.84V (standard hydrogen electrode)

Cl₂ + 2²⁺ → ClO⁻ + H₂O

[Reaction formula 1]

MoS₂ + 6ClO⁻ + 4OH⁻ → MoO₄²⁻ + SO₄²⁻ + 6Cl⁻ + 3H₂O

S + 3ClO⁻ + 2H₂O → H₂SO₄ + 3Cl⁻

[Reaction formula 2]

[0040] In the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme according to the present invention, it is preferred that the current is in the range of 10 mA/cm² to 100 mA/cm². If the current is less than 10 mA/cm², Cl₂ is not sufficiently produced, so that the leaching yield of molybdenum (Mo) is degraded. If the current exceeds 100 mA/cm², the leaching yield of molybdenum (Mo) is not increased any more. Accordingly, it is preferred that the current is 100 mA/cm² or less in terms of energy saving.

[0041] When the current is applied to the solution, the pH of the solution is preferably 9. If the pH of the solution is 9, the leaching yield represents the highest value. If the pH of the solution is less than 9 or more than 9, the leaching yield of molybdenum (Mo) represents a low value.

[0042] When the current is applied to the solution, the solution temperature is preferably in the range of 25°C to 80°C. If the solution temperature is less than 25°C, the leaching yield of molybdenum (Mo) represents a low value. If the solution temperature is more than 80°C, the solubility of Cl₂ is reduced, so that ClO⁻ is less produced. Accordingly, the leaching yield of molybdenum (Mo) is degraded.

[0043] In addition, the present invention provides the method of leaching Mo from the sulfide mineral containing Mo and Cu through the electrolytic oxidation scheme, characterized in that the method includes a step of dipping the sulfide mineral containing molybdenum (Mo) and copper (Cu) into the solution having chloride dissolved therein, loading the electrode into the solution and applying a current to the solution, and an ultrasonic wave is irradiated when the current is applied.

[0044] In the method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme according to the present invention, the ultrasonic wave is irradiated when the current is applied, the production of ClO⁻ may be increased in the solution. Accordingly, the leaching yield of molybdenum (Mo) can be increased to 90% or more.

[0045] The ultrasonic wave is preferably irradiated during the leaching reaction while supplying power of 15 W to 65 W at the frequency of 20 kHz. If the power is less than 15 W, an influence is significantly slightly exerted on the improvement of the leaching yield. If the power exceeds 65 W, the leaching yield is not improved any more. Accordingly, it is preferred that the power is 65 W in terms of power saving.

### Embodiment 1

#### Leaching 1 of Mo

[0046] After dipping MoS₂ into a solution having 3 M of NaCl dissolved therein, a platinum (Pt) electrode and a glassy carbon electrode were loaded, and a current of 90 mA/cm² was applied. In this case, the pulp density of MoS₂ was 1% (w/v), the pH of the solution was adjusted to 9, and the solution temperature of the solution was increased to 50°C.

### Embodiment 2

#### Leaching 2 of Mo

[0047] Molybdenum (Mo) in the second embodiment was leached in the same manner as that of the first embodiment except that molybdenum disulfide (MoS₂) was obtained by secondarily concentrating a mineral from the Geum-um mine located at Hupoup, Uijin-gun, Gyeongsangbuk-do, was used, and 5 M of NaCl was used. Following table 1 represents contents of the molybdenum disulfide (MoS₂) obtained through the secondary concentrate.

| TABLE 1 |
|-----------------|------|-----|-----|-----|-------|-------|------|
| SiO₂ | Fe | Mg | Al | K | Na | MoS₂ | Cu | Zn |
| Primary Concentrate | 1.93 | 0.1 | 1.15 | 0.14 | 0.03 | 68.24 | 8.61 | 0.53 |

### Embodiment 3

#### Leaching 3 of Mo

[0048] Molybdenum (Mo) in the third embodiment was leached in the same manner as that of the second embodiment except that, when the current was applied, the ultrasonic wave was irradiated during the leaching reaction while supplying power of 65 W at the frequency of 20 kHz.

### Leaching Yield Analysis According to Leaching Reaction Time

[0049] In the method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme according to the present invention, the leaching yield of the molybdenum (Mo) according to the leaching reaction time was analyzed, and the result was shown in FIG. 3. The molybdenum (Mo) was leached from MoS₂ in the first embodiment.

[0050] As shown in FIG. 3, the leaching yield is rapidly increased to 80% or more till 120 minutes, and then the increment of the leaching speed is decreased after 120 minutes. After 240 minutes, the high leaching yield corresponding to about 94% is shown.
Embodiment 2

Leaching Yield Analysis According to pH of Solution

[0051] In the method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme according to the present invention, the leaching yield of the molybdenum (Mo) according to the pH of the solution was analyzed, and the result was shown in FIG. 4. The molybdenum (Mo) was leached from MoS₂ in the first embodiment.

[0052] Referring to FIG. 4, after the leaching has been performed for three hours while changing the pH of the solution, 91.3% of a Mo leaching yield is represented at pH 0, and the Mo leaching yield is decreased to 55.2% at pH 10, and more decreased to 8.4% at pH 14. The leaching yield is decreased at pH 0 because Mo is dissolved to Mo⁴⁺ ions in the initial stage, and precipitated to MoO₃ according to the lapse of the time, so that an amount of Mo existing in the form of ions is decreased, and a portion of MoO₃ is precipitated on the surface of MoS₂ to restrain the reaction. For example, after Mo is leached at pH 0, NaOH is added to the solution, so that the pH of the solution is adjusted to the alkaline atmosphere of pH 9. In this case, the leaching yield of molybdenum (Mo) is increased and MoO₃ which is produced at pH 0, is re-dissolved at pH 0→Al (Alkal)Meanwhile, the leaching yield represents a significantly low value at pH 14 because the oxidizing power of ClO⁻ is reduced by the high pH. In other words, the oxidation/reduction potential of ClO⁻ greatly depends on pH. In addition, as the pH is increased, the oxidation/reduction potential is rapidly reduced. Accordingly, the oxidizing power is reduced.

Embodiment 3

Leaching Yield Analysis According to Reaction Temperature

[0053] In the method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme according to the present invention, the leaching yield of the molybdenum (Mo) by changing the reaction temperature of Embodiment 2, and the result was shown in FIG. 5.

[0054] As shown in FIG. 5, if the reaction temperature is increased from 25°C to 50°C, the leaching yield of Mo is increased to 68% from 32%. The leaching yield is slightly decreased to 63% at 80°C. The reaction to produce Cl₂ is decreased at the carbon electrode as the temperature is increased. As Cl₂ solubility is decreased, the production of ClO⁻ is decreased, so that the leaching yield may be reduced.

Embodiment 4

Leaching Yield Analysis of Metal Contained in Secondary Concentrate and Leaching Yield Analysis According to Irradiation of Ultrasonic Wave in Electrolytic Oxidation Process

[0055] The leaching yield of metal in the second embodiment was analyzed, and the result was shown in FIG. 6. In addition, the leaching yield was analyzed according to the power variation of the ultrasonic wave in the third embodiment of irradiating the ultrasonic wave to the second embodiment, and the result was shown in FIG. 7.

[0056] As shown in FIG. 6, in the method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme according to the present invention, Cu and Fe were not leached, but only Mo was selectively leached.

[0057] In addition, as shown in FIG. 7, when the ultrasonic wave is irradiated with the power of 65 W, the leaching yield of Mo is represented as 91.7%. In addition, the leaching yield is increased in the case of ultrasonic wave is irradiated as compared with the case that the ultrasonic wave is not irradiated.

[0058] Although the detailed embodiment of the method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu) through the electrolytic oxidation scheme according to the present invention has been described, it is obvious that various variations and modifications are possible.

[0059] Although exemplary embodiments of the present invention have been described for the illustrative purpose, it is understood that the present invention should not be limited to these exemplary embodiments but various changes, modifications, equivalents can be made by one ordinary skilled in the art within the spirit and scope of the present invention as hereinafter claimed.

1. A method of leaching molybdenum (Mo) from a sulfide mineral containing molybdenum (Mo) and copper (Cu) through an electrolytic oxidation scheme, the method comprising dipping the sulfide mineral containing the molybdenum (Mo) and the copper (Cu) into a solution having chloride dissolved therein, loading an electrode into the solution, and then applying a current to the solution, wherein:

an ultrasonic wave is irradiated when the current is applied, the ultrasonic wave being irradiated while supplying power in a range of 15 W to 65 W at a frequency of 20 kHz, and
in the method of leaching molybdenum (Mo) from the sulfide mineral containing molybdenum (Mo) and copper (Cu), only Mo is leached and not Cu.

2. The method of claim 1, wherein the sulfide mineral containing the molybdenum (Mo) and the copper (Cu) is a molybdenum disulfide (MoS₂).

3. The method of claim 1, wherein the chloride comprises at least one selected from the group consisting of NaCl, KCl, and NH₄Cl.

4. The method of claim 1, wherein the chloride has a concentration in a range of 1 M to 6 M.

5. The method of claim 1, wherein an anode of the electrode comprises one selected from the group consisting of platinum (Pt), iridium dioxide (IrO₂), stainless steel, gold (Au), silver (Ag), titanium (Ti), zirconium (Zr), iron (Fe), cobalt (Co), and nickel (Ni).

6. The method of claim 1, wherein a cathode of the electrode comprises one selected from the group consisting of glowy carbon, platinum (Pt), gold (Au), iridium dioxide (IrO₂), and graphite.

7. The method of claim 1, wherein the current is in a range of 10 mA/cm² to 100 mA/cm².

8. The method of claim 1, wherein the solution has a temperature in a range of 25°C to 80°C when the current is applied.

9. The method of claim 1, wherein the solution has a pH of 9 when the current is applied.

10. (canceled)

11. (canceled)