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Martin et al.

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[54] **RHENIUM AND MOLYBDENUM SEPARATION FROM SULFIDE ORES**

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[51] **Int. Cl.**...**C01g 39/00,** C01g 47/00, C22b 49/00, C22b 61/00

[58] **Field of Search**.....423/49, 61, 53

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

A process is disclosed for the initial removal of rhenium and other metallic impurities from a sulfide bearing molybdenite ore. A relatively small amount of the molybdenum remains with the rhenium while a major portion is dissolved in water. The rhenium and this portion of the molybdenum are recovered from the other metallic impurities. The process does not evolve sulfur dioxide thus eliminates a potential air pollution problem. The process comprises reacting the ores with at least about 15 percent excess of the amount of alkali metal carbonate theoretically required to convert the molybdenum and sulfur in the ore to water soluble compound under controlled temperatures, leaching 95 percent of the molybdenum from the resulting fusion mass, oxidizing the leached fusion mass, treating the oxidized mass with water to extract the rhenium and molybdenum from the other metallic impurities and recovering the rhenium and molybdenum.

5 Claims, No Drawings

RHENIUM AND MOLYBDENUM SEPARATION FROM SULFIDE ORES

CROSS-REFERENCES TO RELATED APPLICATIONS

In co-pending U.S. Pat. application Ser. No. 123,310, filed Mar. 11, 1971, and assigned to the same assignee as the present invention, there is disclosed a process for the recovery of a variety of metals from a variety of sulfur bearing ores using sodium carbonate under conditions which prevent the evolution of certain vapors.

In co-pending U.S. Pat. application Ser. No. 255,012, filed concurrently herewith and assigned to the same assignee as the present invention, another process is disclosed which recovers the rhenium and molybdenum values. The complete molybdenum bearing stream contains the rhenium, therefore, the potential concentration of rhenium is more limited than by the present process. By separating about 95 percent of the molybdenum from the rhenium as in the present process a more concentrated aqueous solution of sodium perrhenate can be prepared.

BACKGROUND OF THE INVENTION

This invention relates to recovering molybdenum from ores. More particularly it relates to a process enabling the recovery of molybdenum and rhenium from sulfur-bearing ores without the evolution of sulfur dioxide gases.

Certain molybdenum ores are obtained as a by-product during the upgrading of copper ores. These ores are sulfide ores and contain a small amount of rhenium. Heretofore, the first step in the recovery of molybdenum from ores by one prior art process is to convert molybdenum to the oxides by heating in the presence of air. This technique has two distinct disadvantages when applied to the foregoing copper by-product ores. The sulfur is converted to sulfur dioxide and evolves a gas which either causes atmospheric pollution or requires additional equipment to prevent the pollution. Additionally, a major portion of the rhenium is oxidized to Re_2O_7 sublimes from the ore during the heating. This metal is a valuable material in short supply and recovery is desired from an economic and material availability standpoint. Another process as disclosed in U.S. Pat. No. 3,376,104 enables molybdenum and rhenium recovery by calcium hydroxide addition, however, sulfur dioxide is evolved.

It is believed, therefore, that a process which enables efficient recovery of molybdenum from sulfide ores without the evolution of sulfur dioxide and without an appreciable loss in rhenium is an advancement in the art.

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of this invention to provide a process enabling the recovery of molybdenum and rhenium from sulfide ores without an atmospheric pollution problem.

It is a further object of this invention to provide a process for the selective recovery of molybdenum and rhenium from ores containing other metallic impurities.

It is still another object of this invention to provide an aqueous solution containing molybdenum and rhenium values substantially free of other impurities and having a relatively high concentration of rhenium.

It is an additional object of this invention to provide a process for the selective recovery of molybdenum and rhenium from sulfide ores containing other metallic impurities without an appreciable loss of molybdenum or rhenium.

In accordance with one aspect of this invention these and other objects are achieved by a process employing alkali metal carbonate fusion, water leaching the fusion mass to remove a major portion of the molybdenum and the sulfur values, oxidizing the water insolubles and a subsequent water leaching step to remove the rhenium and residual molybdenum from the insolubles. The process comprises reacting the molybdenum and rhenium-bearing, sulfide ore containing other metallic impurities with controlled amounts of an alkali metal carbonate under controlled temperature to form water-soluble molybdenum, rhenium and sulfur compounds, leaching the resulting fusion mass under controlled conditions to remove about 95 percent by weight of the molybdenum, thereafter oxidizing the insolubles, water leaching these insolubles to remove the residual molybdenum and rhenium values and recovering molybdenum and rhenium values from the water used to leach the insolubles. The metallic impurities are water insoluble and remain insoluble. The oxidation can be done with oxidizing agents such as hydrogen peroxide.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

For a better understanding of the present invention, together with other and further objects, advantages, and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above description of some of the aspects of the invention.

As disclosed in previously mentioned U.S. Pat. application Ser. No. 123,310, fusion of sulfide ores prevents the evolution of sulfur dioxide and the problems associated therewith and converts the metals to a recoverable form.

In recovering both molybdenum and rhenium certain additional process control limitations are necessary to achieve high percentage recovery of both of the desired metals which are not essential when only a single metal or some other metals are recovered.

The molybdenite ores are in general sulfide ores and other metals are present in addition to rhenium and molybdenum. These metals typically include silicon, copper, iron and minor amounts of tungsten. Although rhenium is present at low levels, that is below 0.1 percent, the scarcity of the metal and its high values because of the beneficial effects imparted to other metals, particularly tungsten, make its recovery highly attractive.

The alkali metal carbonate fusion step achieves conversion of about 95 percent of the molybdenum sulfide present in the ore to alkali metal molybdate with the concurrent conversion of most of the sulfides to alkali metal sulfate. After leaching with water under proper conditions as disclosed herein, the resulting water solution contains dissolved therein greater than 95 percent of the molybdenum originally in the ore.

In the carbonate fusion step, an excess of the amount of an alkali metal carbonate theoretically required to convert the molybdenum, rhenium and sulfur to water soluble compounds is added to insure conversion of about 95 percent of the molybdenum. In theory, one mole of alkali metal carbonate is required for each mole of molybdenum, one mole for sulfur and one-half mole for rhenium. In the present process a molar excess of at least about 15 percent of that required for the theoretical conversion of the molybdenum and sulfur is necessary to prevent the sublimation of rhenium during the fusion. Generally greater than about 70 percent excess is not used for economic reasons. About 3.5 moles of carbonate per atom of molybdenum is used for most sulfide ores. Any of the alkali metal carbonates such as sodium carbonate, potassium carbonate, lithium carbonate and the like can be used, however, sodium and potassium carbonates are preferred with sodium carbonate being especially preferred.

The fusion temperatures are from about 700° to about 950°C in the absence of air. At temperatures below about 700°C the fusion mass can solidify and since no additional benefits are achieved by heating to about 950°C and some of the materials which can be formed can be evolved under certain conditions fusion temperatures above 950°C are not used.

After the ore and the alkali metal carbonates are blended together and heated to the desired temperature in the absence of air, the temperature is maintained until the evolution of carbon dioxide ceases. In most instances the fusion is complete in about 0.25 hour after the reactants have reached 700°C. Higher temperatures require less fusion time.

After the evolution of gases, primarily carbon dioxide, ceases, the molten fusion mass is cooled, crushed and leached with water.

The amount of water used to leach can be varied. Sufficient water is added so that a sample of leached insolubles do not indicate any transparent material when viewed with a microscope under polarized light. Generally about 10 to 20 parts of water per part of fusion mass on a weight basis is sufficient. Generally, a two step leaching or washing procedure is preferred with from about two-thirds to about three-fourths of the total water being initially added and the remainder added later. The two washes are then combined and concentrated to about one-third of the original volume before subsequent separation and recovery. About 95 percent of the molybdenum originally in the ore is extracted from the insolubles.

The insolubles contain, in addition to the copper, iron and other metallic impurities, essentially all of the rhenium and about 5 percent of the molybdenum. These insolubles are oxidized with an excess of an oxidizing agent such as air, oxygen or hydrogen peroxide to oxidize the sulfur values to sulfate and to insure the rhenium is in the water-soluble alkali metal perrhenate form.

The oxidized material is leached with about 3 to about 5 parts per water per part of oxidized material to recover all of the rhenium and molybdenum. The ratio of molybdenum to rhenium is about 90:1 in the resulting solution as compared to about 885:1 in the ore. This enables the production of a relatively concentrated rhenium solution which has advantages in subsequent recovery operations such as disclosed in copending application Ser. No. 255,234 and Ser. No. 255,232, both filed concurrently herewith.

Any of the various means known in the art, such as solvent extraction using alcohols, ketones and esters, various amines and tetraphenyl phosphonium and arsonium chloride, can be used to extract rhenium from the residual molybdenum. Silicate is removed by adjusting the pH with sulfuric acid as known in the art. Molybdenum can thereafter be combined with the original stream containing 95 percent of the molybdenum which is either extracted from sulfate or the sulfate is extracted from the molybdenum by techniques known in the art.

EXAMPLE 1

About 25 parts of molybdenite concentrate (assay 45% Mo, 0.051% Re, 36 percent total sulfur) is blended with about 43.2 parts of Na_2CO_3 (mole ratio of Na_2 to MoS_2 of about 3.5:1) and fused at about 750° to about 800°C in the absence of air. When the evolution of CO_2 ceases (when the foaming subsides,) the melt is poured from the container, cooled, and leached with water and filtered. The leach solution contains greater than about 95 percent of the original molybdenum and less than 5 percent of the rhenium. The insolubles contain greater than 95 percent of the rhenium and less than 5 percent of the molybdenum. The insolubles are then leached with water, and an oxidizing agent, preferably hydrogen peroxide. The insolubles are removed by filtration and contained < 1 percent of the original rhenium and < 0.05 percent of the original molybdenum. This leach solution contains the remainder of the molybdenum and approximately 95 percent of the rhenium. This solution is then in the form to separate sodium molybdate from the sodium perrhenate by either ion exchange or solvent extraction or some other technique, with the rhenium going to rhenium recovery and the molybdenum recycled to the molybdenum purification system.

While there has been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. A process for the recovery of molybdenum and rhenium values from sulfide ores containing said molybdenum and rhenium and other metallic impurities, said process comprising:

a. reacting an excess amount alkali metal carbonate with said ores in the absence of air, said excess being at least 15 percent in excess of the theoretical amount required to convert the molybdenum and sulfide present in said ore to water soluble molybdenum and sulfur compounds, and at a temperature of from about 700° to about 950°C,

b. maintaining said temperature until the evolution of carbon dioxide from said fusion mass ceases thereafter,

c. cooling and leaching said fusion mass with water to remove at least about 95 percent of the molybdenum from said fusion mass,

d. separating the leach solution from said fusion mass,

e. oxidizing the water leached fusion mass with an excess amount of an oxidizing agent that is theoretically required to convert any sulfide present to sulfate and rhenium to perrhenate, and

f. leaching the resulting oxidized material with water to recover the rhenium and remaining molybdenum values therefrom.

2. A process according to claim 1 wherein said alkali metal carbonate is sodium carbonate.

3. A process according to claim 2 wherein 3.5 moles of sodium carbonate are used per atom of molybdenum.

4. A process according to claim 3 wherein said fusion mass before oxidization is leached with about 10 to about 20 parts by weight of water per part by weight of fusion mass.

5. A process according to claim 4 wherein said oxidizing agent is selected from the group consisting of air, oxygen and hydrogen peroxide.

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