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PROCESS FOR EXTRACTING MOLYBDENUM FROM WULFENITE ORE

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CRUSHING ORE TO 60-80 MESH

MIXING ORE WITH NaNO₃ OR WITH NaOH

HEATING MIXTURE TO ABOUT 700°C (DECOMPOSING)

LEACHING WITH WATER

FILTERING

Na₂MoO₄ SOLUTION AGITATED WITH SOLUTION OF MgCl₂

INSOLUBLE RESIDUES HYDROXIDES OF Fe, Al, Zn, Cu, Mn, Pb, ALSO Au AND Ag IF ORIGINALLY PRESENT

FILTERING

Mo-SOLUTION ADDING CaCl₂, OR FeCl₂, OR OTHER CHLORIDES, HEATING AND AGITATING

WASTE (MIXED PRECIPITATES) CONTAINING P, As, ETC.

FILTERING

Desired product: calcium, iron, or other molybdate

Tailings solution

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The present invention relates to ore treatments, and more particularly to improved methods of producing molybdenum compounds from wulfenite ores by reacting these ores with sodium compounds.

One object of this invention is to produce substantially pure molybdenum compounds from wulfenite ore in a more economic and efficient manner.

Another object of the invention is to treat wulfenite ore with sodium compounds in such a manner that any undecomposed excess of the reagent used produces no insoluble or contaminating compound in the product obtained.

A further object of this invention is to extract molybdenum from wulfenite ore, with a high percentage yield of extraction, without requiring the high degree of comminution necessary herebefore.

Hence, when treating molybdenum ores such as wulfenite (PbMoO₄) with aqueous solutions of NaOH, Na₂CO₃, or Na₂S, the lead contained in the ore was converted into an insoluble lead compound which formed an envelope on the surface of the wulfenite grains. This envelope considerably retarded or entirely prevented the solution reaction. In order partly to overcome this, it was necessary to crush the ore to a grain size of about 200 mesh more or less. I have discovered that it is possible to obtain a 100% extraction of the molybdenum contained in wulfenite, without its being necessary to crush the ore to a fineness beyond 60 to 80 mesh (0.246 to 0.175 millimeter sieve opening), while at the same time the molybdate obtained is purer than that obtained by prior art methods. This improved result may be due to the fact that there is no formation of an interfering lead compound during the first step in the process as practiced by me. Such a water-insoluble lead compound is formed in the case of sulphide, sulphate and carbonate reagents used heretofore. However, this explanation of the reason why it is not necessary to crush the ore fine is merely a theory, and the advantageous results may be due to other causes.

The above objects of this invention are attained by treating the molybdenum ore with certain sodium compounds, preferably with sodium nitrate or sodium hydroxide, for example, and heating the mixture to the temperature range which is necessary to promote the desired reaction. In the case of sodium nitrate this temperature is considerably above the melting point of the salt. In this manner sodium molybdate is obtained which is then extracted and purified as described below.

One example of the present invention is set forth diagrammatically in the accompanying drawing in which the invention is more particularly described as applied to the treatment of wulfenite.

The ore is first pulverized to 60 to 80 mesh, and then mixed with dry sodium compound, preferably Chile saltpeter (NaNO₃). I have found that a sufficient amount of the nitrate is about five times the weight of molybdenum present in the ore. When caustic soda is used, a suitable amount is about 2.5 times the weight of the molybdenum present in the ore. A preferred method of employing the latter reagent is to dissolve it in the least amount of water required to moisten the ore uniformly, when thoroughly mixed therewith.

The mixture obtained by either of the above methods is then heated at least to the temperature of reaction of the sodium compound, to produce sodium molybdate. I have found 700° C. to be satisfactory in the case of NaNO₃. This temperature is maintained until the formation of sodium molybdate is completed. The time required has been found to be about one hour. It is not necessary to stir or rabble the ore mixture during this step.

The sintered ore is then leached with water and filtered. It has been found to be unnecessary to remove the last traces of solid matter at this stage.

Magnesium chloride, preferably in aqueous solution, is then added to the extracted molybdenum solution which is vigorously agitated, while heating, until the sodium molybdate solution is almost neutral, and until carbon dioxide (if present) is entirely eliminated. Alternatively, the magnesium chloride may be partly replaced by some other neutralizing agent, such as nitric acid, which may be economically obtained by suitable treatment of the fumes escaping from the sintering furnace when employing sodium nitrate as decomposition agent. It is not usually advisable, however, to dispense entirely with magnesium chloride as neutralizing agent, since one of its functions is to form insoluble magnesium compounds of arsenic and phosphorus, and thus eliminate these objectionable impurities from the molybdenum solution.

The molybdenum solution is then filtered free from the mixed precipitate formed, and calcium, iron, or other chloride is added to the sodium molybdate solution. The solution is heated to
boiling temperature and simultaneously agitated, until the molybdenum present is substantially all precipitated as calcium, iron, or other molybdate. The molybdate precipitated is then filtered, washed and dried.

If an objectionably large proportion of sulphur is present, it is advantageous to wash the precipitated molybdate with a considerable volume of warm water (optimum temperature about 35° C.) after decanting the waste solution and before the final filtering.

An important advantage of the use of NaNO₃ as decomposition agent is that, if any excess of NaNO₃ remains undecomposed by the initial stirring, this excess cannot react with CaCl₂ and thus contaminate the CaMoO₄ with any by-product. This advantage is most apparent by contrast with both sulphide and sulphate reagents, an excess of which would produce CaS or CaSO₄, both of which are particularly objectionable in CaMoO₄; but NaNO₃ is also almost equally advantageous as compared with carbonate or hydroxide reagents, by avoiding the formation of CaCO₃ or Ca(OH)₂ during the precipitation of CaMoO₄ by CaCl₂.

Important advantages of the use of sodium hydroxide as compared with sodium carbonate are as follows: First, NaOH has a larger proportion of available sodium. Second, it has a lower melting point and is chemically more active. Third, it is easier to decompose by magnesium chloride prior to the calcium chloride treatment; this is of considerable practical importance because any carbon dioxide entering the finally purified sodium molybdate solution will cause dilution of the product by calcium carbonate.

I claim:

1. Process for extracting molybdenum from wolframite ore which comprises comminuting and roasting the ore; mixing said roasted ore with a sodium compound selected from the group consisting of sodium nitrate and sodium hydroxide, said sodium compound being present in sufficient proportion to combine with substantially all of the molybdenum contained in the ore to form a water soluble compound of molybdenum; heating said mixture to an elevated reaction temperature; leaching the resultant mass with water to dissolve sodium molybdate therefrom; filtering off the clear impure solution of sodium molybdate; neutralizing said solution; adding thereto a quantity of magnesium chloride, sufficient to precipitate magnesium phosphate and arsenate; filtering off the purified sodium molybdate solution; and precipitating a substantially pure molybdate compound by adding to the solution a quantity of a water-soluble chloride of a metal which forms an insoluble molybdate, sufficient to precipitate substantially all of the molybdenum contained in said solution.

2. Process for extracting molybdenum from wolframite ore which comprises comminuting and roasting the ore; mixing said roasted ore with a sodium compound selected from the group consisting of sodium nitrate and sodium hydroxide, said sodium compound being present in sufficient proportion to combine with substantially all of the molybdenum contained in the ore to form a water soluble compound of molybdenum; heating said mixture to an elevated reaction temperature; leaching the resultant mass with water to dissolve sodium molybdate therefrom; filtering off the clear impure solution of sodium molybdate; adding thereto magnesium chloride in an amount sufficient to neutralize the solution and to precipitate therefrom substantially all carbonates, phosphates, and arsenates; filtering off the purified sodium molybdate solution; and precipitating a substantially pure molybdate compound by adding to the solution a quantity of a water-soluble chloride of a metal which forms an insoluble molybdate, sufficient to precipitate substantially all of the molybdenum contained in said solution.

3. Process for extracting molybdenum from wolframite ore which comprises comminuting and roasting the ore; mixing said roasted ore with a quantity of sodium nitrate sufficient to combine with substantially all of the molybdenum contained in the ore to form sodium molybdate; heating said mixture to a temperature of about 700° C. sufficient to ensure chemical reaction; leaching the resultant mass with water to dissolve sodium molybdate therefrom; filtering off the impure solution of sodium molybdate; neutralizing said solution and adding thereto a quantity of magnesium chloride sufficient to precipitate magnesium phosphate and arsenate; filtering off the purified sodium molybdate solution; and adding calcium chloride to said solution to precipitate therefrom substantially pure calcium molybdate.

4. Process for extracting molybdenum from wolframite ore which comprises comminuting and roasting the ore; mixing said roasted ore with a quantity of sodium hydroxide sufficient to combine with substantially all of the molybdenum contained in the ore to form sodium molybdate; heating said mixture to a temperature sufficient to ensure chemical reaction; leaching the resultant mass with water to dissolve sodium molybdate therefrom; filtering off the impure solution of sodium molybdate; neutralizing said solution and adding thereto a quantity of magnesium chloride sufficient to precipitate magnesium phosphate and arsenate; filtering off the purified sodium molybdate solution; and adding ferric chloride to said solution to precipitate therefrom substantially pure ferric molybdate.

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