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**PROCESS FOR RECOVERING COPPER AND MOLYBDENUM FROM ORE CONCENTRATES**

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No Drawing. Filed Apr. 27, 1967, Ser. No. 634,085

Int. Cl. C22b 3/00, 1/02, 49/00

U.S. Cl. 75-84

18 Claims

**ABSTRACT OF THE DISCLOSURE**

A process for recovering molybdenum from ore concentrates containing copper and molybdenum sulfides which comprises roasting the concentrates in a fluid bed reactor to produce a variety of copper and molybdenum compounds; dissolving these compounds in dilute sulfuric acid; extracting the molybdenum compounds from the acid solution with a tertiary amine solvent; stripping the solvent of molybdenum and other metals with an aqueous solution of ammonium hydroxide; precipitating metals other than molybdenum from the strip solution; recovering the molybdenum by precipitation as ammonium paramolybdate, dimolybdate or tetramolybdate; and optionally, converting the ammonium paramolybdate, dimolybdate, or tetramolybdate so obtained to molybdenum trioxide by calcining or to molybdenum dioxide or molybdenum metal by reduction with hydrogen.

This invention relates to a process for recovering copper and molybdenum from ore concentrates of copper and molybdenum sulfides.

Copper and molybdenum are frequently found together as sulfides in ore bodies throughout the world, and are customarily removed from these ore bodies and separated from each other by differential froth flotation. However, both minerals float rather easily so that it is difficult to separate the two minerals from each other. As a result, the recovery of marketable molybdenum concentrates [concentrates containing less than one percent (1%) copper] is usually poor, e.g., of the order of 60 percent to 80 percent. Further, the cleaning of these molybdenum concentrates usually requires additional grinding in which further molybdenum is lost as non-floatable slimes, thereby further reducing the yield of molybdenum.

Molybdenum is generally recovered from the molybdenum concentrates obtained in such manner by first roasting the concentrates to convert the molybdenum sulfide to molybdenum trioxide, and then purifying the molybdenum trioxide so obtained and reducing it to the metallic state by any of a number of practices. The copper concentrates recovered are reduced to metal by standard copper smelting procedures.

In accordance with the instant invention, separation of copper and molybdenum from ores containing sulfides of these minerals is attained by a process which permits the use of concentrates of copper and molybdenum sulfides obtained by the bulk flotation of such ores rather than by differential flotation as in the prior art processes, and which does not require that the concentrates be completely cleaned out of the gangue material. As a result of this procedure, a greater recovery of copper and molybdenum from the ore bodies is obtained.

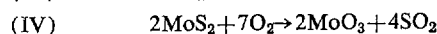
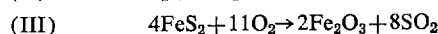
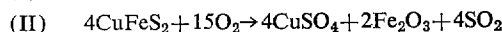
Thus, according to the instant invention, copper and molybdenum can be recovered from bulk concentrates of gangue materials containing copper and molybdenum sulfides, or from mixtures of copper and molybdenum sulfide concentrates obtained by the bulk flotation of ores containing these materials, by a process which comprises roasting the concentrates in a fluid bed reactor to produce a variety of copper and molybdenum compounds; dissolving these compounds in dilute sulfuric acid; extracting

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the molybdenum compounds from the acid solution with a tertiary amine solvent; stripping the solvent of molybdenum and other metals with an aqueous solution of ammonium hydroxide; precipitating metals other than molybdenum from the strip solution; recovering the molybdenum by precipitation as ammonium paramolybdate, dimolybdate, or tetramolybdate; and optionally, converting the ammonium paramolybdate, dimolybdate or tetramolybdate so obtained to molybdenum trioxide by calcining or to molybdenum dioxide or molybdenum metal by reduction with hydrogen; and recovering copper, if desired, from the sulfuric acid extraction raffinate by electrolysis.

Low grade concentrates of copper and molybdenum sulfides can be employed in the process of the instant invention as well as high grade concentrates containing, for example, as much as forty percent (40%) molybdenum and eight percent (8%) copper. The only requirement is that sufficient sulfur be present in the concentrate to sustain autogenous combustion in the fluid bed reactor, otherwise a secondary source of fuel must be supplied to sustain combustion.

Roasting of the concentrate in the fluid bed reactor is effected at temperatures and with a sufficient amount of oxygen to substantially convert any copper present to copper sulfate and copper oxide, and to convert most of the molybdenum present to a molybdenum complex containing molybdenum oxides wherein the molybdenum has a valence of both 5 and 6. Some molybdenum sulfate and/or sulfite is also produced during the roasting, and any iron present is converted to acid insoluble ferric oxide. The total amount of oxygen fed to the roaster should be at least about 130 percent, preferably at least about 150 percent, of the theoretical amount necessary to convert the copper sulfide, molybdenum sulfide and iron sulfide present to copper sulfate, molybdenum trioxide, ferric oxide, and sulfur dioxide according to the equations:



The oxygen can be fed to the roaster either as oxygen gas itself, or diluted with other gases. Any inert gas which is unreactive under the roasting conditions can be employed as a diluent for the oxygen. When oxygen is employed with other diluent gases, it is most preferably employed in the form of air.

The oxygen or oxygen-containing gas should be fed to the roaster at a rate sufficient to fluidize the ore concentrates in the roaster and for a sufficient period of time to effect the desired degree of oxidation. Since the ore concentrates readily agglomerate as roasting continues, it may be necessary to increase the velocity rate of the gas as roasting continues to maintain the concentrates in a fluidized condition. In general, a space velocity of from about 1.0 cubic foot per second to about 2.5 cubic feet per second (determined at reactor temperatures) of fluidizing gas per square foot of reactor area can be employed, with about 1.5 cubic feet per second to about 2.0 cubic feet per second of fluidizing gas per square foot of reactor area being preferred. By "reactor area" is meant the minimum cross sectional area of the fluidized zone of the reactor.

Roasting of the ore concentrates in the fluid bed is conducted at a temperature above about 580° C., preferably above about 640° C., as lower temperatures tend to increase the solubility of the iron in the sulfuric acid during the acid extraction step. Temperatures above about 720° C. are not recommended as such temperatures tend to decrease the acid solubility of the copper.

If desired, a small amount of sodium sulfate may be added to the roaster feed to enhance agglomeration of the ore concentrates and increase sulfation of the copper. Generally, from about 0.1 part by weight to about 5 parts by weight, preferably from about 1 part by weight to about 3 parts by weight, of the sodium sulfate per 100 parts by weight of the ore concentrate is employed.

After the ore concentrates have been roasted to the desired degree, the resulting agglomerates are treated with dilute sulfuric acid to dissolve the copper and molybdenum compounds present. Sulfuric acid solutions containing about 100 grams of sulfuric acid per liter are generally suitable. Heating is unnecessary as these compounds readily dissolve in the acid without heating. Temperatures of from about 30° C. to about 105° C. are preferred. A sufficient amount of acid should be employed to avoid supersaturating the solution with copper and molybdenum, and preferably, the amount of acid employed should be sufficient so that the extract solution contains no more than about 30 grams of molybdenum and 100 grams of copper per liter of solution. While the initial acid concentration is in no way critical, it is preferred that the final solution containing the extract have a pH of no more than about 1. Higher pH values than 1 lower extraction and no improvement in results is obtained with lower pH values.

After the copper and molybdenum compounds have dissolved in the sulfuric acid, the solution is separated from insolubles such as ferric oxide by conventional means, e.g., by filtration. The molybdenum is then extracted from the acid solution by means of a water insoluble, high molecular weight tertiary amine (including amides), and the copper is recovered from the solvent extraction raffinate by conventional electrolysis procedures. During the electrolysis, sulfuric acid is recovered which can be re-employed in the extraction of copper and molybdenum from the roasted ore concentrates.

Any water insoluble, high molecular weight tertiary amine can be employed to extract the molybdenum from the sulfuric acid solution. The amine forms a complex with the molybdenum anions and other heavy metal anions present, including arsenic, phosphorous, bismuth, antimony, lead, selenium, and silicon, and readily separates from the aqueous extraction raffinate which contains the copper.

The most preferred tertiary amines are those in which the groups attached to nitrogen contain from 6 to 10 carbon atoms, although any tertiary amine of sufficiently high molecular weight to be insoluble in water can be employed. Illustrative of the amines which can be employed are trihexylamine, triheptylamine, trioctylamine, triisooctylamine, trinonylamine, tridecylamine, triisodecylamine, tridodecylamine, trioctadecylamine, tricaprylamine, N,N-dioctylaniline, and the like.

The tertiary amine should be employed in an amount of from about 5 parts by weight to about 150 parts by weight per 100 parts by weight of the sulfuric acid solution.

Most preferably the amine is employed in an amount sufficient to provide an extract solution containing about two and one-half (2½) parts by weight of the amine for each one (1) part by weight of molybdenum. To aid in the extraction, it is desirable to employ an aromatic diluent with the amine together with a small amount of a high molecular weight alcohol modifier which acts as a wetting agent and prevents the formation of third phases and emulsions. Generally from about 50 parts by volume to about 100 parts by volume of the aromatic diluent and from about 2 parts by volume to about 5 parts by volume of the high molecular weight alcohol modifier per 5 parts by volume of the amine are suitable. Any aromatic diluent which is inert under the conditions of its use can be employed, while any alcohol containing at least about 8 carbon atoms, preferably from about 10 to about 12 carbon atoms, can be employed. Typical aromatic diluents include benzene, toluene, xylene, naphthalene, anthracene, aromatic petroleum solvents, and the like. Among the al-

cohols which can be employed are octanol, nonanol, decanol, isodecanol and the like.

An aqueous solution of ammonium hydroxide is then employed to strip the tertiary amine of molybdenum and other metals which may be present. Generally, as little solution as possible should be used so that the final strip solution will be as concentrated with molybdenum as possible, e.g. solutions containing as much as 200 grams per liter of molybdenum can be obtained. While the initial concentration of ammonium hydroxide in the solution is in no way critical, the final solution should have a pH of above 7.5.

After the molybdenum and other metals have been stripped from the tertiary amine mixture, the metals other than molybdenum can be precipitated from the strip solution. Precipitation of compounds containing such metals can be effected by heating the strip solution at a temperature of about 50° C. at a pH of 7.3 or higher. A strong mineral acid, i.e., sulfuric acid, hydrochloric acid or nitric acid, can be used to lower the pH if desired. If desired, a small amount of an aluminum, iron or magnesium compound, such as aluminum sulfate, magnesium sulfate, ferric sulfate, magnesium hydroxide, magnesium oxide, and the like, e.g., from about 5 grams to about 50 grams per liter of solution, can be added to the solution to aid in the precipitation of the metal compounds. The molybdenum is not precipitated and remains in solution as ammonium paramolybdate. To help prevent precipitation of the molybdenum as a partially reduced silicomolybdate, a small amount of an oxidizing agent such as hydrogen peroxide, sodium chlorate, and the like can be added, e.g., as little as about one milliliter of a 30 percent aqueous solution of hydrogen peroxide per liter of solution is often sufficient to maintain the molybdenum in solution as the paramolybdate.

Any metal compound impurities which separate from the strip solution are removed by conventional means, e.g., by filtration. The molybdenum is then recovered from the strip solution by precipitation as ammonium paramolybdate by evaporating the solution below 50° C., or as ammonium dimolybdate by evaporating above 50° C., or as ammonium tetramolybdate by heating to a temperature of 70° C. or higher and adjusting the pH of the solution to about 2.5 with a strong mineral acid, i.e., sulfuric acid, hydrochloric acid, or nitric acid.

If desired, the ammonium paramolybdate, dimolybdate or tetramolybdate so obtained may be converted to molybdenum trioxide by calcining at a temperature of from about 350° C. to about 600° C., preferably from about 400° C. to about 450° C. Alternatively, these molybdates may be converted to molybdenum dioxide or molybdenum metal by hydrogen reduction, e.g., by heating at a temperature of from about 500° C. to about 750° C., preferably from about 575° C. to about 675° C., to convert to molybdenum dioxide, and then at a temperature of from about 800° C. to about 1100° C., preferably from about 950° C. to about 1000° C. to convert the molybdenum.

The following are illustrative of the various steps employed in the process of the instant invention.

#### ROASTING-LEACHING

A concentrate of copper and molybdenum sulfides obtained by the bulk flotation of ore containing such sulfides was roasted at the rate of approximately twenty-five (25) grams per minute in a fluid bed roaster at an average temperature of 640° C. The bed of the roaster was four feet deep and four inches in diameter. The concentrate contained 5.6% molybdenum, 21.4% copper, 29.6% sulfur, and 22.3% iron, and was mixed with 2.5 parts by weight of sodium sulfate per 100 parts by weight concentrate. Air was fed to the reactor at a space velocity of 1.7 cubic feet per second per square foot of reactor area until 190 percent of the theoretical

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amount required for oxidation in accordance with equations I through IV had been supplied.

The flue gas from the reactor was passed through a cyclone situated above the bed where solid particles entrained in the gas were removed. These particles amounted to ten (10) percent of the total solids, with the remaining ninety (90) percent remaining as bed product. The bed product contained 6.0% molybdenum and 23.3% copper.

Fifty (50) grams of the bed product was leached with one hundred and ninety (190) grams of water containing ten (10) grams of sulfuric acid at a temperature at 80° C. for two hours. The resulting slurry had a pH of 0.9 and contained 19.3 grams of undissolved solids. The solid residue, which was removed by filtration, contained 0.28% copper and 1.12% molybdenum. The residue was washed with water and the wash water added to the filtrate to produce a total of 250 milliliters. The combined filtrate and wash water contained 11 grams per liter of molybdenum and 47 grams per liter of copper. This represented a recovery of 99.6% copper and 92.7% molybdenum from the calcined ore concentrate.

#### MOLYBDENUM EXTRACTION—STRIPPING

A sulfuric acid leach solution obtained in a manner similar to that described above and containing from 54 to 58 grams per liter of copper and 13.0 to 13.6 grams per liter of molybdenum was continuously fed to a solvent extraction unit at a rate of 144 milliliters per minute over a 24 hour period where it was contacted with 103 milliliters per minute of an extraction solvent containing 5 volume percent of Adogen 364 (a mixture of trinonyl amines), 2 volume per cent of isodecanol and 93 volume percent of SC-150 (an aromatic petroleum solvent). The extract solution contained an average of 19 grams per liter of molybdenum, and the solvent extraction raffinate contained an average of 0.006 gram per liter of molybdenum. This represented an average recovery of molybdenum from the leach solution of 99.95%.

The extract solution was continuously washed with 22 milliliters per minute of water, and stripped with 11 milliliters per minute of 3 molar ammonium hydroxide solution. The final strip solution had a pH of about 9 and contained 151 to 173 grams of molybdenum per liter and only 0.05 to 0.08 gram of copper per liter.

#### PURIFICATION OF STRIP SOLUTION

A strip solution obtained in a manner similar to that described above was analyzed and found to contain 141 grams per liter of molybdenum, 0.9 gram per liter of phosphorus, 0.034 gram per liter of arsenic, 0.1 gram per liter of silicon, 0.02 gram per liter of copper, 0.01 gram per liter of bismuth, and 0.01 gram per liter of iron. The pH of the solution was 9.0.

Six tenths of a gram (0.6 g.) of magnesium oxide was added to a 120 milliliter portion of the solution and the solution was heated at a temperature of 50° C. for two hours with stirring and then filtered. The filtrate contained less than 0.03 gram per liter of phosphorus, arsenic and silicon.

#### CRYSTALLIZATION OR PRECIPITATION

##### (A) Crystallization as ammonium dimolybdate

One liter of purified strip solution obtained in a manner similar to that described above and containing 113 grams per liter of molybdenum was evaporated at approximately 100° C. until a 95 percent reduction in volume had been effected. Approximately 81 percent of the molybdenum present crystallized as ammonium dimolybdate.

##### (B) Precipitation as ammonium tetramolybdate

Three hundred (300) milliliters of purified strip solution obtained in a manner similar to that described above and containing 124 grams per liter of molybdenum was heated to 70° C. and acidified to a pH of 2.5 with 30

grams of sulfuric acid. After stirring for 6½ hours, approximately 99.5 percent of the molybdenum present precipitated as anhydrous ammonium tetramolybdate. Less than 0.1 percent of the tetramolybdate dissolved when washed with 60 milliliters of water.

#### MOLYBDENUM REDUCTION

Twenty (20) pounds per hour of ammonium tetramolybdate was fed to a seven foot long, externally heated calciner having an inner diameter of 6½ inches. One hundred and fifty (150) standard cubic feet of hydrogen per hour was fed counter currently through the calciner. The calciner discharge temperature was 593° C. The product obtained in this manner was molybdenum dioxide.

Five and three-tenths pounds per hour (5.3 lbs./hr.) of the molybdenum dioxide so produced was again fed to the calciner while 230 standard cubic feet of hydrogen per hour was fed counter currently through the calciner. The calciner discharge temperature was 936° C. The product obtained in this manner contained 99.5 percent molybdenum and only 0.53 percent oxygen.

What is claimed is:

1. A process for recovering molybdenum from concentrates containing copper and molybdenum sulfides which comprises roasting the concentrates in a fluid bed reactor at a temperature and with a sufficient amount of oxygen to substantially convert any copper present to copper sulfate and copper oxide, and to convert most of the molybdenum present to a molybdenum complex containing molybdenum oxides wherein the molybdenum has a valence of both 5 and 6; treating the roasted concentrates with dilute sulfuric acid to dissolve the copper and molybdenum compounds; removing insolubles from the sulfuric acid solution; extracting the molybdenum from the sulfuric acid solution with a water insoluble tertiary amine; stripping the tertiary amine of molybdenum with an aqueous solution of ammonium hydroxide to produce a final solution having a pH above 7.5; precipitating metals other than molybdenum from the solution by heating the solution at a temperature of about 50° C. at a pH of at least 7.3, and removing the precipitated metal compounds from the solution; and evaporating the solution below 50° C. to precipitate the molybdenum as ammonium paramolybdate.

2. A process as in claim 1 wherein the ammonium paramolybdate is reduced with hydrogen to produce a member selected from the group consisting of molybdenum dioxide and molybdenum metal.

3. A process as in claim 1 wherein roasting of the concentrates is effected at a temperature above about 580° C. with an amount of oxygen at least about 130 percent of the theoretical amount necessary to convert the copper sulfide, molybdenum sulfide and any iron sulfide present to copper sulfate, molybdenum trioxide, ferric oxide, and sulfur dioxide; the roasted concentrates are treated with dilute sulfuric acid at a temperature of from about 30° C. to about 105° C. to produce a solution having a pH of no more than about 1 and containing no more than about 30 grams of molybdenum and 100 grams of copper per liter of solution; and the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is one in which the groups attached to nitrogen contain from 6 to 10 carbon atoms and is employed in an amount of from about 5 parts by weight to about 150 parts by weight per 100 parts by weight of the sulfuric acid solution.

4. A process as in claim 3 wherein roasting of the concentrates is effected at a temperature above about 640° C. to about 720° C. with an amount of oxygen at least about 150 percent of the theoretical amount necessary to convert the copper sulfide, molybdenum sulfide and any iron sulfide present to copper sulfate, molybdenum trioxide, ferric oxide, and sulfur dioxide, with the fluidizing gas being supplied at a space velocity of from about 1.0 cubic foot per second to about 2.5 cubic feet per second per square foot of reactor area;

and the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is employed with from about 50 parts by volume to about 100 parts by volume of an aromatic diluent and from about 2 parts by volume to about 5 parts by volume of an alcohol per 5 parts by volume of the amine, said alcohol containing at least about 8 carbon atoms.

5. A process as in claim 4 wherein the fluidizing gas is supplied at a space velocity of from about 1.5 cubic feet per second to about 2.0 cubic feet per second per square foot of reactor area; the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is employed in an amount sufficient to provide an extract solution containing about 2.5 parts by weight of the amine for each 1 part by weight of molybdenum; and the alcohol employed with the tertiary amine contains from about 10 to about 12 carbon atoms.

6. A process as in claim 5 wherein the ammonium paramolybdate is reduced with hydrogen to produce a member selected from the group consisting of molybdenum dioxide and molybdenum metal.

7. A process for recovering molybdenum from concentrates containing copper and molybdenum sulfides which comprises roasting the concentrates in a fluid bed reactor at a temperature and with a sufficient amount of oxygen to substantially convert any copper present to copper sulfate and copper oxide, and to convert most of the molybdenum present to a molybdenum complex containing molybdenum oxides wherein the molybdenum has a valence of both 5 and 6; treating the roasted concentrates with dilute sulfuric acid to dissolve the copper and molybdenum compounds; removing insolubles from the sulfuric acid solution; extracting the molybdenum from the sulfuric acid solution with a water insoluble tertiary amine; stripping the tertiary amine of molybdenum with an aqueous solution of ammonium hydroxide to produce a final solution having a pH above 7.5; precipitating metals other than molybdenum from the solution by heating the solution at a temperature of about 50° C. at a pH of at least 7.3, and removing the precipitated metal compounds from the solution; and evaporating the solution above 50° C. to precipitate the molybdenum as ammonium dimolybdate.

8. A process as in claim 7 wherein the ammonium dimolybdate is reduced with hydrogen to produce a member selected from the group consisting of molybdenum dioxide and molybdenum metal.

9. A process as in claim 7 wherein roasting of the concentrates is effected at a temperature above about 580° C. with an amount of oxygen at least about 130 percent of the theoretical amount necessary to convert the copper sulfide, molybdenum sulfide and any iron sulfide present to copper sulfate, molybdenum trioxide, ferric oxide, and sulfur dioxide; the roasted concentrates are treated with dilute sulfuric acid at a temperature of from about 30° C. to about 105° C. to produce a solution having a pH of no more than about 1 and containing no more than about 30 grams of molybdenum and 100 grams of copper per liter of solution; and the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is one in which the groups attached to nitrogen contain from 6 to 10 carbon atoms and is employed in an amount of from about 5 parts by weight to about 150 parts by weight per 100 parts by weight of the sulfuric acid solution.

10. A process as in claim 9 wherein roasting of the concentrates is effected at a temperature above about 640° C. to about 720° C. with an amount of oxygen at least about 150 percent of the theoretical amount necessary to convert the copper sulfide, molybdenum sulfide and any iron sulfide present to copper sulfate, molybdenum trioxide, ferric oxide, and sulfur dioxide, with the fluidizing gas being supplied at a space velocity of from about 1.0 cubic foot per second to about 2.5 cubic feet per second per square foot of reactor area; and the water

insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is employed with from about 50 parts by volume to about 100 parts by volume of an aromatic diluent and from about 2 parts by volume to about 5 parts by volume of an alcohol per 5 parts by volume of the amine, said alcohol containing at least about 8 carbon atoms.

11. A process as in claim 10 wherein the fluidizing gas is supplied at a space velocity of from about 1.5 cubic feet per second to about 2.0 cubic feet per second per square foot of reactor area; the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is employed in an amount sufficient to provide an extract solution containing about 2.5 parts by weight of the amine for each 1 part by weight of molybdenum; and the alcohol employed with the tertiary amine contains from about 10 to about 12 carbon atoms.

12. A process as in claim 11 wherein the ammonium dimolybdate is reduced with hydrogen to produce a member selected from the group consisting of molybdenum dioxide and molybdenum metal.

13. A process for recovering molybdenum from concentrates containing copper and molybdenum sulfides which comprises roasting the concentrates in a fluid bed reactor at a temperature and with a sufficient amount of oxygen to substantially convert any copper present to copper sulfate and copper oxide, and to convert most of the molybdenum present to a molybdenum complex containing molybdenum oxides wherein the molybdenum has a valence of both 5 and 6; treating the roasted concentrates with dilute sulfuric acid to dissolve the copper and molybdenum compounds; removing insolubles from the sulfuric acid solution; extracting the molybdenum from the sulfuric acid solution with a water insoluble tertiary amine; stripping the tertiary amine of molybdenum with an aqueous solution of ammonium hydroxide to produce a final solution having a pH above 7.5; precipitating metals other than molybdenum from the solution by heating the solution at a temperature of about 50° C. at a pH of at least 7.3, and removing the precipitated metal compounds from the solution; and heating the solution to a temperature of at least 70° C. and adjusting the pH of the solution to about 2.5 with a strong mineral acid to precipitate the molybdenum present as ammonium tetramolybdate.

14. A process as in claim 13 wherein the ammonium tetramolybdate is reduced with hydrogen to produce a member selected from the group consisting of molybdenum dioxide and molybdenum metal.

15. A process as in claim 13 wherein roasting of the concentrates is effected at a temperature above about 580° C. with an amount of oxygen at least about 130 percent of the theoretical amount necessary to convert the copper sulfide, molybdenum sulfide and any iron sulfide present to copper sulfate, molybdenum trioxide, ferric oxide, and sulfur dioxide; the roasted concentrates are treated with dilute sulfuric acid at a temperature of from about 30° C. to about 105° C. to produce a solution having a pH of no more than about 1 and containing no more than about 30 grams of molybdenum and 100 grams of copper per liter of solution; and the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is one in which the groups attached to nitrogen contain from 6 to 10 carbon atoms and is employed in an amount of from about 5 parts by weight to about 150 parts by weight per 100 parts by weight of the sulfuric acid solution.

16. A process as in claim 15 wherein roasting of the concentrates is effected at a temperature above about 640° C. to about 720° C. with an amount of oxygen at least about 150 percent of the theoretical amount necessary to convert the copper sulfide, molybdenum sulfide and any iron sulfide present to copper sulfate, molybdenum trioxide, ferric oxide, and sulfur dioxide, with the fluidizing gas being supplied at a space velocity of from about 1.0 cubic foot per second to about 2.5 cubic feet per second

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per square foot of reactor area; and the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is employed with from about 50 parts by volume to about 100 parts by volume of an aromatic diluent and from about 2 parts by volume to about 5 parts by volume of an alcohol per 5 parts by volume of the amine, said alcohol containing at least about 8 carbon atoms.

17. A process as in claim 16 wherein the fluidizing gas is supplied at a space velocity of from about 1.5 cubic feet per second to about 2.0 cubic feet per second per square foot of reactor area; the water insoluble tertiary amine employed to extract the molybdenum from the sulfuric acid solution is employed in an amount sufficient to provide an extract solution containing about 2.5 parts by weight of the amine for each 1 part by weight of molybdenum; and the alcohol employed with the tertiary amine contains from about 10 to about 12 carbon atoms.

18. A process as in claim 17 wherein the ammonium

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tetramolybdate is reduced with hydrogen to produce a member selected from the group consisting of molybdenum dioxide and molybdenum metal.

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23—19, 23, 24, 51, 140; 75—109, 117, 121