MOLYBDENUM REFINING METHOD

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ABSTRACT
A molybdenum refining method collects molybdenum with high purity and yield by simple means. The molybdenum refining method includes mixing and grinding a molybdenum ore or concentrate containing molybdenum sulfide, an oxidizing agent, and an alkali or alkaline earth metal salt to produce an alkali or alkaline earth metal salt of molybdic acid from molybdenum sulfide.
**Fig. 1**

The diagram shows the binding energy (eV) against intensity (c/s) for different states of molybdenum (Mo). The peaks labeled Mo$_{3d}^{5/2}$ and Mo$_{3d}^{3/2}$ represent different spin-orbit components of the Mo$_{3d}$ orbital. The diagram also notes the presence of sulfide and tetravalent oxide, with peaks labeled Mo$_{3d}^{5/2}$ and Mo$_{3d}^{3/2}$ corresponding to these states.
MOLYBDENUM REFINING METHOD

RELATED APPLICATIONS


TECHNICAL FIELD

This disclosure relates to a molybdenum refining method, which includes refining a molybdenum ore or concentrate containing molybdenum sulfide.

BACKGROUND

Molybdenum is an important element widely used in industrial and research applications such as steels, special steel raw materials, semiconductors, metal materials for lightning fixtures and the like, catalysts, dyes, and other inorganic chemistry materials. Molybdenum for use in these applications is produced from oxide-based compounds.

Known molybdenum refining methods generally include a roasting method in which a molybdenum concentrate obtained by flotation of a molybdenum ore including sulfide mineral is oxidized by roasting, and a pressure oxidation method in which oxidation is performed using an autoclave.

The roasting method includes oxidizing a molybdenum concentrate (MoS₂) by roasting at 600° C. or higher to convert molybdenum and sulfur into a crude oxide (MoO₃) and sulfuric acid gas (SO₃), respectively, and then performing a wet or dry purification process on the crude oxide obtained by the roasting so that impurities are removed from the crude oxide.

On the other hand, the method for pressure oxidation of a molybdenum concentrate with an autoclave includes grinding a molybdenum ore or concentrate without roasting it, placing the ground product and water in an autoclave, and subjecting them to pressure oxidation at high temperature and high pressure so that molybdate acid is directly precipitated.

In the roasting method, if the roasting temperature is too low, molybdenum will be insufficiently oxidized so that molybdenum sulfide may remain. The roasting time must be enough to prevent that and, in such a case, the problem of reduction in productivity occurs.

On the other hand, if the roasting temperature is too high, the crude oxide produced will be lost through melting or sublimation which causes the problem of a reduction in collection yield. In addition, sulfuric acid gas produced during the roasting is an air pollutant and, therefore, a waste gas treatment using desulfurization equipment is indispensable, which is expensive.

When wet refining is performed to remove impurities from the crude oxide obtained by the roasting, there is a problem in which molybdenum is partially dissolved in a process that includes treating the crude oxide with nitric acid to completely oxidize lower molybdenum oxide and dissolve and remove impurities including copper and the like.

On the other hand, dry refining, which includes heating the crude oxide at 1,270 to 1,370 K or higher in an electric furnace and collecting the sublimed molybdenum oxide with a bag filter has a problem in which not only it is difficult to collect all the sublimed molybdenum oxide, but also the heat treatment at a high temperature of 1,200 K or more is costly.

As described above, the roasting method has various problems.

On the other hand, the method for pressure oxidation of a molybdenum concentrate with an autoclave includes applying a pressure as high as 1,000 to 2,000 KPa to a 1:10 mixture of a molybdenum ore or concentrate and water at a temperature of 150 to 200° C. in an autoclave using an excess of oxygen and also requires a treatment time of 3 to 6 hours (see JP ’207 and JP ’457).

Therefore, the autoclave for use in pressure oxidation is very costly to be installed and maintained and also requires complicated operation. The fact is, therefore, that refining methods using an autoclave are not so widely used as a molybdenum refining method.

It could therefore be helpful to provide a molybdenum refining method capable of collecting molybdenum with high purity and yield by simple means.

SUMMARY

We thus provide:

(1) A molybdenum refining method, including the steps of:

- providing at least one molybdenum-containing ore selected from the group consisting of a molybdenum ore containing molybdenum sulfide and a molybdenum concentrate containing molybdenum sulfide, an oxidizing agent, and at least one metal salt selected from the group consisting of an alkali metal salt and an alkaline earth metal salt; and

- mixing and grinding the at least one molybdenum-containing ore, the oxidizing agent, and the at least one metal salt to produce a metal salt of molybdic acid from molybdenum sulfide.

(2) A molybdenum refining method, including the steps of:

- providing at least one molybdenum-containing ore selected from the group consisting of a molybdenum ore containing molybdenum sulfide and a molybdenum concentrate containing molybdenum sulfide, an oxidizing agent, and at least one metal salt selected from the group consisting of an alkali metal salt and an alkaline earth metal salt;

- mixing and grinding the at least one molybdenum-containing ore, the oxidizing agent, and the at least one metal salt to produce a reaction product containing a metal salt of molybdic acid from molybdenum sulfide; and

- extracting molybdate ions from the reaction product using an aqueous solvent to collect molybdic acid in the aqueous solvent.

(3) The molybdenum refining method according to item (1) or (2), wherein the oxidizing agent is an oxoacid or an oxoacid salt.

(4) The molybdenum refining method according to item (3), wherein the oxoacid is at least one selected from the group consisting of manganese dioxide, lead oxide, silver oxide, a peroxy acid, nitrous acid, nitric acid, manganic acid,
permanganic acid, bichromic acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, and percarbonic acid.

(0026) The molybdenum refining method according to item (1) or (2), wherein the at least one molybdenum-containing ore is a molybdenum ore containing molybdenum sulfide.

(0027) The molybdenum refining method according to item (1) or (2), wherein the at least one molybdenum-containing ore is a molybdenum concentrate.

(0028) The molybdenum refining method according to item (1) or (2), wherein the at least one metal salt is an alkali metal salt.

(0029) The molybdenum refining method according to item (1) or (2), wherein the alkali metal salt is at least one selected from the group consisting of a carbonate, a bicarbonate, a halide, a sulfate, a sulfite, a nitrate, and a hydroxide.

(0030) The molybdenum refining method according to item (1) or (2), wherein the at least one metal salt is an alkali earth metal salt.

(0031) The molybdenum refining method according to item (1) or (2), wherein the alkali earth metal salt is at least one selected from the group consisting of a carbonate, a bicarbonate, a halide, a sulfate, a sulfite, a nitrate, and a hydroxide.

(0032) A molybdenum ore or concentrate containing molybdenum sulfide, an oxidizing agent, and an alkali or alkali earth metal salt are mixed and ground so that an alkali or alkali earth metal salt of molybdic acid is produced and, therefore, refining of molybdenum can be performed with high purity and yield without production of sulfuric acid gas, which has been a problem in the roasting step of a roasting method, without loss of a crude oxide which would otherwise be caused by sublimation, and without purification for removal of impurities.

(0033) In addition, a mild and simple process can be performed using a grinder and, therefore, it is unnecessary to perform a complicated process at high temperature and high pressure, such as autoclaving used in conventional techniques so that the cost of equipment operation and maintenance can be reduced.

BRIEF DESCRIPTION OF THE DRAWING

(0034) FIG. 1 is a schematic diagram illustrating the advantageous effect of Example 1.

DETAILED DESCRIPTION

(0035) We discovered that when a molybdenum ore, an oxidizing agent and an alkali or alkali earth metal compound are mixed and ground (which is hereinafter also referred to as "co-grinding"), active surfaces of the molybdenum ore, the oxidizing agent and the alkali or alkali earth metal compound are exposed and contact one another so that an alkali or alkali earth metal salt of molybdic acid and an alkali or alkali earth metal sulfide are produced.

(0036) Thus, molybdenum sulfide in the molybdenum ore can be oxidized without using a roasting process which is accompanied by production of sulfuric acid gas, or without using a high-temperature, high-pressure autoclave. This reaction proceeds as the active surfaces formed by the co-grinding come into contact with one another. Therefore, when sufficient time is provided for the co-grinding, the whole amount of molybdenum sulfide in a molybdenum ore can be converted into an alkali or alkali earth metal salt of molybdic acid which enables the extraction of molybdenum into an aqueous solvent.

(0037) On the other hand, sulfides of copper or iron contained as impurities in the molybdenum ore are also oxidized by the co-grinding to form oxides, but there is no soluble alkali acid salt of copper or iron. Therefore, when the ground product is subjected to an extraction procedure with an aqueous solvent, copper or iron remains as an oxide in the dissolution residue, while the alkali or alkaline earth metal salt of molybdic acid is dissolved in the solvent. Thus, our methods are also applicable to low-quality ores with a high copper content which is not suitable for the roasting method.

(0038) Therefore, the molybdenum ore co-ground product containing an alkali or alkaline earth metal salt of molybdic acid produced by the co-grinding can be subjected to leaching with an aqueous solvent so that molybdenum can be collected with high purity and yield by simple means.

(0039) Hereinafter, a representative description is given of our molybdenum refining method.

(0040) A molybdenum refining method includes: a co-grinding step including mixing and grinding a molybdenum ore or concentrate containing molybdenum sulfide, an oxidizing agent, and an alkali or alkaline earth metal salt to produce from molybdenum sulfide a reaction product containing an alkali or alkaline earth metal salt of molybdic acid; a leaching step including leaching with an aqueous solvent the reaction product produced in the co-grinding step to elute the alkali or alkaline earth metal salt of molybdic acid and to separate a residue containing copper, iron, or other metals; and a precipitating step including precipitating and collecting molybdic acid from the leachate containing molybdic acid leached in the leaching step so that molybdic acid is separated from the dissolved impurities.

(0041) Hereinafter, a more detailed description is given of the respective steps of the molybdenum refining method, specifically, the co-grinding step, the leaching step, and the precipitating step.

Molybdenum Sulfide Co-Grinding Step

(0042) The molybdenum sulfide co-grinding step includes mixing and grinding a molybdenum ore or concentrate containing molybdenum sulfide, an oxidizing agent, and an alkali or alkaline earth metal salt to produce from molybdenum sulfide a reaction product containing an alkali or alkaline earth metal salt of molybdic acid.

(0043) In the grinding process, a mechanochemical reaction occurs in which molybdenum sulfide in the ore is oxidized with the oxidizing agent and further reacts with the alkali or alkaline earth metal salt to form an alkali or alkaline earth metal salt of molybdic acid.

(0044) The molybdenum sulfide before the grinding may have a particle size of about 0.3 mm or less so that a mechanochemical reaction can sufficiently occur in the grinding process.

(0045) The lower content of molybdenum sulfide in the molybdenum ore or concentrate to be co-ground is disadvantageous in terms of process cost, waste production, or the like. It is therefore preferred that a molybdenum ore or concentrate with a high molybdenum sulfide content should be used. It will be understood, however, that the content of molybdenum sulfide in the molybdenum ore or concentrate is not particul-
larly restricted and that the content of impurities such as copper and iron in the molybdenum ore or concentrate is also not particularly restricted.

[0046] While the molybdenum ore may be co-ground with any oxidizing agent and any alkali or alkaline earth metal salt, the oxidizing agent and the alkali or alkaline earth metal salt should be selected such that the oxidizing agent and alkali or alkaline earth metal salt can react with molybdenum sulfide in the molybdenum ore to form an alkali or alkaline earth metal salt through a mechanochemical effect caused by the grinding.

[0047] The oxidizing agent may be any material capable of causing oxidation of molybdenum sulfide during grinding, which should be solid rather than gaseous or liquid and preferably an oxide with a high oxidation number, a peroxide such as a percarbonate or a persulfate, or an o xo acid or a salt thereof. Specific examples of the oxidizing agent which can be used include manganese dioxide (MnO₂), lead oxide (PbO₂), silver oxide, a peroxide, and an o xo acid such as nitric acid, nitric acid, manganic acid, permanganic acid, bichromic acid, chloric acid, chromic acid, hypochlorous acid, bromic acid, or percarbonic acid, or a salt thereof, such as sodium chloride or sodium percarbonate. Among the above oxidizing agents, manganese dioxide is more preferred because it is easily industrially available and serves as an oxidizing agent to cause a relatively mild reaction.

[0048] To improve reaction efficiency, the amount of the oxidizing agent added to the co-grinding process is preferably about one to three times the theoretical equivalent necessary to produce the desired molybdc acid.

[0049] The alkali or alkaline earth metal salt is preferably an alkali or alkaline earth metal carbonate, bicarbonate, halide, sulfate, sulfite, nitrate, nitrite, or hydroxide capable of forming a soluble alkali or alkaline earth metal salt of molybdc acid. For example, sodium carbonate, sodium hydroxide, or the like may be used. To improve reaction efficiency, the amount of the alkali or alkaline earth metal salt added to the co-grinding process is preferably about once to twice the theoretical equivalent necessary to produce the desired molybdc acid.

[0050] The co-grinding may be performed using any grinder. High collision energy during the grinding is effective in allowing the reaction to proceed efficiently in a short time and, therefore, a planet mill, a vibrating mill, or a grinding machine capable of applying an acceleration of several G or more is preferred.

Leaching Step

[0051] The leaching step includes leaching with an aqueous solvent the alkali or alkaline earth metal salt of molybdic acid produced in the co-grinding to elute the alkali or alkaline earth metal salt of molybdic acid and to separate a residue containing copper, iron, or other metals.

[0052] While the leaching solvent used in the leaching step is not restricted, pure water containing no impurities is preferably used. The temperature of the leaching water used is preferably, but not limited to, from 30 to 80°C for the dissolution of the alkali or alkaline earth metal salt of molybdic acid.

Precipitating Step

[0053] The precipitating step includes precipitating and collecting molybdic acid from the leachate containing molybdic acid leached in the leaching step so that molybdic acid is separated from the dissolved impurities.

[0054] The method of collecting molybdic acid may be performed using a known wet process that includes adding an acid such as nitric acid to the leachate to control the pH of the leachate so that molybdic acid can be collected as a precipitate from the leachate. In this process, even when copper, iron, or the like is dissolved in the leachate, iron or copper compounds do not precipitate from the acid solution and, therefore, are separated from molybdic acid.

[0055] Some Examples of the molybdenum refining method using the co-grinding process are described below.

[0056] It will be understood that the Examples described below are not intended to limit this disclosure.

EXAMPLE 1

[0057] To a stainless steel pot (1.2 liters in volume) of a vibrating mill (manufactured by URAS TECHNOCO., LTD.) were added 49.6 g of a molybdenum concentrate having the composition shown in Table 1, 141.9 g of manganese dioxide, and 48.5 g of sodium carbonate.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mo</th>
<th>S</th>
<th>Cu</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃</td>
<td>41.5</td>
<td>28.9</td>
<td>0.72</td>
<td>11.5</td>
</tr>
</tbody>
</table>

[0058] In this case, the molar ratio of molybdenum sulfide/manganese dioxide/sodium carbonate is 1:7:2 based on the molybdenum content shown in Table 1.

[0059] To the pot were added 146 stainless steel balls 19 mm in diameter and 146 stainless steel balls 10 mm in diameter. Subsequently, the pot was attached to the vibrating mill, and co-grinding was performed for 240 minutes. After the co-grinding was completed, the stainless steel pot was detached, and the ground product was collected.

[0060] In Example 1, the following reaction is considered to occur:

\[
\text{MoS}_3 + 4.5\text{MnO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{NaN}_2\text{Mn}_3\text{O}_7 + 1.5\text{Mn}_2\text{O}_4 + 2\text{Na}_2\text{O} + 5\text{CO}_2.
\]

[0061] Twenty g of the co-ground product was added into 200 ml of distilled water heated at 80°C and subjected to leaching for 1 hour. The resulting liquid was filtered through a reduced pressure filter so that an aqueous molybdenum solution was obtained. Molybdenum was collected with a yield of 88.4% in the aqueous solution.

[0062] FIG. 1 shows the result of X-ray photoelectron spectroscopy (XPS) measurement of the co-ground product. In FIG. 1, the horizontal axis represents binding energy (eV), and the vertical axis represents e/s (counts per second). It is apparent that molybdenum sulfide in the ore was converted into a molybdate by the co-grinding because as the solid phase reaction proceeds, the peak indicating the binding energy corresponding to a hexavalent molybdate becomes much more prominent than the peak indicating the corresponding to tetravalent molybdenum sulfide.

[0063] The pH of the resulting aqueous solution was adjusted to about 0.8 with nitric acid so that molybdc acid was precipitated. The resulting liquid was filtered through a reduced pressure filter and the molybdc acid precipitate was collected. Table 2 shows the composition of the resulting
molybdic acid precipitate. It is shown that none of copper, sulfur, and iron, which have been a problem in conventional techniques, were not detected and that molybdic acid was collected with a high purity.

**TABLE 2**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mo</th>
<th>S</th>
<th>Cu</th>
<th>Fe</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1 molybdic acid (wt %)</td>
<td>66.3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.02</td>
<td>n.d.</td>
</tr>
<tr>
<td>Example 2 molybdic acid (wt %)</td>
<td>66.2</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.02</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

n.d.: undetectable

**EXAMPLE 2**

[0064] To a stainless steel pot (1.2 liters in volume) of a vibrating mill (manufactured by URAS TECHNO CO., LTD.) were added 49.6 g of a molybdenum concentrate having the composition shown in Table 1, 141.9 g of manganese dioxide, 0.5 g of potassium nitrate, and 48.5 g of sodium carbonate. Co-grinding was performed under the same conditions as those in Example 1, except that the time of the co-grinding with the vibrating mill was changed to 120 minutes.

[0065] After the co-grinding was completed, the stainless steel pot was detached and the ground product was collected. Twenty g of the ground product was added into 200 ml of distilled water heated at 80 °C and subjected to leaching for 1 hour. The resulting liquid was filtered through a reduced pressure filter so that an aqueous molybdenum solution was obtained. Molybdenum was collected with a yield of 84.2% in the aqueous solution.

[0066] The pH of the resulting aqueous solution was adjusted to about 0.8 with nitric acid so that molybdic acid was precipitated. The resulting liquid was filtered through a reduced pressure filter and the molybdic acid precipitate was collected. Table 2 shows the composition of the resulting molybdic acid precipitate.

[0067] It is apparent that the same dissolved amount as that in Example 1 was successfully obtained by grinding for a time shorter than that in Example 1 and that from the resulting molybdic acid solution, molybdic acid was collected with a purity as high as that in Example 1.

1. **A molybdenum refining method comprising:**
   - providing at least one molybdenum-containing ore selected from the group consisting of a molybdenum ore containing molybdenum sulfide and a molybdenum concentrate containing molybdenum sulfide, an oxidizing agent, and at least one metal salt selected from the group consisting of an alkali metal salt and an alkaline earth metal salt; and
   - mixing and grinding the at least one molybdenum-containing ore, the oxidizing agent, and the at least one metal salt to produce a reaction product containing a metal salt of molybdic acid from molybdenum sulfide; and
   - extracting molybdate ions from the reaction product using an aqueous solvent to collect molybdic acid in the aqueous solvent.

2. **The molybdenum refining method according to claim 1,** wherein the oxidizing agent is an oxidant or an oxidant salt.

3. **The molybdenum refining method according to claim 1,** wherein the oxoacid is at least one selected from the group consisting of manganous dioxide, lead oxide, silver oxide, a peroxide, nitrous acid, nitric acid, manganese acid, permanganic acid, bichromic acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, and percarbonic acid.

4. **The molybdenum refining method according to claim 3,** wherein the oxoacid is at least one selected from the group consisting of manganous dioxide, lead oxide, silver oxide, a peroxide, nitrous acid, nitric acid, manganese acid, permanganic acid, bichromic acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, and percarbonic acid.

5. **The molybdenum refining method according to claim 1,** wherein the at least one molybdenum-containing ore is a molybdenum ore containing molybdenum sulfide.

6. **The molybdenum refining method according to claim 1,** wherein the at least one molybdenum-containing ore is a molybdenum concentrate.

7. **The molybdenum refining method according to claim 1,** wherein the at least one metal salt is an alkali metal salt.

8. **The molybdenum refining method according to claim 1,** wherein the alkali metal salt is at least one selected from the group consisting of a carbonate, a bicarbonate, a halide, a sulfite, a sulfide, a nitrate, and a hydroxide.

9. **The molybdenum refining method according to claim 1,** wherein the at least one metal salt is an alkali earth metal salt.

10. **The molybdenum refining method according to claim 1,** wherein the alkali earth metal salt is at least one selected from the group consisting of a carbonate, a bicarbonate, a halide, a sulfite, a sulfide, a nitrate, and a hydroxide.

11. **The molybdenum refining method according to claim 2,** wherein the oxidizing agent is an oxidant or an oxidant salt.

12. **The molybdenum refining method according to claim 1,** wherein the oxoacid is at least one selected from the group consisting of manganous dioxide, lead oxide, silver oxide, a peroxide, nitrous acid, nitric acid, manganese acid, permanganic acid, bichromic acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, and percarbonic acid.

13. **The molybdenum refining method according to claim 2,** wherein the at least one molybdenum-containing ore is a molybdenum ore containing molybdenum sulfide.

14. **The molybdenum refining method according to claim 2,** wherein the at least one molybdenum-containing ore is a molybdenum concentrate.

15. **The molybdenum refining method according to claim 2,** wherein the at least one metal salt is an alkali metal salt.

16. **The molybdenum refining method according to claim 2,** wherein the alkali metal salt is at least one selected from the group consisting of a carbonate, a bicarbonate, a halide, a sulfite, a sulfide, a nitrate, and a hydroxide.

17. **The molybdenum refining method according to claim 2,** wherein the at least one metal salt is an alkali earth metal salt.

18. **The molybdenum refining method according to claim 2,** wherein the alkali earth metal salt is at least one selected from the group consisting of a carbonate, a bicarbonate, a halide, a sulfite, a sulfide, a nitrate, and a hydroxide.