



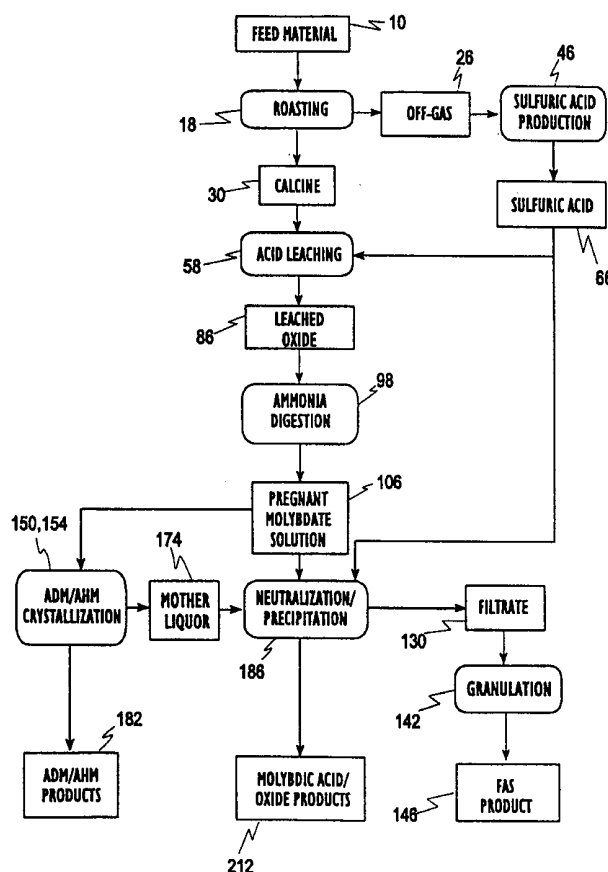
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(54) Title: METHOD FOR PRODUCING MOLYBDENUM CHEMICALS FROM SULFIDIC MATERIALS

(57) Abstract

The integrated process of the subject invention is directed to the production of high purity molybdenum chemical products from molybdenum sulfide containing materials by a series of steps, including roasting, sulfuric acid leaching of the calcine to remove impurities from the calcine, ammonia digesting of the calcine to form a pregnant molybdate solution containing dissolved molybdenum, and recovery of the dissolved molybdenum by crystallization and/or molybdic acid precipitation. The process is a "zero discharge" process in that all process waste streams are combined to produce a ferrous ammonium sulfate fertilizer byproduct.



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METHOD FOR PRODUCING MOLYBDENUM CHEMICALS FROM SULFIDIC MATERIALS

FIELD OF THE INVENTION

5 The present invention relates generally to the recovery of molybdenum from molybdenum sulfides and specifically to the production of high-purity molybdenum chemicals from molybdenum oxides derived from oxidation of molybdenum sulfides containing impurities.

BACKGROUND OF THE INVENTION

10 Molybdenum is an important raw material in many industrial processes. Molybdenum is used as an alloying metal in steel making, as catalysts in the petroleum refining and petrochemical industries, as a metal and alloy in high-tech applications, and as lubricants. The major source of molybdenum is no longer primary molybdenum sulfide concentrates from molybdenum mining operations but is byproduct molybdenum sulfide concentrates from copper mining operations. Another emerging source is 15 molybdenum sulfides produced during chemical processing of molybdenum containing catalysts, scraps and other materials. These sulfidic materials may contain one or more metal impurities such as calcium, copper, iron, nickel etc. that are not acceptable in high-purity molybdenum chemicals, particularly in molybdic oxide and ammonium molybdates used in the production of molybdenum metal, superalloys and catalysts.

20 Molybdenum sulfide concentrates are commonly air roasted in multiple-hearth roasters to convert molybdenum sulfide to technical-grade molybdenum trioxide, MoO_3 , (known as "Tech Oxide"). To remove sulfur dioxide from the roaster off-gas, molybdenum roasting operations use an acid plant or a scrubber. The acid plant is expensive to operate because additional sulfur typically has to be purchased to facilitate 25 sulfuric acid production. The scrubber is also expensive to operate because the sulfuric acid neutralization product, gypsum, has high disposal costs.

To remove additional impurities, such as copper and lead from the calcined product of the roasting step, molybdenum producers leach it with hydrochloric acid or pug mix the calcined product with sulfuric acid followed by secondary roasting and water 30 leaching. The hydrochloric acid leach causes the leach residue to have a relatively high chlorine content(0.17 to 0.38 weight percent) which is not commercially acceptable. The

secondary roasting process requires several reagents and additional cost intensive steps and is therefore very expensive. Due to low recoveries, a significant amount of molybdenum can also be lost in the wastes from either of these processes.

5 For applications requiring high purity molybdates such as catalyst manufacture, the calcined product can be chemically purified to remove silica, alumina, calcium or lead molybdate and other gangue materials. In the process, ammonia dissolves molybdenum trioxide, thereby rejecting silica and other mineral impurities. The process, however, can fail to dissolve 5% or more of the molybdenum trioxide, which is lost to the residue, and can have metallic impurities such as alkali metals build up in the large volume of
10 ammonium molybdate solution that is recirculated from a crystallization step, thereby adversely affecting the quality of the product.

In the current commercial practice, production of high-purity molybdenum chemicals requires high-grade primary molybdenite concentrates as starting feedstock. At the same time, an increasing quantity of low-cost byproduct molybdenite concentrates
15 are being produced by copper mines and molybdenum sulfide precipitates are being produced at molybdenum processing plants. Thus, there is a need for a conversion process to produce high-purity molybdenum chemicals from low-grade sulfidic feed materials.

20 There is also a need for a process for converting molybdenum sulfides into molybdenum oxides in which sulfur is disposed of in a form other than sulfuric acid or gypsum.

25 There is a further need for a process for converting molybdenum sulfides into molybdenum oxides in which the recovery of molybdenum is relatively high and therefore a significant part of the molybdenum is not lost in residues and downgraded products.

There is a further need for a process for converting molybdenum sulfides into molybdenum oxides and/or molybdenum sulfides into molybdates which does not consume large amounts of energy and/or pose environmental problems.

30 There is a further need for a process for converting low-grade molybdenum sulfides into high-purity molybdenum oxides and/or ammonium molybdates in which impurities such as aluminum, copper, calcium, iron and silica are totally removed and do not end up in waste streams that require costly disposal.

SUMMARY OF THE INVENTION

These and other needs are addressed by the molybdenum recovery process of the present invention. In one configuration, the method removes metal impurities from a molybdenum oxide-containing material by contacting the material with sulfuric acid in a slurry to solubilize the metal impurities in a leach solution, while maintaining a substantial portion of the molybdenum oxide in the material. Typically, no more than about 3% of the molybdenum oxide is solubilized during leaching. The metal impurities that are solubilized in the leach solution include aluminum, cadmium, calcium, copper, iron, lead, magnesium, nickel, potassium, sodium, zinc and mixtures thereof. The material may be any molybdenum oxide-containing material, such as the calcined material from a roasting process.

The leaching conditions are selected to solubilize the metal impurities but not the molybdenum oxide. The lixiviant preferably has, during the leaching step, a pH ranging from about pH 0.5 to about pH 1.5, and a temperature ranging from about 80 °C to about 100 °C. During leaching, the slurry preferably contains from about 10 to about 50 percent solids by weight. After the leaching step, the leach solution preferably comprises no more than about 5 g/l molybdenum-containing compounds.

Following leaching, the slurry can be passed through a filter to form (a) a filter cake containing the leached material and (b) a metal sulfate solution. The filter cake is washed with a sulfuric acid solution having a pH ranging from about pH 0.5 to about pH 1.5 to remove residual leach solution without dissolving molybdenum.

The heavy metal impurities such as copper, cadmium and nickel can be recovered from the metal sulfate leach solution by an iron cementation process to form a metal by-product and a ferrous sulfate solution. The metal by-product, such as cement copper, can then be sold commercially.

The ferrous sulfate solution can be contacted with a sulfide to precipitate any molybdenum in the solution as molybdenum sulfide. The molybdenum sulfide precipitate can be filtered and recycled to a roaster. The filtrate, ferrous sulfate solution, can be combined with ammonium sulfate solution from another process step discussed later, to produce ferrous ammonium sulfate (FAS) fertilizer byproduct.

The leached filter cake is digested in an ammonia lixiviant to solubilize molybdenum oxide and form a pregnant molybdate solution while rejecting mineral impurities such as silica, gypsum and iron oxide. A portion of the solubilized molybdenum can be crystallized from the pregnant molybdate solution as a high purity molybdate. The molybdate can be in the form of ammonium dimolybdate (ADM), or ammonium heptamolybdate (AHM), depending upon the market demand. It is preferred that no more than about 20% of the solubilized molybdenum in the pregnant molybdate solution be crystallized to maintain relatively high purity levels of the crystals.

The pH of the pregnant molybdate solution, after the crystallizing step, can be adjusted to precipitate any molybdenum remaining in the solution after the crystallizing step. The ammonium molybdate solution is neutralized with sulfuric acid to a pH of about pH 2 to pH 3, forming an ammonium sulfate solution and a molybdic acid (ammonium polymolybdate) precipitate. The polymolybdate is filtered, washed, and dried to a molybdic acid product or calcined to pure molybdic oxide which is the main product of the process. The filtrate, ammonium sulfate solution, can be treated with a sulfide to recover any residual molybdenum as molybdenum sulfide, which can be recycled to a roaster. The ammonium sulfate solution can be combined with ferrous sulfate solution from the copper cementation step discussed above to produce ferrous ammonium sulfate (FAS) fertilizer by a drying/granulation process. The mineral residue from the ammonia digestion step can be mixed as an inert binder. The water evaporated during drying is condensed and recycled as process water. Thus, the process results in a "zero-discharge" process.

Impurities, including oxide minerals, such as clay and silica, and acid-insoluble iron oxide and calcium sulfate formed during roasting remain insoluble in ammonia, and therefore remain in the residue after the ammonia digestion step. The combination of crystallization and the subsequent molybdenum precipitation operations together can produce high-purity molybdenum chemicals from ammonium molybdate solutions. As will be appreciated, the process is applicable to any ammonium molybdate solution prepared by ammonia dissolution of molybdenum trioxides. The molybdenum trioxides can be produced by other means such as multiple-hearth roasting, aqueous oxidation of molybdenite concentrates or molybdenum sulfides, or treatment of spent molybdenum-containing catalysts.

The process has a number of advantages relative to other processes. First, the operating costs of the process can be low. Sulfuric acid, derived from sulfur dioxide contained in the roasting off-gas, can be used as the lixiviant for the leaching process, thereby reducing leaching costs. The process can integrate its various unit operations in a flowsheet that allows for maximum recovery of products at minimum energy consumption. Energy released during roasting and sulfuric acid production can be recovered as steam and utilized for evaporation of water during the ferrous ammonium sulfate (fertilizer) production step. Second, the process can be a "zero discharge" process for molybdenite conversion and therefore is environmentally friendly. All solid products and byproducts from the process can be sold as commercial products or readily disposed of at no cost. Water from aqueous streams in the process can be evaporated, condensed, and reused in the process. The gaseous emissions are all constituents of air (i.e., nitrogen, oxygen, carbon dioxide, and moisture). Sulfur is converted into sulfuric acid which is utilized in several process steps and finally leaves the plant as a ferrous ammonium sulfate (FAS) fertilizer byproduct. Other by-products include rhenium as ammonium perrhenate and copper as cement copper. Finally, the process can produce high purity molybdenum chemicals from an ammonium molybdate solution at high levels of molybdenum recovery. The process can produce high purity ammonium dimolybdate (ADM), ammonium heptamolybdate (AHM), ammonium polymolybdate (molybdic acid), and molybdic oxide from ammonium molybdate solutions obtained by ammonia dissolution of molybdenum trioxide. The process allows the production of these molybdenum products in varying proportions to satisfy changing market conditions. The process can produce these high purity molybdates while eliminating recycling of mother liquors from the various crystallization steps, thereby avoiding impurity buildup in the solutions, which results in high- purity molybdenum chemical products recovered from such solutions.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a high-level flow schematic of a process according to the present invention; and

Figs. 2 A-C are detailed flow schematics of various embodiments of a process according to the present invention.

DETAILED DESCRIPTION

The process of the present invention combines several unit operations of molybdenite conversion in a way that maximizes the recovery of very high purity molybdenum chemical products, minimizes the energy consumption, and eliminates the discharge of waste streams by converting the sulfur and other impurities in molybdenite into marketable byproducts. The main features of these unit operations are discussed below and illustrated further in the examples that follow.

General Overview

A general overview of a preferred embodiment of the process of the present invention is depicted in Fig. 1. A feed material 10 containing molybdenum is roasted in an oxidizing environment to produce a roasting off-gas 26 and a calcine 30 containing oxidized molybdenum compounds. The calcine 30 is subjected to acid leaching 58 to produce a leached oxide 86. The calcine 30 contains molybdenum oxide as well as various contaminant metals. In the acid leaching step 58, a majority of the contaminant metals is solubilized in the lixiviant while a majority of the molybdenum remains in the calcine 30. After liquid/solid separation is performed, the leached oxide 86 is subjected to ammonia digestion 98 to remove other impurities, such as silica, gypsum, and iron oxide, to form a pregnant molybdate solution 106. The filtrate containing the dissolved contaminant metals is subjected to further treatment to recover the contaminant metals as a byproduct (not shown). In ammonia digestion 98, the leached calcine is contacted with an ammonia solution under conditions sufficient to maximize solubilization of molybdenum while minimizing solubilization of the remaining impurities. The pregnant molybdate solution 106 is subjected to liquid/solid separation to form a pregnant molybdate solution 106 containing dissolved molybdenum.

To recover the dissolved molybdenum in the pregnant molybdate solution, the process has alternative steps. In a first alternative, the pregnant molybdate solution is subjected to ADM/AHM crystallization 150, 154 to partially crystallize the dissolved molybdenum as ammonium dimolybdate or ammonium heptamolybdate crystals as ADM/AHM products. Ammonium dimolybdate crystals are produced by evaporative crystallization at or near the boiling point of the pregnant molybdate solution. Ammonium heptamolybdate crystals are produced by heating the pregnant molybdate

solution to a temperature sufficient to expel ammonia gas and to increase the concentration of molybdenum in the solution and thereby favor the formation of ammonium heptamolybdate. The ammonium heptamolybdate is thereafter crystallized by cooling the solution. In a second alternative, the pregnant molybdate solution is subjected to neutralization/precipitation 186 to form molybdic acid/oxide products 212 and a filtrate 130. In neutralization/precipitation, the pH of the pregnant molybdate solution is adjusted to an acidic pH to cause molybdic acid, or ammonium polymolybdate with low ammonia content, to precipitate from the pregnant molybdate solution. At the low pH, any residual metals other than molybdenum remain in solution and do not contaminate the molybdic acid precipitate. In a third alternative, ADM/AHM crystallization 150, 154 and neutralization/precipitation 186 are combined to produce two products of high purity, namely ADM/AHM crystals 170 and molybdic acid/oxide product 212. In this approach, the mother liquor 174 from ADM/AHM crystallization 150, 154 is subjected to neutralization/precipitation 186 to form the molybdic acid/oxide product 212.

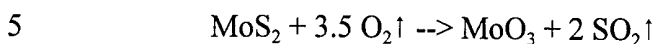
Regardless of the approach, the filtrate 130 produced by liquid/solid separation of the pregnant molybdate solution after molybdenum removal, which is essentially an ammonium sulfate solution, is mixed with ferrous sulfate solution and subjected to drying/granulation 142 to form a granulated ferrous ammonium sulfate product 146. In drying/granulation 142, the filtrate 130, which contains ferrous ammonium sulfate, is concentrated and dried by evaporating water both by indirect and direct heating. As a result, ferrous ammonium sulfate granules are formed.

Sulfuric acid 66 that is used in the acid leaching step 58 and in the neutralization/precipitation step 186 can be produced from the off-gas 26. The scrubbed off-gas is sent to a sulfuric acid production plant 46 where sulfuric acid is produced from the sulfur dioxide in the scrubbed off-gas. The treated off-gas is thereafter scrubbed with ammonia to remove residual sulfur dioxide and sulfur trioxide to form an off-gas that is in compliance with pertinent environmental regulations.

The Conversion of Molybdenum Sulfides to Molybdenum Oxides

Referring to Figs. 2A, 2B, and 2C, a more detailed flowchart of the preferred process, a feed material 10 and recycled molybdenum sulfide 14 are fed continuously to

a roaster to perform roasting 18 in the presence of air 22 to produce a roasting off-gas 26 and calcine 30. Air is used for fluidization as well as for oxidation of metal sulfides to metal oxides and sulfur dioxide (SO₂). Molybdenite roasting occurs according to the following reaction:



The feed material 10 can be any molybdenum sulfide-containing material, particularly molybdenite (MoS₂) concentrates. The feed material 10 has a P size preferably ranging from about 100 to about 500 mesh (Tyler).

10 Roasting 18 may be performed in any suitable fixed or fluidized bed roasting reactor or other suitable device, such as a kiln, with a fluidized bed roasting reactor being most preferred.

15 The preferred fluidized bed roaster design and roasting conditions are set forth in detail in co-pending U.S. Patent Application entitled "Fluidized Bed Roasting of Molybdenite Concentrates", Serial No. 08/907,373, filed August 7, 1997, which is incorporated by reference fully herein.

20 The roasting temperature is preferably controlled by passing cooling water through coils immersed in the fluidized bed. The steam produced in the coils can be used to heat and thereby concentrate process solutions in the plant. Because heat is removed as steam in the cooling coils, the amount of excess (i.e. superstoichiometric) air used in roasting is significantly less than that used in a conventional multiple-hearth roaster.

25 The roaster off-gas 26 commonly contains from about 5 to about 10 percent by volume SO₂, in comparison to the 1 to 3 percent by volume obtained with conventional multiple-hearth roasters. The higher SO₂ concentration allows for more economic conversion of the SO₂ in the off-gas 26 to sulfuric acid which can be used in the molybdenum purification process (discussed below) and to produce the ferrous ammonium sulfate by-product (discussed below).

30 The higher SO₂ partial pressure in the off-gas 26 combined with relatively low roasting temperatures (preferably from about 450 to about 600°C and more preferably from about 500 to about 570°C) results in the formation of molybdenum trioxide, which is readily soluble in ammonia, and impurity metal compounds that are soluble in hot sulfuric acid. Almost all (i.e., commonly at least about 95% and most commonly at least about 99%) of the molybdenum is converted to a soluble oxide form while almost all

(i.e., commonly at least about 90% and most commonly at least about 95%) of the other impurity metals are converted to either oxides or sulfates. Example 1 presents an example of typical roasting conditions and the results obtained in a continuous pilot-scale roaster.

5 Cyclones, filters, or other similar devices can be used to separate the entrained fine particles from the hot off-gas 26 as it leaves the roaster. The fine particles can be recycled to the fluidized bed.

The fluidized bed is maintained at a constant level and the calcine 30 is discharged continuously. The calcine 30 is cooled and stored for further processing or
10 fed directly to an acid leaching tank discussed below.

Treatment of Roasting Off-Gas

Referring to Figs. 2A, 2B, and 2C, the roasting off-gas 26 is subjected to further treatment steps to remove rhenium and sulfur dioxide impurities prior to discharge of the off-gas into the environment.

15 The off-gas 26 is subjected to rhenium scrubbing 34 to produce a scrubbing solution 38 and a scrubbed off-gas 42. The hot off-gas 26 exiting the roaster is preferably maintained at temperatures above about 300°C and more preferably above about 350°C until rhenium scrubbing 34 is performed so that rhenium oxide will stay in the vapor phase and not condense on the conduit walls. The gas is thereafter quenched in the
20 rhenium scrubber. The rhenium scrubber is preferably a venturi scrubber or other similar device, using a recirculating solution. Fresh, cold, deionized water is added to the scrubber to maintain a constant sump level. Under the conditions prevailing in the scrubber (i.e., a saturated concentration of sulfurous acid vapor in the off-gas which is at or near the boiling temperature of the scrubbing solution), all or substantially all (i.e.,
25 preferably at least about 90%) of the rhenium present in the off-gas 26 is solubilized in the scrubbing solution 38 as perrhenic acid. Some molybdenum and other metal impurities present in the very fine dust may also dissolve in the scrubbing solution 38. Any undissolved solids (unroasted sulfides or inert oxide minerals) collect as sludge in the scrubber sump, and can be recycled back to the roasting step 18. Recirculation of the
30 scrubbing solution increases the rhenium concentration in the scrubbing solution so that only a small bleed stream has to be processed in the purification and crystallization steps

40 to yield ammonium perrhenate as a rhenium by-product 44 of the process. The purification step consists of selective loading of rhenium as perrhenic acid on an activated carbon or on an ion exchange resin followed by elution with ammonia. From the eluate, ammonium perrhenate is recovered by evaporative crystallization.

5 The scrubbed off-gas 42 from the rhenium scrubber is sent to a sulfuric acid production plant where sulfuric acid is produced 46 from the sulfur dioxide (SO_2) in the scrubbed off-gas 42. The conversion of SO_2 to H_2SO_4 is accomplished by catalytic oxidation of SO_2 to SO_3 followed by water absorption of SO_3 to form H_2SO_4 . Since in the process of this invention, H_2SO_4 is consumed within the process as discussed later,
10 it is possible to use a less expensive single absorption process to produce 93% H_2SO_4 rather than the more expensive double absorption process necessary for production of 98% H_2SO_4 required for commercial sale. As noted below, a portion of the acid is utilized in the calcine leach step discussed below, another portion is utilized in neutralization of ammonium molybdate solution to precipitate ammonium polymolybdate
15 (discussed below) and the remainder is used to dissolve scrap steel to make ferrous sulfate solution in the iron contacting step 50 (discussed below).

 The treated off-gas 54 is scrubbed with ammonia to remove residual SO_2/SO_3 in compliance with pertinent environmental regulations. It can therefore be readily discharged into the environment.

20 Leaching of Calcine

 A three-step purification process is used to remove impurities and produce high-purity molybdenum chemicals.

 In the first step, the hot calcine 30 (which contains molybdenum oxide contaminated with various metal impurities) from the roasting step 18 is subjected to acid
25 leaching 58 to produce a leach slurry 62. Sulfuric acid 66 is used in the acid leaching step 58. Calcine 30 discharged from the roaster is fed directly to the leaching tank or it can be cooled, stored, and then fed to the leaching tank depending upon the operational requirement of the plant.

 Acid leaching may be conducted in any suitable vessel, such as a leaching tank.
30 The leaching tank can be a single-stirred tank of required capacity, or several tanks

connected in a series. The tank is maintained at a constant level, and the leached solids are discharged continuously to a filtering and washing step 74.

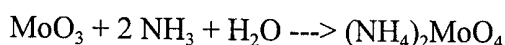
5 In acid leaching 58, the calcine 30 is leached under conditions sufficient to cause most of the copper and other impurity metals that form metal sulfates, such as aluminum, cadmium, calcium, iron, magnesium, potassium, tin, nickel and sodium, to be dissolved, while minimizing the amount of molybdenum dissolved. The calcine 30 is slurried with a recycled wash solution 70 from the filtering and washing step 74 to form a slurry and sulfuric acid 66 is added to maintain the desired pH. Preferred conditions for the leaching step 58 are: (i) a pH ranging from about pH 0.5 to about pH 2, and more preferably from about pH 1 to about pH 1.5; (ii) a temperature ranging from about 70°C to about 100°C, and more preferably from about 85°C to about 95°C; and (iii) a solid content of the slurry ranging from about 10 to about 50 wt% solids, and more preferably from about 30 to about 40 wt% solids. Sulfuric acid is added during leaching 58 as required to maintain the desired pH. Example 2 shows the typical results obtained under preferred conditions in bench-scale tests. Examples 14, 15 and 16 show the effects of process variables.

15 In the filtering and washing step 74, the leach slurry 62 is filtered to produce a filtrate 82 and leached oxide 86. The leached oxide 86 is washed to remove liquid from the voids and solid surfaces in the filter cake. Filtering and washing 74 can be performed with a horizontal vacuum-belt filter or other similar device equipped with washing sprays and separate chambers for collection of filtrate 82 and wash solution 70. The filtrate 82, an acidic metal sulfate solution, contains copper, iron, and potassium (the primary targets of the acid leaching step) as well as other metals, such as aluminum, cadmium, cobalt, magnesium, nickel, sodium, tin, and zinc, which form soluble sulfates. The filtrate 82 is forwarded to the metal recovery step 90 as discussed below. The washing step is performed using the wash solution which contains fresh dilute sulfuric acid solution to minimize the solubilization of molybdenum oxide. After use, the wash solution 70, which now contains metal sulfates, is recycled to the acid leaching step 58. The concentration of sulfuric acid in the wash solution 70 is controlled preferably to maintain a pH ranging from about pH 0.5 to about pH 2 and more preferably from about pH 1 to about pH 1.5.

The leached oxide 86 can be dried and sold as a Tech Oxide product 94, or, alternatively, forwarded to the ammonia digestion step 98 discussed below.

Ammonia Digestion

In the second step of the purification process to separate metal impurities from molybdenum, the leached oxide 86 is digested 98 in an excess of ammonia solution to remove silica, gypsum, iron oxide and other mineral impurities and form a pregnant slurry 99. In ammonia digestion, molybdenum oxide is dissolved as ammonium molybdate according to the following reaction:



The digestion conditions are, of course, selected to maximize solubilization of molybdenum and minimize solubilization of impurities. The leached oxide 86 and ammonia lixiviant are added continuously to the digestion vessel which could be one large vessel or preferably a number of vessels operating in series. The digestion temperature preferably ranges from about 50°C to about 80°C, and more preferably from about 60 to about 70°C. The pH of the pregnant slurry is maintained at a pH preferably of at least about pH 8, and more preferably ranging from about pH 8.5 to pH 9.5. Ammonia is added to the system to control the pH in the desired range. Example 4 presents the typical digestion conditions used and results obtained in bench-scale tests. Aluminum and iron concentrations in the solution are reduced to low levels by precipitating them as hydroxides at a pH of at least about pH 8 and preferably a pH from about pH 8.5 to pH 9.5 by the addition of ammonia. The Eh of the pregnant leach solution should be maintained above about -20mv to insure that all the iron is present in ferric form. If necessary, an oxidant such as hydrogen peroxide can be added to the solution. Example 9 presents results from bench-scale tests performed to remove iron and other impurities from an ammonium molybdate solution.

A residue 102 is separated from a pregnant molybdate solution 106 by subjecting the pregnant slurry 99 to solid/liquid separation 100, such as filtration and forwarded to a mixing step 110 discussed in detail below.

After solid/liquid separation, the residue 102 is washed thoroughly with deionized water to recover molybdenum entrained in the residue as ammonium molybdate solution. The pregnant molybdate solution 106 and wash solution from this washing step are

combined (not shown). Since fresh deionized water is used for digestion and washing, and since the mother liquor from the crystallization step (discussed below) is not recycled, the concentration of metallic impurities in the pregnant molybdate solution 106 remains very low. The washed residue is mixed 110 with ferrous ammonium sulfate solution as discussed below. Since the residue was insoluble in acid leaching and insoluble in ammonia digestion, it will act only as an inert binder in the sulfate fertilizer.

Depending upon the origin (i.e., fluidized bed or multiple-hearth roasting or aqueous oxidation of primary or byproduct molybdenite concentrate or recovery from spent catalysts) of the molybdenum trioxide, the molybdenum trioxide could have different physical and chemical characteristics. This, in turn, may determine the concentration of molybdenum and other impurities in the pregnant molybdate solution 106. Under the conditions noted above, preferably at least about 95%, and more preferably at least about 98% of the molybdenum present in the leached oxide 86 is dissolved in the pregnant molybdate solution 106 containing solubilized ammonium molybdates. Impurities, such as clay, gypsum, and silica, present in the original feed material 10 as well as acid-insoluble iron oxide and calcium sulfate formed during roasting 18 remain insoluble in the ammonia slurry and report to the residue 102.

Crystallization of Molybdates

Removal of Impurities

In the third step of the purification process, molybdenum is recovered as a high purity molybdate after removal of metal impurities. The impurities present in the pregnant molybdate solution can be classified into two groups. The first group consists of metals like sodium, potassium, magnesium, etc., which remain soluble under the crystallization and precipitation conditions used for production of molybdenum chemicals. The second group consists of iron, copper, cadmium and other heavy metals which are likely to precipitate and contaminate the product. The goal of solution purification is primarily the removal of the impurities of the second group.

As will be appreciated, a relatively pure ammonium molybdate solution is colorless. The presence of a copper impurity imparts a pale blue-green color to the solution. Purification is aimed primarily at the removal of copper, and other heavy metal impurities by precipitation techniques to produce a clear solution.

To remove residual copper and other heavy metals from the solution, ammonium sulfide is added to precipitate them as sulfides. The amount of ammonium sulfide added to the pregnant molybdate solution is at least the stoichiometric amount of ammonium sulfide required to convert the dissolved impurities into their respective sulfide compounds. During copper sulfide precipitation 103, the pregnant molybdate solution is agitated and maintained at a temperature ranging from about 50°C to about 70°C and more preferably from about 60°C to about 70°C. The pH of the solution is preferably maintained in the range of from about pH 8.5 to about pH 9.5. Example 9 presents results from a bench-scale test performed to remove copper and other impurities from an ammonium molybdate solution.

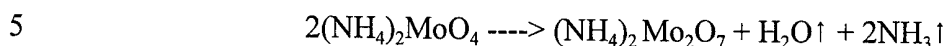
The solution is thereafter filtered 108 to remove the sulfide precipitate 111 and the filtered pregnant molybdate solution 113 fed to a crystallizer to produce ADM or AHM as described below or forwarded to the molybdic acid precipitation step 186. The recovered sulfide precipitate 111 can be recycled to the roasting step 18.

Depending upon market demand, all or a portion of the dissolved molybdenum oxide in the filtered pregnant molybdate solution 113 can be converted into either ammonium dimolybdate (ADM) or ammonium heptamolybdate (AHM) by either ADM evaporative crystallization 150 or AHM cooling crystallization 154. ADM and AHM are standard items of commerce. ADM is more commonly sold in the metallurgical and chemical markets. AHM is preferred in the catalyst market because of its higher solubility in water in comparison to ADM.

To perform crystallization, the filtered pregnant molybdate solution 113 can be fed to a crystallizer equipped with a heating or cooling coil (the same crystallizer and the same coil may be used for both ADM and AHM crystallization by simply passing steam or cold water through the coil at a desired rate) to maintain the desired temperature in the crystallizer. Alternatively, the solution can be fed to separate ADM and AHM crystallizers arranged in parallel. The crystallization can be performed in a batch or continuous mode. The pH of the filtered pregnant molybdate solution 113 prior to crystallization, is preferably at least about pH 8 and more preferably from about pH 8.5 to about pH 9.5.

ADM Crystallization

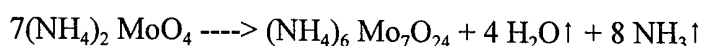
Ammonium dimolybdate (ADM) crystals are produced by evaporative crystallization 150 at or near the boiling point of the filtered pregnant molybdate solution 113 according to the following reaction:



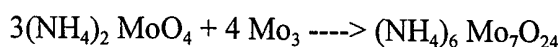
Since the solubility of ADM is substantially constant, the amount of ADM recovered from the solution 113 can be controlled simply by controlling the amount of water evaporation, which in turn is controlled by controlling the residence time of the solution 113 in the crystallizer. The pH during ADM crystallization preferably ranges from about pH 7.5 to about pH 9, and more preferably is maintained around 8. The released ammonia gas can be scrubbed with water and the scrubbing solution recycled to the ammonia digestion step 98. Examples 5 and 10 provide further details on the ADM crystallization conditions and the results obtained.

AHM Crystallization

15 Ammonium heptamolybdate (AHM) is preferred over ADM in the production of catalysts because of its higher solubility. AHM becomes a stable form of ammonium molybdate commonly when the pH is about 7 or less and more commonly when the pH is about 6.5 or less. AHM can be formed by expulsion of ammonia and addition of molybdic oxide to the filtered pregnant molybdate solution 113 as represented by the following reactions:



and



The ammonia gas released from the solution 113 can be scrubbed and the scrubbing solution recycled back to the digestion step 98 to dissolve additional amounts of molybdenum oxide. The temperature is maintained preferably in the range of about 50°C to about 80°C and more preferably from about 60°C to about 70°C. The pH of the solution is maintained in the range from about pH 5 to about pH 7 and more preferably from about pH 5.5 to about pH 6.5 by addition of molybdic oxide.

30 The added molybdic oxide increases the concentration of molybdenum in the solution 113 to near saturation point and lowers the pH. Thus, the addition of molybdic

oxide to the filtered pregnant molybdate solution 113 at a temperature preferably ranging from about 50°C to about 70°C and more preferably about 60 to about 70°C accomplishes both the concentration of solution and the conversion of molybdate ion from normal molybdate to heptamolybdate form. The solution pH is lowered to the range
5 from about pH 5 to about pH 7 and preferably from about pH 5.5 to about pH 6.5.

After the AHM is formed, AHM crystals can be produced by cooling the solution in a crystallizer 154. The solubility of AHM in water is high, typically about 500 grams per liter at 80 to 90°C. The solubility decreases with the decrease in temperature to about 400 gpl at 50 to 60°C and about 300 gpl at 20°C. Therefore, for production of AHM,
10 cooling crystallization is used, as illustrated by Examples 6 and 11. Cold water is passed through a coil submerged in the slurry in the crystallizer. The amount of molybdenum recovered is controlled by controlling the final temperature of the crystallizer in the 20°C to 30°C range.

In either ADM or AHM crystallization, preferably only a portion of the molybdenum is crystallized to maintain low impurity levels. In fractional crystallization,
15 only a portion of the product is recovered while the rest remains in solution. By its nature, the crystallization process rejects impurities and the initial crystals obtained are of the highest purity. It is only after continued crystallization that impurities build up in the solution and begin to get incorporated in the product crystals. Thus, fractional
20 crystallization enables recovery of higher purity products while impurities remain behind in the solution (mother liquor) 174. Preferably no more than about 30 percent and more preferably no more than about 20 percent of the solubilized molybdenum in the pregnant molybdate solution is crystallized as ADM/AHM.

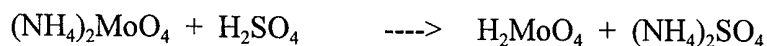
In either event, the ADM crystal slurry 158 or the AHM crystal slurry 162 are
25 subjected to solid/liquid separation 166 to separate crystals 170 from mother liquor 174. Solid/liquid separation 166 can be performed by a centrifuge or other similar gravity separation devices. The crystals 170 are dried 178, typically at moderate temperatures preferably ranging from about 60 to 70°C, to produce ADM/AHM products 182 for sale.

Neutralization/Precipitation

30 The mother liquor 174, which contains the remainder of the molybdenum as ammonium di- or heptamolybdate, or alternatively the filtered pregnant molybdate

solution 113 is, with reference to Fig. 2B, subjected to neutralization/precipitation 186, to precipitate molybdic acid (ammonium polymolybdate)190. Neutralization/precipitation 186 is performed using an acid, preferably sulfuric acid 66, to adjust the pH of the mother liquor 174 to a pH preferably ranging from about pH 1.5 to about pH 4, and most preferably from about pH 2 to about pH 3. The temperature during neutralization/precipitation 186 ranges from about 30°C to about 80°C, and preferably from about 50 to about 60°C. The temperature is controlled in the 30°C to 80°C range by using a water cooling coil to remove the heat of neutralization. The altered pH causes molybdic acid (also known as ammonium polymolybdate) with low ammonia content, to precipitate from the mother liquor 174 while converting ammonium molybdate to ammonium sulfate (when sulfuric acid is used to lower the pH). At the low pH used in the process, any residual metals (most likely aluminum, iron, magnesium, potassium and sodium in small concentrations) present in the mother liquor remain in solution and do not contaminate the molybdic acid precipitate. Therefore, the molybdenum product is of very high purity.

The neutralization/precipitation reaction is performed according to the following reaction:



The process can be operated in a batch or continuous mode. As illustrated by Examples 7 and 12, continuous neutralization to a pH range of 2 to 3 at 50 to 60°C results in the formation of a granular product that is easy to filter.

In practice, the solution would contain dimolybdate or heptamolybdate ions instead of normal molybdate ions represented in the above reaction. Similarly, the product may be true molybdic acid of the formula shown in the equation or commercial molybdic acid which includes ammonium polymolybdates that may contain varying amounts of ammonia and water of hydration depending upon the temperature and pH of the precipitation.

The precipitate-containing polymolybdate slurry 190 is subjected to solid/liquid separation 194, preferably by centrifuging, to produce the filtrate 130 and a precipitate 198. The filtrate 130 is predominantly an ammonium sulfate solution produced during the neutralization/precipitation step. The precipitate 198 is washed 200 with a suitable solution, preferably a saturated pure molybdic acid solution, to remove ammonium

sulfate solution from the precipitate 202, thereby minimizing sulfur contamination. The wash liquor 204 is then recycled to the neutralization/ precipitation step 186.

The washed precipitate 202 can be either dried 208 at a temperature of no more than about 90°C, and more preferably ranging from about 60 to about 80°C, to produce a molybdic acid product 212.

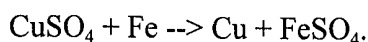
Alternatively, the washed precipitate 202 can be dried and calcined 216 at a temperature of no more than about 550°C, and more preferably ranging from about 400 to about 450°C, in a suitable reactor to expel ammonia and water and to produce a molybdic oxide product 212. Pure molybdic oxide is a common molybdenum product used in both catalyst and metal industries. As illustrated by Examples 8 and 13, it is easily produced by calcining the molybdic acid at a temperature of about 400 to about 450°C. Water and ammonia are expelled and MoO₃ is left behind. In comparison to calcination of ADM to produce molybdic oxide, calcination of molybdic acid is advantageous because the amount of ammonia released is significantly lower. Any ammonia released during the process is captured by scrubbing and recycled to the digestion step to produce more ammonium molybdate solution.

The molybdenum-containing products produced by the above-described process have a high level of purity. The ADM/AHM Products typically contain no more than about 500 and more typically no more than about 200 ppm metal impurities. The molybdic acid product 212 typically contains no more than 500 and more typically no more than about 200 ppm metal impurities. The recovery of molybdenum in this process is high. The collective recovery of molybdenum in the ADM/AHM Products 182 and/or the molybdic acid product 212 is typically at least about 99% and more typically at least about 99.5%.

Metal Recovery

Referring to Figs. 2A and 2C, the metal recovery step 90 can be performed using any technique suitable for recovering heavy metals from an acidic sulfate solution. Preferably, the metal recovery step 90 is performed by cementation techniques. As will be appreciated, iron powder, scraps, steel turnings, and other similar materials can be used as a cementing reagent that will precipitate copper and other heavy metals like

cadmium and nickel from the filtrate 82 while also dissolving iron. Copper is cemented out according to the following reaction:



5 The metal recovery step 90 can performed in a tank, column, or specially-designed launders commonly used in the industry for this purpose. The metal by-product 114 is filtered, washed, and dried. The common metal by-product is cement copper. The cement copper is a standard item of commerce that will be sold to a copper smelter.

10 To verify its applicability for recovery of copper from the leach solutions of the process of this invention, several batch cementation tests were performed using steel turnings. Details are presented in Example 3. It is noted that copper concentration was reduced from a few grams per liter to a few ppm, indicating 99.9% recovery. Some molybdenum was also cemented out. Analysis of timed samples indicated that copper cementation was much faster than molybdenum cementation and a residence time of 1 hour or less is adequate to remove all the copper while minimizing molybdenum removal.

15 The two process streams, the treated solution 118 from the metal recovery step 90 and filtrate 130 from the solid/liquid precipitation step 194 contain small concentrations of molybdenum. In the sulfide precipitation step 122, they are combined in a sulfide precipitation tank. The pH is adjusted, if necessary, by adding sulfuric acid to a pH ranging from about pH 2 to about pH 3 and the temperature is raised to a temperature ranging from about 50°C to about 90°C by indirect steam heating.
20 Hydrogen sulfide gas or ammonium sulfide can be used as the precipitating agent. The precipitate-containing liquor is filtered to form a filter-cake and a barren solution 126. The filter-cake is filtered, washed, and recycled to the roaster. Thus, the process recovers essentially 100% of the molybdenum present in the feed. Example 17 provides further
25 details on molybdenum sulfide precipitation.

FAS Production

The barren solution 126 is essentially an ammonium sulfate solution, with small concentrations of iron, potassium and other light metals such as aluminum, magnesium, and sodium. The barren solution 126 is mixed 110 with the residue 102, and ferrous
30 sulfate solution 134, to form a ferrous ammonium sulfate slurry 138. Excess sulfuric acid 66 produced in the sulfuric acid production step 46 is neutralized with iron (e.g., steel

scrap 50) to produce ferrous sulfate solution 134. Alternatively, the excess acid can be neutralized with ammonia in the mixing tank 110 to form additional ammonium sulfate. The combined ferrous ammonium sulfate slurry 138 is concentrated by evaporating water both by indirect and direct heating. The indirect heating is provided by the steam produced in the roaster and in the acid plant. The direct heating is provided by the hot gas coming from the FAS drying/granulation step as it is scrubbed by the recirculating FAS solution. The residue contains inert mineral matter such as gypsum, silica and iron oxide which act as a binder in the drying/granulation step. The concentrated FAS slurry is converted to FAS granules of a desired size using a fluidized-bed dryer/granulator, flaker, a curtain granulator, or other similar equipment. The water evaporated during the concentration of FAS solution is condensed and recycled as deionized water to the process. The sulfate solution is dried/evaporated 142 to produce ferrous ammonium sulfate (FAS) product 146. Drying/granulation is performed in a fluidized-bed dryer or other similar device fired with natural gas. Coarse-sized product is removed for shipping and the fines are recycled to the dryer for further growth. The hot exit gas passes through cyclones for capture and recycle of dust to provide seed. The gas is then scrubbed with recirculating ferrous ammonium sulfate solution to evaporate water and concentrate the slurry. The leach residue from the ammonia digestion step is added to this tank since it is innocuous (insoluble in either acid or alkaline media) and acts as a binder in the production of ferrous ammonium sulfate (FAS) granules in the fluidized bed. Thus, there is no solid waste stream to be discharged from the plant. All the sulfur entering the plant is converted to a ferrous ammonium sulfate (FAS) by-product for sale in the fertilizer chemical market. Alternatively, the filtrate (ammonium sulfate solution) can be dried and granulated into an ammonium sulfate byproduct.

25 **Heat Exchange Loops**

There are two heat exchange loops in the process which are not shown in Fig. 1. They significantly improve the energy efficiency of the process. The first heat exchange loop consists of demineralized water/steam flowing through coils submersed in the roaster, acid plant converters, and several process tanks. This system removes heat from the roaster and acid plant by converting water to steam. It provides heat to the process

tanks while converting steam back to water. If necessary, the water can be further cooled by heat exchange in a water cooler.

The second heat exchange loop is open. Water evaporated during drying of ferrous ammonium sulfate solution to granules is condensed, cooled, and recycled to the plant as process water (various leaching and digestion tanks as well as washing of the filter cakes). Depending upon water balance and ambient conditions, either fresh deionized water may be added to the system or excess water may be removed as water vapor in the gaseous emissions from the FAS production loop. Thus, there is no liquid discharged from the plant.

As for the gaseous emissions, there are several sources - the roasting step 18, the sulfuric acid production step 46, the molybdic acid drying/calcination steps 208 and 216, and the FAS drying/granulation step 142. In all these cases, the exhaust gases (basically combustion products) consist of components naturally present in the air - nitrogen, oxygen, carbon dioxide, and water vapor. The acid plant design will ensure that the SO₂ gas concentration in the exhaust gas meets the local and federal standards. Similarly, the gas from the molybdic acid calcination step will be scrubbed to ensure that the ammonia concentration in the exhaust gas is below the local and federal standards. Technologies for control of these two gases are well proven on commercial scale. There will be no polluting gas emission from the plant.

EXAMPLES

The following examples are provided to further illustrate the various unit operations of the novel process of this invention. They are not intended to limit the scope of the invention as described above and set forth in the claims. These examples are based on a batch bench-scale roaster and a continuous pilot-scale roaster operation followed by bench-scale batch/continuous tests for chemical purification unit operations.

Example 1 - Continuous Fluidized-Bed Roasting

A by-product molybdenite concentrate containing approximately 90% molybdenum disulfide, 1.5% iron, 1.0% copper, 0.3% calcium, 0.7% residual flotation oil and 0.6% moisture was roasted in a pilot-scale vibratory three-zone fluidized-bed reactor by continuously feeding the concentrate at a rate of 8 lb/hr while passing

fluidizing air through the reactor at nominally 10 scfm. The temperature of the fluidized bed, comprised of a mixture of molybdenum sulfide plus molybdenum oxide, was controlled between 500°C and 560°C by passing cooling water through coils submerged within the fluidized bed.

5 Molybdic oxide product was removed from the reactor at approximately 7 lb/hr after a nominal 3-hour residence time via a water-cooled overflow-type discharge port. The rate of product discharge was proportional to the feed rate taking into account the stoichiometric weight change due to the conversion of molybdenum sulfide to molybdenum oxide. The resulting gas, which contained 6-8% sulfur dioxide, low levels
10 of volatile rhenium oxide and a significant quantity of carry-over fines (small particle size bed material) was passed through primary and secondary hot cyclones which returned greater than 99% of the fines back to the reactor. The reactor off-gas was then passed through a wet vortex-type scrubber which removed any residual particulate solids and the water-soluble volatile rhenium oxide. Prior to discharge to the atmosphere, the sulfur
15 dioxide in the off-gas was removed by contact with a caustic solution in a packed tower scrubber.

Example 2 - Acid Leaching

A sample of roasted molybdenum oxide weighing 200 grams was slowly added to a beaker containing 600 ml of a rapidly stirred pH 1.0 sulfuric acid solution. Once all
20 of the oxide was added to the beaker, the solution temperature was raised to the boiling point and held at that temperature for 3 hours while additional deionized water was added to maintain the initial slurry volume. The slurry was then filtered on a standard Buchner funnel and the solids filter cake was washed twice with 50 ml quantities of pH 1.0 sulfuric acid solution.

25 Upon drying, the leached oxide was found to have lost 2.9 wt % due primarily to the removal of greater than 95% of the copper impurity, 93% of the calcium impurity and some molybdenum dissolution. The leachate was analyzed and found to contain nominally 5 gpl molybdenum, 2.6 gpl copper, 1 gpl calcium and 150 ppm potassium. The leached oxide product from this step is equivalent to the "technical grade" molybdic
30 oxide which is sold to the steel-making industry.

Example 3 - Copper Cementation

A 300 ml sample of acid leachate solution containing 2.9 gpl copper was heated to 70°C and stirred for 1 hour with 3.0 grams of iron in the form of steel wool. The quantity of iron used represented a 3.7 times stoichiometric excess based on the quantity of copper in the leachate. At the completion of 1 hour, the solution plus iron was filtered. The solids residue on the filter contained a significant quantity of the original steel wool and a noticeable quantity of copper powder. Analysis of the filtrate showed that the residual copper concentration was below 3 ppm suggesting the copper had been quantitatively removed from solution. The cement copper powder produced by this process is marketable as feedstock for a copper smelter.

Example 4 - Ammonia Digestion

A 200 gram sample of roasted oxide which had been leached in hot sulfuric acid as described above was digested in an aqueous ammonia solution as follows. Approximately 100 ml of deionized water was added to a beaker along with 50 ml of 28% ammonium hydroxide solution. The solution was then heated to 50°C. The leached oxide and additional aqua ammonia solution were then added slowly in alternating small quantities so as to maintain the solution temperature around 60°C and the pH between 8.5 and 9.5. In this case, as the final aqua ammonia solution addition was made, care was taken to maintain the final solution pH between 9.2 and 9.4.

Two drops of 30% hydrogen peroxide solution were then added to the slurry to ensure oxidizing conditions and thereby full conversion of any iron impurity to the insoluble ferric hydroxide form.

The digestion slurry was stirred and held at 60°C for 3 hours after which 6 drops of 20% ammonium sulfide solution were added to precipitate residual copper. Following an additional 15 minute hold time at temperature, the slurry was filtered hot and the solids residue was washed lightly with deionized water and dried at 110°C. The resulting clear colorless ammonium molybdate solution had a specific gravity of 1.29 g/cc. It will be appreciated that the measured specific gravity of the resulting ammonium molybdate solution suggests a concentration of nominally 250 gpl molybdenum.

Example 5 - ADM Crystallization

An ammonium molybdate solution with a specific gravity of 1.30 g/cc and a pH of 9.2, prepared in a similar fashion as described previously above, was heated to the boiling point with vigorous agitation in a stainless steel beaker. After boiling the solution for 2 hours, it was observed that the pH had dropped to 8.3, the specific gravity had risen to 1.33g/cc and white crystals were beginning to form in the solution. After 30 minutes of additional boiling, the solution volume had been reduced to approximately 60% of the initial volume and it contained a substantial quantity of white crystal product.

By filtering the resulting slurry while still hot, a "crop" of coarse white ammonium dimolybdate crystals was obtained. These crystals, which accounted for nominally 30-40% of the total molybdenum in the initial ammonium molybdate solution, were dried in air at 70°C. The remaining ammonium molybdate mother liquor was then used for molybdic acid precipitation tests as described in a subsequent example. The crystalline ammonium dimolybdate product is used as a feedstock in a hydrogen reduction process for the production of molybdenum metal powders as well as in numerous applications in the chemical industry.

Example 6 - AHM Crystallization

Alternately, the ammonium molybdate solution described in Example 5, was heated to 70°C with mild agitation and the pH was lowered to below 7.0 by addition of pure molybdic oxide. By continuing to hold the solution temperature at 70°C, evaporation resulted in the eventual formation of a small quantity of white crystals. The solution, which was observed to have a specific gravity of approximately 1.36 was then allowed to cool with continued stirring. When the temperature of the slurry had reached 20°C, a large quantity of white crystals was evident and the slurry was filtered. The crystal product, which represented approximately 30% of the total molybdenum in the initial ammonium molybdate solution, was dried at 60°C. The remaining ammonium molybdate mother liquor was then used for molybdic acid precipitation tests as described in the next example. The crystalline ammonium heptamolybdate product is preferred in the catalyst industry because of its high solubility in water in comparison to ammonium dimolybdate or pure molybdic oxide.

Example 7 - Molybdic Acid Precipitation

Ammonium molybdate solution filtrate as described above from the crystallization of either ADM or AHM was used to precipitate an ammonium polymolybdate product sometimes called "commercial molybdic acid" in the literature. Starting with a "heel" of weak sulfuric acid solution vigorously stirred at pH 2.5 in a large glass beaker, both the ammonium molybdate solution and concentrated sulfuric acid were continuously added while maintaining the pH between 2.5 and 3.0 and the temperature between 50°C and 60°C. An internal water cooling coil was used to control the temperature. After a short period of time, the solution turned a pale yellow color and a "crop" of white crystals was evident.

This process was carried out in a continuous manner by pumping the crystal slurry from the beaker to a Buchner funnel filter at the same rate as fresh solutions were being added. During the test, the "average residence time" of slurry in the beaker was observed to be between 20 and 30 minutes. The filter "cake" was washed twice with small quantities of a saturated molybdic acid solution prepared by dissolving pure molybdic oxide in deionized water. This washing action is desirable to remove residual filtrate containing ammonium sulfate from the product prior to drying. The drying was performed at nominally 110°C (it is noteworthy that drying temperature is not critical to the product). This product has recently found acceptance as a feedstock for the molybdenum metal powder market. Alternately, the "molybdic acid" product can be used as feedstock to produce pure molybdic oxide as described in the subsequent example.

Example 8 - Production of Pure Molybdic Oxide

Pure molybdic oxide was produced by calcining precipitated "molybdic acid", the production of which was described in the preceding example. A sample of the molybdic acid, weighing exactly 100 grams, was placed on a flat tray in a muffle furnace under an air atmosphere and heated to 450°C for 4 hours. After cooling, the sample was found to weigh 91.3 grams and was a pale gray-blue color. The pure molybdic oxide thus produced is a standard product of commerce in the molybdenum metal products industry as well as in several applications of the chemical and catalyst manufacturing industries.

Example 9 - Purification of Ammonium Molybdate Solutions

5 A 200-gram sample of fluid-bed roasted molybdenum trioxide which had been leached in a pH 1.0 boiling sulfuric acid solution was digested in deionized water and anhydrous ammonia. Sufficient ammonia was added to result in a final solution pH of approximately 9.2 to 9.4. The solution at this point had an oxidation/reduction potential (ORP) of -143 mv. To insure complete oxidation of iron impurities in the solution to the (insoluble) ferric state, the oxidation potential of the solution (also known as Eh) was increased to -30 mv by the addition of three drops of 30% hydrogen peroxide solution. 10 This solution was then held at 60 to 70°C for 3 hours and then a small sample was filtered through a 1.5 micron filter.

At this point, the filtrate sample had a pale bluish-green color due to the presence of a small concentration of copper impurity which had apparently not been removed totally from the oxide during the sulfuric acid leach. Following the addition of 3 drops 15 of ammonium hydrosulfide, another small sample of the solution was filtered. The color of this filtrate was a very pale blue. Repeating this procedure with 3 additional drops of ammonium hydrosulfide resulted in a clear ammonium molybdate filtrate. Spectrographic analysis of this solution showed that all metal impurities had been reduced to less than 10 ppm in solution.

Example 10 - ADM Crystallization

20 A 4-liter lot of purified ammonium molybdate solution was prepared following the same manner as described in the aforementioned Example 9. The solution was then heated to the boiling point and held at a slow boil with agitation. When the volume had decreased by approximately 20 percent, the solution became opaque due to the presence 25 of precipitated crystals. The specific gravity of the solution at this point was 1.33. Continuous boiling until the volume had decreased by approximately 35 percent resulted in a slurry containing a large quantity of white crystals in solution. It can be appreciated by those schooled in the art that the crystals produced at this point, which represented roughly 30 percent of the contained molybdenum values in solution, are of exceptionally 30 high purity due to this fractional crystallization technique.

The solution was then filtered while hot and the crystals were allowed to filter dry for 10 minutes to minimize retention of the filtrate in the crystal product. The white crystalline ammonium dimolybdate product was then dried at 70°C for 3 hours. Chemical analysis indicated the purity to be 99.95+%. This ADM product is useful to both the chemical industry as a source of molybdenum and to the metallurgical industry as a starting material for the production of pure molybdenum metal powder.

The mother liquor (filtrate) from this test was held for further processing to remove the remaining molybdenum values as described in Example 12 below.

Example 11 - AHM Crystallization

A 4-liter lot of purified ammonium molybdate solution was prepared following the same manner as described in the aforementioned Example 9. The solution was then heated to 70°C and held at that temperature with mild agitation. Small 50 gram additions of pure molybdic oxide were then made until the pH had been lowered to approximately 6.7 and the solution's specific gravity was approximately 1.36. The solution was then filtered hot (at 70°C) and allowed to cool to room temperature (18°C) with agitation. As the solution began to cool, it turned from clear to opaque due to the presence of precipitated crystals. As in the previous example, the crystals produced at this point, which represented roughly 25 percent of the contained molybdenum values in solution, are of exceptionally high purity due to this fractional crystallization technique.

The room temperature solution was then filtered and the crystals were allowed to filter dry for 10 minutes to minimize retention of the filtrate in the crystal product. The white crystalline ammonium heptamolybdate product was then dried at 60°C for 3 hours. The chemical analysis of the product indicated its purity to be 99.95+%. The AHM product is useful to the catalyst industry as a source of highly soluble molybdenum for coating catalysis substrates.

The mother liquor (filtrate) from this test was held for further processing to remove the remaining molybdenum values as described in Example 12 below.

Example 12 - Molybdic Acid Precipitation

A saturated ammonium molybdate mother liquor, similar to that generated in the previous two examples following ADM or AHM crystallization, was processed to recover all molybdenum values as follows.

5 A 2-liter beaker, equipped with agitation and a cooling coil, was filled nominally one-third full with a concentrated ammonium sulfate solution at pH 2.5. The saturated ammonium molybdate mother liquor was then diluted with deionized water to a specific gravity of 1.25 and pumped into the beaker at approximately 100 milliliters per minute while concentrated (98%) sulfuric acid was added continuously to maintain the pH between 2.5 and 3.0. Cooling water was supplied to the cooling coil to maintain the
10 temperature of the bath between 50°C and 60°C.

Shortly after starting the additions, the solution in the beaker became semi-opaque due to the formation of a granular white precipitate. When the beaker was nominally three-quarters full, the slurry was continuously pumped out of the beaker to a filter at a rate to maintain constant volume in the beaker. In this manner, ammonium molybdate
15 solution and concentrated sulfuric acid were continuously added to the beaker while an ammonium sulfate and molybdic acid (ammonium polymolybdate) precipitate were continuously removed for filtration.

Filtration of the granular precipitate was very rapid. Following filtration, which was conducted semi-batch wise with multiple filters, the white precipitate granules were
20 washed twice with a saturated molybdic acid solution produced by dissolving pure molybdic oxide in deionized water. The washing step was desirable to remove any residual ammonium sulfate solution from the filter cake. The white precipitate which is sometimes referred to as "molybdic acid" or "ammonium polymolybdate" was then dried at 110°C for 2 hours. The chemical analysis of the product indicated its purity to be
25 99.95+%. The "molybdic acid" produced in this manner may be useful to the metallurgical industry as a source of starting material for the production of molybdenum metal powder or may be calcined to produce pure molybdic oxide which is a standard commercial molybdenum chemical product.

Example 13 - Calcination of Molybdic Acid to Molybdic Oxide

30 "Molybdic Acid" produced in a similar fashion as the aforementioned Example 12 was converted to pure molybdic oxide as follows.

Nominally 7 kilograms of "molybdic acid" which had been thoroughly dried was spread 1 inch deep in trays and heated to 450°C in a convection furnace over a 2-hour period. The trays were then held for 4 hours at temperature and allowed to cool to room temperature in the furnace. During heat-up, a very small quantity of ammonia was detected in the furnace off-gas.

Upon removal from the furnace, it was observed that the white "molybdic acid" had changed to a blue/gray color common to commercial pure molybdic oxide. The chemical analysis of the product indicated its purity to be 99.95+%.

Example 14 Acid Leaching of Calcine - Effect of pH

In one test, a sample of roasted molybdenum oxide weighing 200 grams was slowly added to a beaker containing 600 ml of a rapidly stirred deionized water. Once all of the oxide was added to the beaker, the solution temperature was raised to above 90°C and held at that temperature for 3 hours while additional deionized water was added to maintain the initial slurry volume. The slurry was then filtered on a standard Buchner funnel and the solids filter cake was washed twice with 50 ml quantities of deionized water. The pH of the leach filtrate was 2.2. In a second test, a 200 gram molybdic oxide sample was added to 600 ml of a sulfuric acid solution at pH 1 and the test was conducted as described above with the exception that the filter cake was washed twice with 50 ml quantities of pH 1 sulfuric acid solution. The pH of filtrate was 1.3.

Upon drying, the leached oxide from the deionized water leach test was found to have lost 10.9 wt% due primarily to the dissolution of a significant quantity of molybdenum. The oxide from the pH 1 acid leach test lost only 2.9 wt % due to decreased molybdenum loss. As shown in Table 1, the use of sulfuric acid in the leach step reduced the quantity of molybdenum dissolved by over 70%. The use of the acid leach also resulted in a slight increase in copper removal and significantly increased the removal of iron, calcium, and aluminum. Note that the acid leach did not affect the removal of magnesium, potassium, or sodium. The leached oxide product from this step is equivalent to the "technical grade" molybdic oxide which is sold in the steel-making industry.

TABLE 1

Lixiviant	pH	Mo	Cu	Ca	Fe	Al	Mg	K	Na
Water	7	17.9	2.5	620	290	355	165	150	35
Acid	1	5.1	2.6	950	3500	460	185	150	35

5 All results are expressed in parts per million except for Mo and Cu, which are in grams per liter.

Example 15 Leaching of Calcine - Effect of Recycling Leachate

A sample of as-roasted molybdenum oxide weighing 100 grams was leached in 300 ml of pH 1.0 boiling sulfuric acid solution for 1 hour and filtered. A small aliquot of the leachate was then removed for analysis and the remaining solution was used to
 10 leach a second 100 gram sample of as-roasted oxide in a manner similar to the first leach test. A sample from the leachate after the second leach test was removed and both leachate samples were analyzed for impurity pickup.

It is evident from the results presented in Table 2 that multiple recycles of the leach solution would result in continued impurity removal from the roasted molybdenum oxide while minimizing commercial production costs due to lower water/acid usage,
 15 lower molybdenum dissolution, and lower volume of metal sulfate solution to be processed in cementation step.

TABLE 2

Test	Cu	Al	Mg	K	Na
First leach	1540	212	128	76	26
Second leach	3193	431	257	152	52

20 All results are expressed in parts per million.

Example 16 Leaching of Calcine- Effect of Time

Samples of as-roasted molybdenum oxide, each weighing 100 grams were leached batch-wise in 300 grams of deionized water with vigorous agitation at 90°C for 1, 2, 3,
 25 and 6 hours. At the end of each leach time, the slurry was filtered and the leachate was submitted for impurity analysis. The results, which are summarized in Table 3 for the 1 hour and 6 hours tests, show that the concentrations of the major impurities in ppm

(parts per million) did not significantly increase with increased leach time beyond the first hour.

TABLE 3

Time	Cu	Ca	Al	Fe	Mg	K	Na
1 hr.	2500	620	355	290	165	150	35
6 hrs.	2600	730	415	260	185	150	38

All results are expressed in parts per million.

Example 17 Precipitation of Molybdenum Sulfide

A cementation liquor, as generated by the process described in Example 3, contained 5.2 gpl molybdenum. To recover these molybdenum values, 800 ml of the liquor was placed in a tall-form beaker and sparged with approximately 21 grams of hydrogen sulfide gas at room temperature. Following sparging, the pH was 2.8. A small amount of sulfuric acid was then added to drop the pH to 2.2 and the solution was filtered. Analysis of the leachate from this test showed the molybdenum concentration had dropped to approximately 1 gpl. The remaining solution was then sparged with an additional 40 grams of hydrogen sulfide gas and filtered. Analysis of this second leachate showed that the molybdenum concentration had been reduced to 0.2 gpl.

It is to be understood that greater than 95% of the molybdenum values lost to the leach circuit during the hot acid leach step were recovered as a sulfide which can be returned to the fluidized-bed roaster as feedstock. Sulfide precipitation at higher temperatures can further increase the molybdenum recovery. Furthermore, the sulfide addition had no effect on the residual iron concentration in solution thereby allowing the iron containing leachate to be used as a feed stream for the ferrous ammonium sulfate fertilizer plant.

While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the scope of the present invention, as set forth in the following claims.

What is claimed is:

1. A method for recovering molybdenum from a feed solution containing a dissolved molybdate, comprising lowering the pH of the feed solution to precipitate the molybdate as a polymolybdate.
- 5 2. The method of Claim 1, wherein the pH of the feed solution after the lowering step is no more than about pH 4.
3. The method of Claim 1, wherein the temperature of the feed solution during the pH lowering step is maintained in the range of about 30°C to about 80°C.
4. The method of Claim 1, wherein the pH lowering step comprises:
10 contacting the feed solution with sulfuric acid.
5. The method of Claim 1, wherein at least about 95 % of the molybdenum in the feed solution is converted into a polymolybdate.
6. The method of Claim 1, further comprising:
filtering the feed solution, after the pH lowering step, to separate the
15 polymolybdate from the feed solution to form a recovered polymolybdate precipitate and a filtrate.
7. The method of Claim 6, further comprising:
washing the recovered polymolybdate precipitate with a wash solution comprising
ammonium molybdate to remove at least a portion of any ammonium sulfate in the
20 precipitate.
8. The method of Claim 7, further comprising:
drying and calcining the recovered polymolybdate precipitate to remove ammonia
and water and thereby produce a molybdenum-containing product.
9. The method of Claim 6, wherein the filtrate comprises dissolved
25 molybdenum, and further comprising:
recovering the dissolved molybdenum from the filtrate by contacting the filtrate
with a sulfide under conditions sufficient to precipitate molybdenum sulfide.
10. The method of Claim 1, further comprising before the pH lowering step:
converting only a portion of the molybdenum in the feed solution into
30 molybdenum-containing crystals including at least one of ammonium heptamolybdate
and ammonium dimolybdate and
removing the molybdenum-containing crystals from the feed solution.

11. The method of Claim 10, wherein the feed solution comprises a dissolved metal besides the dissolved molybdenum and further comprising before the pH lowering step:

precipitating the dissolved metal as a sulfide from the feed solution.

12. The method of Claim 6, wherein the filtrate comprises ferrous ammonium sulfate and further comprising:

evaporating water from the filtrate to form granulated ferrous ammonium sulfate.

13. The method of Claim 1, further comprising, before the pH lowering step: contacting a molybdenum oxide-containing material with an ammonia-containing lixiviant to solubilize the molybdenum contained in the molybdenum oxide-containing material in the feed solution.

14. The method of Claim 1, further comprising, before the pH lowering step: leaching a molybdenum oxide-containing material with a lixiviant comprising an acid or salt thereof to solubilize a metal impurity contained in the molybdenum oxide-containing material in a pregnant leach solution while maintaining a substantial portion of the molybdenum oxide in the material.

15. A method for removing metal impurities from a molybdenum oxide containing material, comprising:

leaching the material with a lixiviant comprising an acid or salt thereof to solubilize the metal impurities in a pregnant molybdate solution while maintaining a substantial portion of the molybdenum oxide in the material.

16. The method of Claim 15, wherein the metal impurities are selected from the group consisting of aluminum, cadmium, calcium, cobalt, copper, iron, lead, magnesium, nickel, potassium, sodium, tin, zinc, and mixtures thereof.

17. The method of Claim 15, wherein the pH of the lixiviant in the leaching step is no more than about pH 2.

18. The method of Claim 15, wherein the lixiviant and molybdenum oxide-containing material together form a slurry containing from about 10 to about 50 wt.% solids.

19. The method of Claim 15, wherein the temperature of the molybdenum oxide-containing material in the leaching step ranges from about 60°C to about 100°C.

20. The method of Claim 15, wherein, after the leaching step, the molybdenum oxide-containing material comprises from about 96 to about 99% of the molybdenum contained in the molybdenum oxide-containing material before the leaching step.

5 21. The method of Claim 15, wherein, after the leaching step, the pregnant leach solution comprises no more than about 7 g/l molybdenum-containing compounds.

22. The method of Claim 15, further comprising after the leaching step:
washing the molybdenum oxide-containing material with an acid to remove the
lixiviant and thereafter recycling the wash solution.

10 23. The method of Claim 15, further comprising:
lowering the pH of a feed solution containing a dissolved molybdate to precipitate
the molybdate as a polymolybdate.

24. A method for recovering molybdenum from a molybdenum sulfide-
containing material, comprising:
15 roasting the molybdenum sulfide-containing material in the presence of oxygen
to form a calcined material comprising molybdenum oxide and metal impurities;
leaching the calcined material with sulfuric acid to solubilize the metal impurities
in a pregnant leach solution while maintaining a substantial portion of the molybdenum
oxide in the material;

20 contacting the leached calcined material with ammonia to form a primary
pregnant leach solution comprising molybdenum from the leached material; and
lowering the pH of the primary pregnant leach solution to precipitate the
molybdenum in the solution as ammonium polymolybdate.

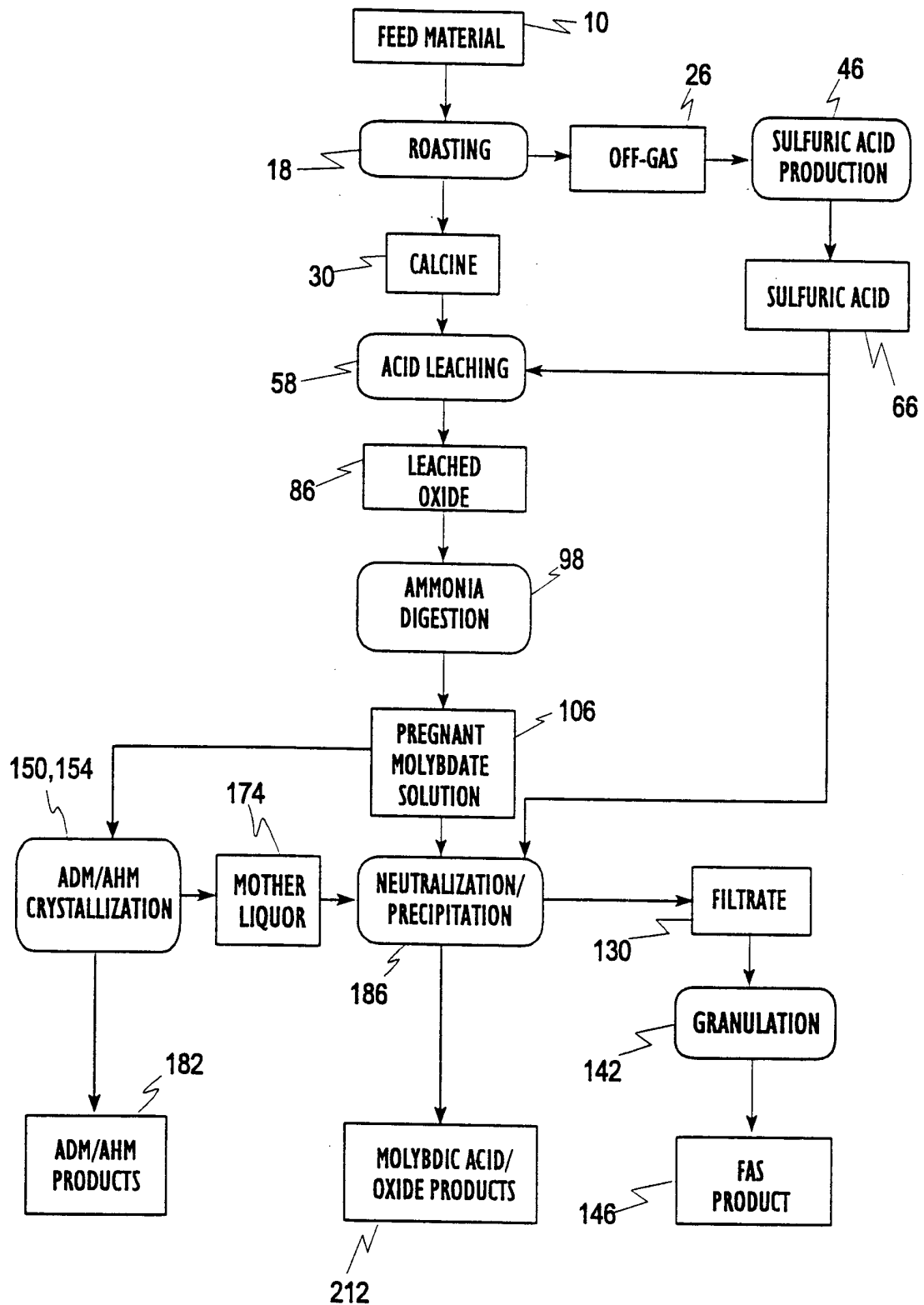
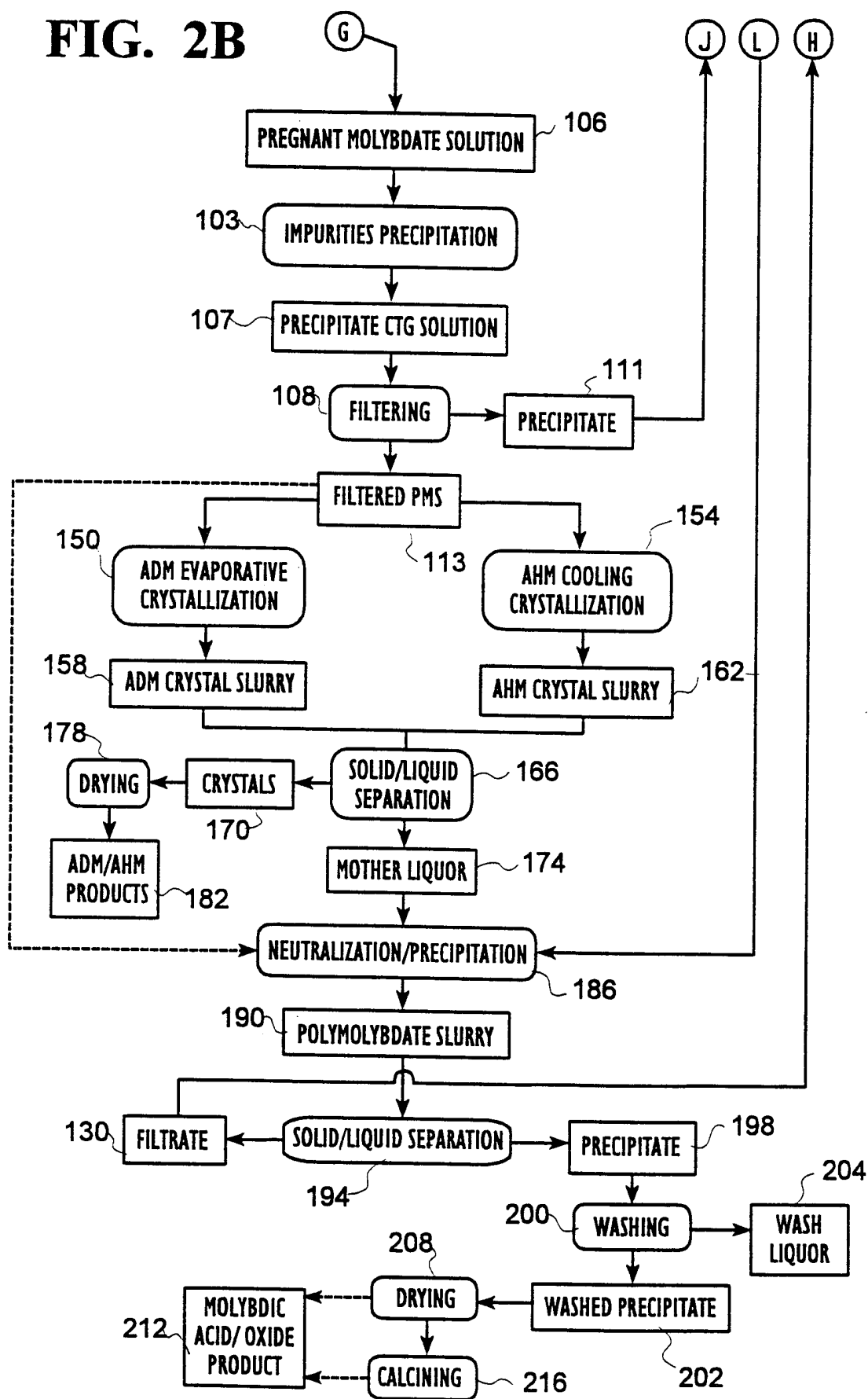
**FIG. 1**

FIG. 2B



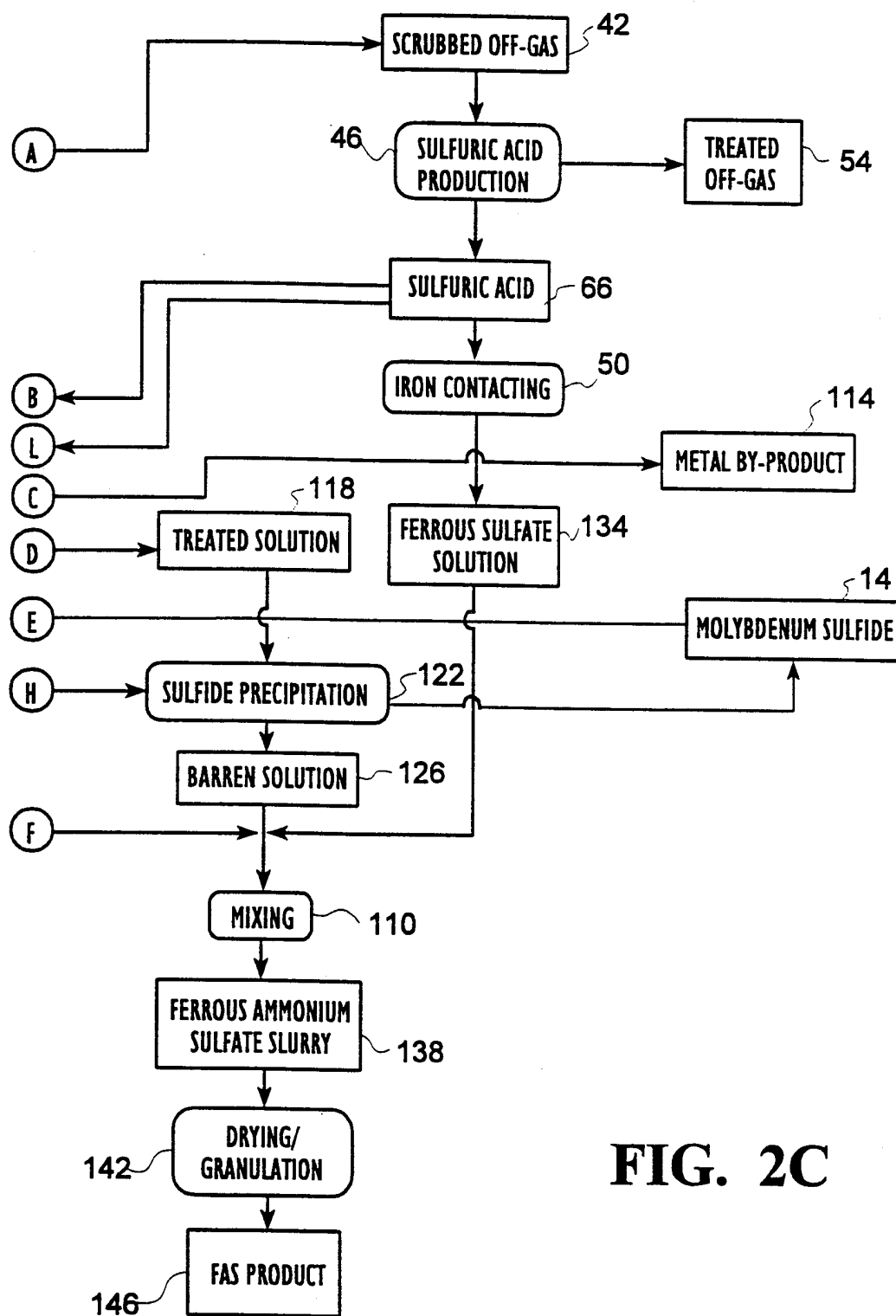


FIG. 2C