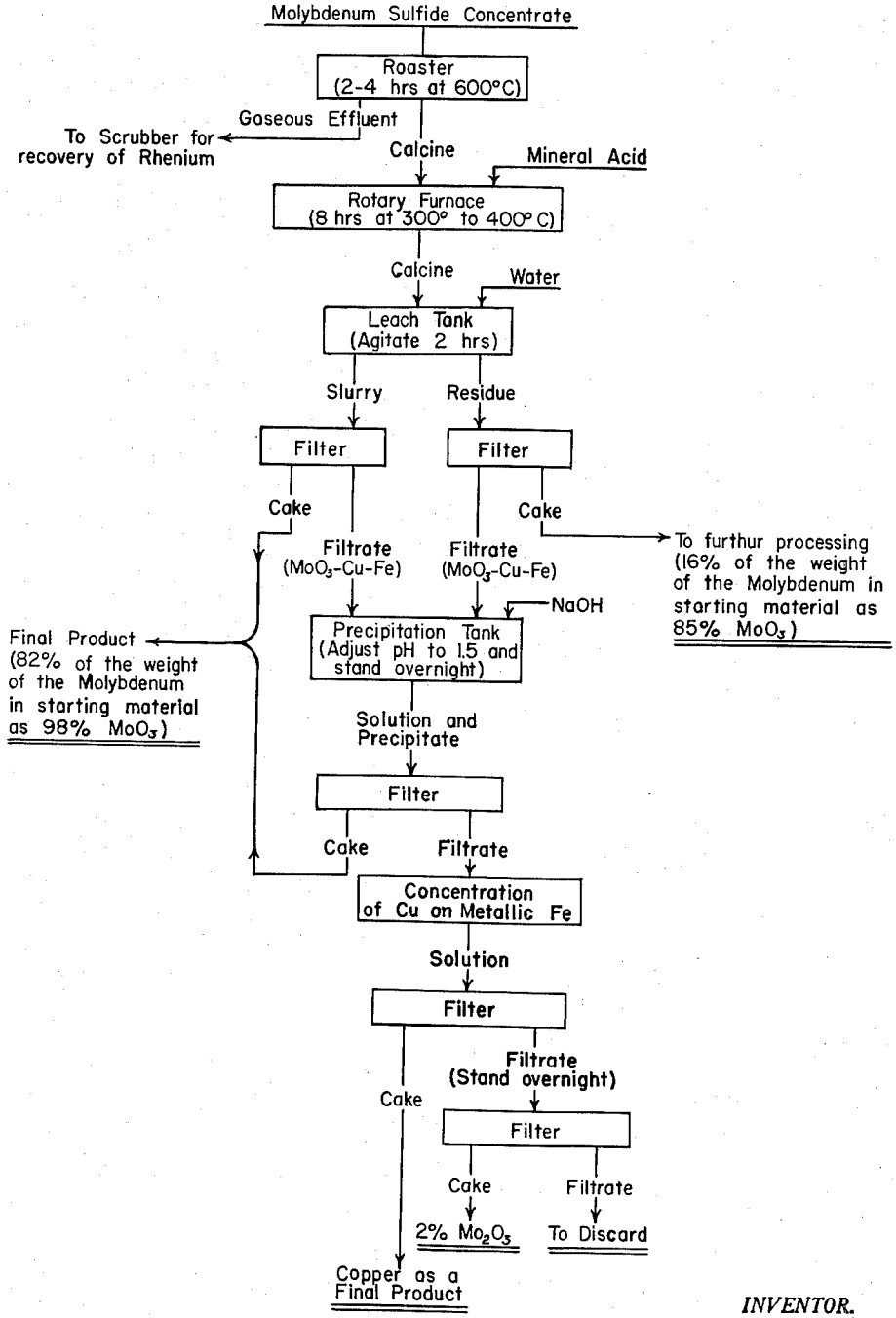
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ACID PROCESS FOR PRODUCTION OF HIGH GRADE MOLYBDENUM OXIDE

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ACID PROCESS FOR PRODUCTION OF HIGH GRADE MOLYBDENUM OXIDE

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9 Claims. (Cl. 23—140)

This invention relates to processes for the production of molybdenum oxide, and is concerned particularly with providing a process applicable to low grade molybdenum sulfide flotation concentrates.

Molybdenum oxide is presently produced commercially from molybdenum sulfide flotation concentrates by passing such concentrates through conventional roasting apparatus, such as the well known Herreshoff multiple hearth furnace, where the sulfides are oxidized by the action of heat in the presence of air.

Much of the concentrates so processed are obtained as a by-product of the recovery, by flotation, of copper minerals from low grade copper sulfide ores.

All of such concentrates are not of the same quality, however. Some are inferior as compared with others, even when run through special and expensive upgrading procedures. Accordingly, they bring a lower price on the market and are difficult to dispose of when plentiful supplies of higher grade concentrates are available. Their inferior quality is due largely to copper and iron contamination. It is to molybdenum sulfide concentrates of this type that our invention is especially, though by no means exclusively, applicable.

The present invention is closely related to one forming the subject of our copending application Serial Number 771,161, filed October 31, 1958, entitled "Acid Process for Recovery of Rhenium from Mineral Materials Containing Same," now abandoned, which is a continuation-in-part of our similarly entitled application Serial Number 592,182, filed June 18, 1956, and now abandoned. When justified by the character of the concentrates being treated, the present process will be normally carried out in conjunction with the recovery of rhenium by means of the process of our aforesaid copending application. Nevertheless, the process of this present invention may be advantageously utilized whether or not a recoverable quantity of rhenium is contained in the molybdenum sulfide concentrate being treated.

By the process, the molybdenum is solubilized, so that the resulting product may be treated by chemical, ion-exchange, or liquid-liquid extraction methods for the recovery of valuable by-products, such as copper, rhenium, and selenium, as well as for the production of an extremely high purity molybdenum oxide. Other decided advantages over the ordinary commercial roasting are that dust loss is reduced appreciably, and the usual loss of molybdenum oxide by volatilization (when roasting to the lowest possible sulfur content) is eliminated.

Impurities and valuable by-products often present in molybdenite flotation concentrates are aluminum, antimony, barium, beryllium, bismuth, calcium, chromium, cobalt, copper, germanium, indium, iron, lead, lithium, magnesium, manganese, nickel, phosphorus, rhenium, selenium, silicon, silver, sodium, sulfur, tin, titanium, vanadium, zinc, and zirconium.

By our process, impurities are removed in three ways. Some impurities, such as selenium, rhenium, phosphorus, and sulfur, are eliminated by volatilization during a preliminary roasting stage and also, thereafter, during an oxidizing acid roast which characterizes the process. Some impurities, such as copper and iron, are converted to water soluble form removable from the final calcines by water leaching. Those impurities that are not volatilized or solubilized form insoluble compounds which settle out as a sludge.

An example of the amount of purification that can be obtained by this process is shown by the upgrading of a molybdenite concentrate from 68.88 percent molybdenum sulfide to 98.7 percent molybdic oxide. By the conventional roasting method of producing molybdic oxide, the 68.88 percent molybdenum sulfide concentrate would have produced only a 62 percent molybdic oxide.

In accordance with the invention, and as a principal object thereof, molybdenum oxide of exceptionally high purity is obtained from even inferior grades of molybdenum sulfide concentrates. In addition, contaminating copper is economcially recoverable.

The process of the invention is characterized by the subjection of the molybdenum sulfide concentrates to the combined action of heat and an oxidizing, strong, mineral acid following the oxidation of a large part or all of the sulfur by preliminary roasting.

Further objects and features of the invention will become apparent from the following detailed description of the preferred procedures indicated by the flow sheet of the accompanying drawing, which represents a particular preferred practice of the process.

Referring to the drawing:

In applying our process to any given molybdenum sulfide flotation concentrate, such concentrate is preferably subjected to a preliminary roasting operation for the oxidation of a large part, if not substantially all, of its sulfur content.

In instances where the rhenium content of the concentrate is sufficiently high to make recovery practical, for example with concentrates from the Nevada Consolidated Division and the Chino Mines Division of Kennecott Copper Corporation, this preliminary roast is carefully controlled to eliminate approximately 40 to 50% of the sulfur without volatilizing any significant quantity of the rhenium or molybdenum. For this purpose, the roasting operation is generally conducted in a multiple hearth, rabble type roaster at a temperature of approximately 600 degrees centigrade for approximately two hours, as is more fully disclosed in our copending application Serial Number 771,161, previously referred to. The gaseous effluent from such operation is advantageously passed through particle collecting apparatus and a gas scrubber for recovery of that rhenium which is volatilized.

In instances where the rhenium content of the concentrate is either too insignificant to be recovered, or for some reason is not of interest to the producer of molybdenum oxide, the preliminary roasting operation is preferably carried on until most or substantially all of the sulfur is oxidized, usually, over a period of approximately four hours at about 600 degrees centigrade.

As mentioned hereinbefore, the present process is most advantageous in its application to molybdenum sulfide concentrates of inferior quality, but it may also be applied to advantage to relatively high grade concentrates where an exceptionally high purity product is desired.

In all instances, the calcine from the roaster is charged into preferably a rotary furnace, for example, a standard Bruckner type furnace, along with a quantity of a concentrated and preferably oxidizing, strong, mineral acid. While any mineral acid may be successfully utilized under oxidizing conditions, it is preferred to employ sulfuric

acid because of its oxidizing character, its availability in quantity, and its comparatively low cost.

The quantity of acid utilized in any given instance will be sufficient to thoroughly wet the concentrate, and will depend largely upon the extent to which the preliminary roasting operation has been carried. Where only 40% to 50% of the sulfur has been eliminated from the concentrate, as where rhenium is being recovered, the quantity of sulfuric acid employed should be approximately two parts of acid to one part of calcine by weight. Where approximately 80% or more of the sulfur has been eliminated, the quantity of acid can be reduced to a ratio of one part of acid to one part of the calcine. It should be borne in mind, however, that in the latter instance, a substantial portion of any rhenium present is volatilized during the preliminary roast, i.e. from 25% to 40%.

The mixture of calcined molybdenum sulfide concentrate and mineral acid is heated to a temperature within the range of from approximately 300 degrees to 400 degrees centigrade for a period of about eight hours, during which time certain of the unvolatilized contaminants in the original concentrate (notably copper and iron) are rendered soluble along with the molybdenum. The material from this acid-heating stage is an easily handled powder.

Where rhenium is to be recovered, the two stage acid-heating of our aforementioned copending application Serial Number 771,161 is applied in order to first oxidize the rhenium, without volatilizing either it or the acid, and subsequently to volatilize both the rhenium and the acid.

In all instances, the material from the rotary furnace is leached with water (preferably an equal weight) in any suitable leach tank and for a period of approximately two hours under conditions of agitation, during which time copper, iron, and any other solubilized contaminants are dissolved and leached out along with the molybdenum oxide.

The insolubles form a residue at the bottom of the tank, while the liquid and some molybdenum oxide which has already precipitated out of solution form a slurry in the upper portion of the tank.

The slurry is decanted from the leach tank and is passed to a filter of any suitable type, for example, a multiple-leaf vacuum filter, where the solids are formed into a filter cake containing a high percentage of the molybdenum present in the starting material. Such molybdenum is in the form of a high grade molybdenum oxide (approximately 82% by weight of 98.7% MoO_3 is typical).

The liquid filtrate, carrying principally molybdenum oxide, copper, and iron in solution, and filtrate resulting from filtration of the residue of the leach tank left after decanting of the slurry, are combined, and the pH thereof is adjusted to a less acid condition (e.g. to 1.5) by the addition of a basic material that will not combine with the molybdate ion (e.g. NaOH), to selectively precipitate molybdenum oxide. The solution containing the precipitated molybdenum oxide is then filtered. The resulting filter cake is combined with the previously recovered filter cake to provide a molybdenum oxide product of grade considerably higher than obtained by ordinary roasting procedures.

The filter cake resulting from filtration of the leach tank residue contains some molybdenum (16% of the weight of the molybdenum in the starting material as 85% MoO_3), which may be recovered by further processing in known manner.

The final filtrate is treated for the recovery of copper, preferably by cementation on iron. Thereafter, further filtration of such final filtrate solution yields a filter cake high in copper and a filtrate, which, after standing, may be filtered further to yield a cake containing sufficient Mo_2O_3 (approximately 2%) to have some commercial value.

Whereas this invention is here specifically set forth with respect to presently preferred procedure, it is to be understood that various changes may be made without departing from the scope of the claims which here follow.

We claim:

1. A process for producing high grade molybdenum oxide, comprising roasting a molybdenum sulfide concentrate containing impurities, including at least copper and iron, at a temperature below that at which molybdenum oxide volatilizes to oxidize a large portion of its sulfur content in the form of a gaseous effluent; thoroughly wetting the calcine from such roasting operation with a concentrated, strong, mineral acid; heating the wetted calcine in the presence of oxygen at a temperature within the range of from approximately 300 degrees to approximately 400 degrees centigrade for a sufficient length of time to oxidize the molybdenum sulfide and solubilize at least the copper and iron present; leaching the resulting calcine with water under conditions of agitation to produce an aqueous solution containing molybdenum oxide and water soluble impurities; separating the pregnant leach solution from the insoluble residue; and recovering molybdenum oxide as a high grade product free of said water soluble impurities by precipitating said molybdenum oxide from said pregnant leach solution on standing, and freeing the precipitate from the solution.

2. The process of claim 1, wherein the molybdenum sulfide concentrate is roasted for a period of approximately two hours at about 600 degrees centigrade, the gaseous effluent therefrom being treated for the recovery of rhenium; and wherein the calcine from such roasting operation is wetted with approximately twice its weight of the mineral acid.

3. The process of claim 1, wherein the molybdenum sulfide concentrate is roasted for a period of approximately four hours at about 600 degrees centigrade; and wherein the calcine from such roasting operation is wetted with approximately an equal weight of the mineral acid.

4. A process for producing high grade molybdenum oxide, comprising roasting a molybdenum sulfide concentrate containing impurities including at least copper and iron at a temperature below that at which molybdenum oxide volatilizes; to oxidize a large portion of its sulfur content in the form of a gaseous effluent; thoroughly wetting the calcine from such roasting operation with a concentrated, strong, mineral acid; heating the wetted calcine in the presence of oxygen at a temperature within the range of from approximately 300 degrees to approximately 400 degrees centigrade for a sufficient length of time to oxidize the molybdenum sulfide and solubilize at least the copper and iron present; leaching the resulting calcine with water under conditions of agitation to produce an aqueous solution containing molybdenum oxide and water soluble impurities; separating the pregnant leach solution from the insoluble residue; raising the pH of the pregnant leach solution until molybdenum oxide precipitates therefrom, leaving said water soluble impurities behind in the solution; and separating the precipitated molybdenum oxide from the solution.

5. The process of claim 4, wherein the molybdenum sulfide concentrate is roasted for a period of approximately two hours at about 600 degrees centigrade, the gaseous effluent therefrom being treated for the recovery of rhenium; and wherein the calcine from such roasting operation is wetted with approximately twice its weight of the mineral acid.

6. The process of claim 4, wherein the molybdenum sulfide concentrate is roasted for a period of approximately four hours at about 600 degrees centigrade; and wherein the calcine from such roasting operation is wetted with approximately an equal weight of the mineral acid.

7. The process of claim 1, wherein the recovery of molybdenum oxide comprises precipitating molybdenum oxide from the pregnant leach solution on standing, leaving less easily precipitated molybdenum oxide in the solution together with the water soluble impurities; sepa-

rating said solution from the precipitated molybdenum oxide; precipitating additional molybdenum oxide from the so-separated solution on standing by raising the pH of that solution to approximately 1.5; and freeing said additional molybdenum oxide from the solution.

8. The process of claim 1, wherein the mineral acid is sulfuric acid.

9. The process of claim 4, wherein the mineral acid is sulfuric acid.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,965,447 December 20, 1960

Stuart R. Zimmerley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 42, strike out "now abandoned,".

Signed and sealed this 16th day of May 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents