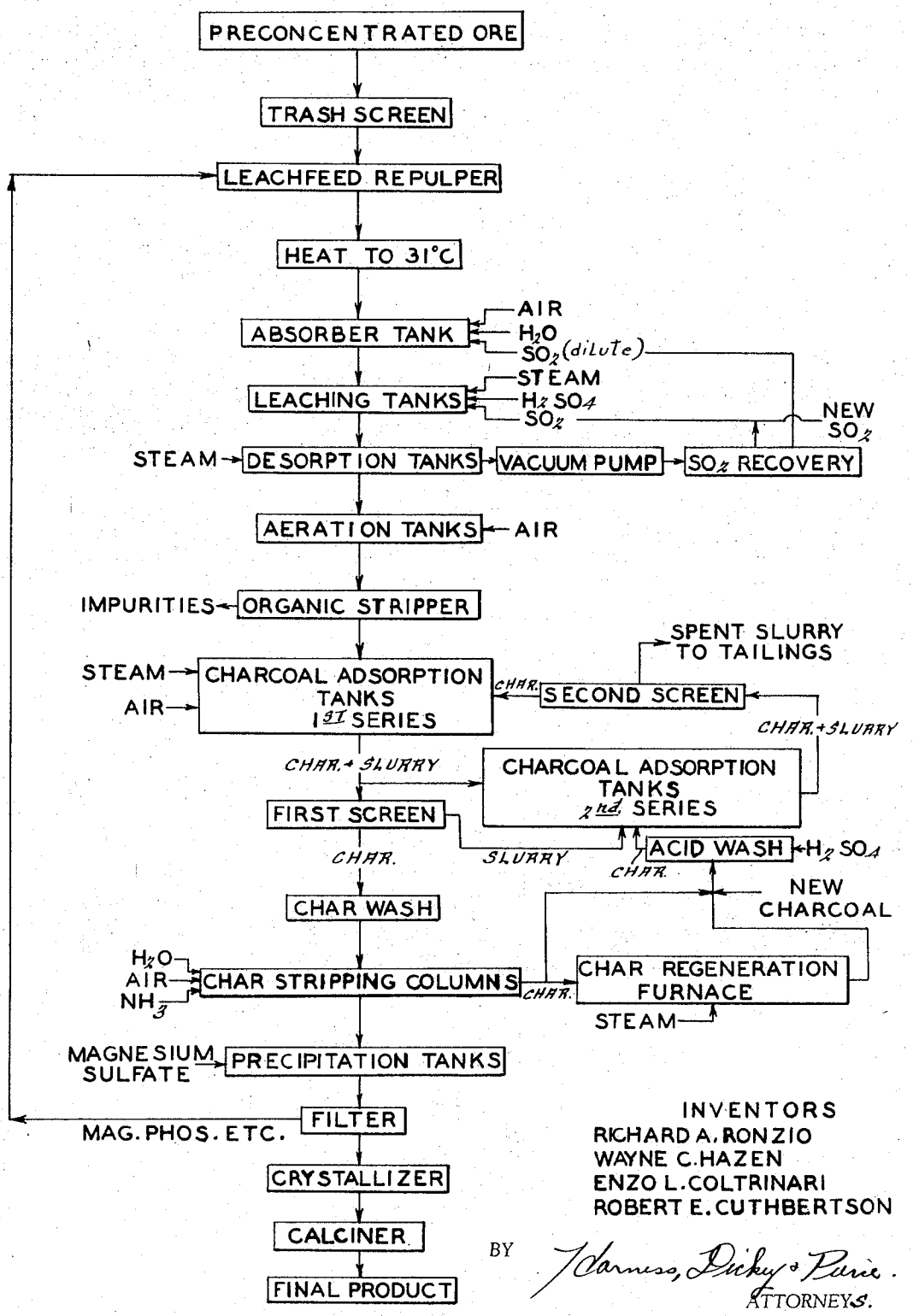
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PROCESS FOR EXTRACTING METAL VALUES

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PROCESS FOR EXTRACTING METAL VALUES

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The present invention relates to the treatment of mineral ores and more particularly to a hydrometallurgical process for recovering molybdenum from molybdenum bearing minerals.

As is known, the most important molybdenum ores contain molybdenite (MoS_2) and/or oxidized molybdenum that is associated with iron. The more important deposits of ore, however, contain molybdenum largely as the sulfide, i.e., as MoS_2. Although these molybdenum bearing ores seldom carry more than 1% or so of the mineral, methods having been developed whereby such ores are concentrated by flotation to produce a concentrate containing 90% or more of the molybdenum disulfide. In such an operation, however, that portion of the molybdenum found in the ore in an oxidized form is not flotated but appears in the tailings. As far as is known, no profitable commercial utilization has yet been made of such oxidized form and it has been simply discarded.

The present invention resides primarily in the discovery of a profitable and economically feasible technique for extracting molybdenum from those oxidized portions of ores which heretofore have been considered a commercially impractical source. It has been recently discovered that in the molybdenum ore deposits at Climax, Colorado, one of the largest deposits of molybdenum in the world, the oxidized molybdenum is associated with an iron oxide hydrate, goethite ($Fe_2O_3 \cdot H_2O$). This goethite contains approximately 1.3 to 9.6% oxidized molybdenum by weight. It is also apparently associated with other iron compounds such as Jarosite ($K_2Fe_6(OH)_{12}(SO_4)_4$) and ferri-molybdite ($Fe_2MoO_4)_3 \cdot XH_2O$). As a consequence of this discovery, a feasible pre-concentration process has been developed for concentrating the oxidized molybdenum values in this ore (approximately .14% molybdenum in a nonsulfide form) to a point where it is commercially practical to extract them. This process operates on the basis of concentrating iron oxide and since the molybdenum is dissolved therein there is thus produced a higher concentration of molybdenum and consequently a reduction in the total amount of material which will have to be handled through the remainder of the extraction process. This concentration can be effected by particle size separation of the finely milled ore (since the iron compounds are more friable they break into smaller particles than the remainder of the ore), by flotation, by magnetic separation, or by any combination of these methods. By such methods it is possible to increase the molybdenum concentration in this ore to approximately .30% (concentrations from .25% to .37% have been achieved). The iron concentration in this concentrate would be approximately 3%, or roughly tenfold.

Considering the present process broadly, the pre-concentrated ore to be processed is preferably introduced in the form of a relatively high pulp density aqueous slurry (approximately 50% solids). This slurry is first heated and then leached with a combination of sulfuric acid and gaseous sulfur dioxide to dissolve the iron and molybdenum compounds therein. The sulfur dioxide is then flashed off and the slurry is aerated. The slurry is then passed through a series of activated charcoal adsorption tanks where the molybdenum values are preferentially picked up by the activated charcoal. The loaded charcoal

is then stripped with air, ammonia, and water to form ammonium molybdate solution. Undesirable phosphorous values may be precipitated as magnesium ammonium phosphate by adding magnesium sulfate to the solution. The ammonium molybdate may be separated from the solution by crystallization and if desired may be converted to molybdenum oxide of a greater than technical grade by a calcining operation.

It is therefore a primary object of the present invention to provide an improved continuous process for economically extracting molybdenum values from ores containing molybdenum in oxidized forms.

A further object of this invention concerns the provision of an improved process for economically leaching molybdenum values from molybdenum bearing ore. A related object concerns the provision of such a leaching process suitable for use on relatively high pulp density slurries, i.e., in the order of 50% solids. Another related object concerns the provision of such a leaching process which is relatively fast acting, thereby reducing the size of the leaching tanks required for a given output capacity, as well as overall cycle time.

Yet another object of this invention resides in the provision of an improved process for preferentially extracting molybdenum values from a leach liquor containing dissolved iron and molybdenum values.

Another object resides in the provision of a novel combined leaching and adsorption process for economically extracting high recovery amounts of molybdenum from ores containing the oxidized forms thereof.

Another object of this invention concerns the provision of a unique activated charcoal extraction process which possesses the desirable characteristics of both cocurrent and countercurrent systems without being subject to the disadvantages thereof. A related object resides in the provision of such a process which is operable upon a slurry, and specifically a high density slurry.

A further object resides in the provision of a novel charcoal stripping process which will yield molybdenum values of increased concentration, which has a heat of reaction operable to increase the speed of the stripping operation, and in which the primary stripping agent is relatively inexpensive and easily recoverable for reuse.

Further objects, features, and advantages of this invention will become apparent from consideration of the following description, the appended claims, and the accompanying drawing in which there is shown schematically a flow diagram of the present process.

The present invention will be described for examplary purposes only embodied in a detailed commercial process which has been found through pilot plant and other studies to give very satisfactory results when applied to the presently obtained tailings from the commercial molybdenite flotation plant now processing the molybdenum ore at Climax, Colorado.

The ore slurry from the pre-concentration process, approximately .30% molybdenum, 50% solids, minus 65 mesh in size, and substantially neutral in pH, is first passed through a 35 mesh trash screen to eliminate any trash. The slurry, which at this point is approximately 4.4° C. because of the cold water used in the pre-concentration process, is fed, as it becomes available, into a surge tank from which it may be pumped continuously at a constant rate to the extraction system. Into this tank may also added, for reprocessing, the filtration precipitate from the magnesium sulfate precipitation step, as will be described in detail later. The tank is under atmospheric pressure. The slurry may be pumped through heat exchangers which will increase its temperature to approximately 31° C. Heating is not essential at this point but since it is required later in the process and since certain of the tailings from a later stage in the process are relatively hot (about

60° C.) this material is used to preheat the slurry at this time. It is then fed into an absorber tank into which also may be introduced a portion of the SO_2 which is recovered from a later portion of the process. This SO_2 is slightly contaminated and dilute with air and moisture but may be economically utilized at this point because the slurry temperature is relatively low and the gas therefor more soluble. The slurry may be agitated to aid absorption. This operation is continuous and the tank is at atmospheric pressure.

The slurry, which is still approximately 50% solids, is then fed through a series of leach tanks in which it is gently agitated at atmospheric pressure. A plurality of tanks are used to prevent any short circuiting of the slurry flow, and to provide flexibility of operation. Although a pressure system would be faster it would not be as economical overall because of the considerably greater cost of pressure equipment. In addition, there may also be fouling as a result of the increased formation of thionates. The operation is continuous and the rate of flow is such that the leach time is approximately 12 hours. To the first of these tanks is added sulfuric acid, gaseous sulfur dioxide and live steam. To SO_2 is bubbled in at the bottom where the pressure and hence solubility are the greatest. It has been found that 53 to 75 and preferably about 72 pounds of 93% H_2SO_4 per ton of dry ore, and 15 to 30 and preferably about 20 pounds of 100% SO_2 per ton of dry ore give very satisfactory results for ore of the type presently being mined at Climax, Colorado. The resulting pH of the solution should range between 1.0 to 1.3 and is preferably approximately 1.2. The SO_2 ion concentration should range between 10 to 15 and is preferably approximately 10 grams per liter of solution, and the oxidation state (E.M.F.) of the solution is about −200 to −250 mv. as measured with a platinum electrode with reference to a saturated calomel electrode. The steam serves to maintain leaching the temperature at approximately 60° C. It has been found that leach temperatures of 60° to 70° C. give the best results, however at 70° C. there is not enough of an improvement to economically justify the cost of the additional heat. Temperatures higher than 70° C. are not satisfactory because of the decrease in SO_2 solubility.

Although it is not completely known in what exact forms the molybdenum exists in the leach liquor, because of the complex manner in which its many valence forms react, the liquor is predominantly iron in the form of ferrous sulfate, and the molybdenum is believed to be in the form of molybdenum blue, a complex acid colloid, and possibly some molybdate. Also there may be a small amount of phosphorous as phosphates, sulfur as sulfates and thionates, and other normally encountered impurities. About 95–96% of the molybdenum can be successfully leached by this operation.

Generally speaking, the leaching operation is an SO_2 leach. The process is greatly improved, however, by the addition of the H_2SO_4, for a number of reasons. First, the acid greatly increases the speed of the operation, the leaching time of SO_2 alone being as much as four times longer than with the combination of SO_2 and H_2SO_4. Second, it makes it possible to obtain high leach extractions while operating in a very high density pulp. There factors substantially reduce the size and amount of equipment required for leaching a given quantity of ore and for tailings disposal. Third, the H_2SO_4 brings the pH level of the solution down to a value which greatly enhances the later charcoal adsorption operation. In the absence of it the pH of the solution would increase to about 4 when the SO_2 was desorbed and as a consequence the ferric iron in the leach solution would precipitate as a hydroxide, which would interfere with charcoal adsorption. Fourth, if it is not used sulfites would be formed which would also interfere with charcoal adsorption since they tend to be adsorbed before some of the molybdenum values. Fifth, it is believed that the acid also prevents the oxidation of some of the molybdenum blue to molybdate, which would not adsorb as well at a pH of 4. The H_2SO_4 will not work satisfactorily alone because it will not dissolve more than about 60% of the iron. It is preferable that the SO_2 and H_2SO_4 be added to the pulp in the same vessel since harmful scale was observed to form if the acid was added first.

The above specified quantities are those which have been found to do the job the most economically overall. Sufficient SO_2 should be used to completely leach the iron and molybdenum values, with a minimum of excess. This amount may vary slightly with temperature, according to known solubility principles. Also, for ores containing greater quantities of iron and molybdenum proportionally greater amounts of SO_2 should be used because there is more leaching to be done. For example, if the ore contained .20% molybdenum approximately 7 pounds SO_2 per ton of ore would be required, and if the ore contained .40% molybdenum approximately 33 pounds of SO_2 per ton would be required. In actual practice the quantity of H_2SO_4 should be sufficient to bring the pH level down to an acceptable point (i.e., 1.0 to 1.3) and to speed the reaction time to where the process is the most economical. It has been found that the amount of acid required does not vary substantially with the grade of ore, unless limestone or other alkaline materials are present in large quantities, in which case it should be increased. Although the use of additional quantities of SO_2 and H_2SO_4 would speed reaction time somewhat, it is wasteful of these materials and less economical on the overall.

From the leaching tanks the slurry is pumped through a series of desorption tanks in which it is agitated a sufficient time to flash off the SO_2. This may take anywhere from about 5 min. to 45 min. the exact time not being critical. The process is continuous. These tanks are maintained under a vacuum of approximately 6" Hg absolute and steam is injected into the tanks to effect vaporization by heating the slurry. The temperature of the slurry in the tanks ranges from about 55° C. to 60° C., from beginning to end, and the SO_2 concentration in the slurry output is reduced to approximately 0.4 grams per liter of solution. If desired, the SO_2 flashed off in the desorption tanks may be recovered using conventional techniques and re-used in the absorbing and leaching operations discussed above. The portion of the SO_2 recovered in a low grade or slightly contaminated state would be used in the absorption process. The E.M.F. oxidation state of the slurry issuing from the desorption tanks is approximately −200 to −250 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, and the pH is 1.3 to 1.8, and preferably about 1.5. Although this process might be performed by boiling the pulp, the high cost of the heat required makes such a technique uneconomical.

The slurry is then fed through a barometric leg to a series of aeration tanks where it is agitated for a total of approximately 30 minutes while air is blown upwardly through it. The tanks are under atmospheric pressure. This is a continuous process and it serves not only to remove the small remaining amount of SO_2 in the slurry, but more importantly to oxidize the slurry in a manner which greatly enhances the charcoal adsorption process. It has been found that the efficiency of the charcoal adsorption process is greater with greater minus E.M.F. levels of oxidation. Taking into account economical considerations, for charcoal adsorption the slurry should have an oxidation state (E.M.F.) of approximately −250 to −300 mv., and preferably about −270 mv., as measured by a platinum electrode with reference to a saturated calomel electrode. Accordingly, air is added in an amount sufficient to raise the oxidation level to this point. More air would give a more negative E.M.F. and a greater percent charcoal adsorption, up to a point (approximately −380 mv.), however it is too costly because of the air

required and because it would take a disproportionally longer time, thus requiring more equipment and so on. The degree of oxidation of the solution appears to be governed primarily by the ferric to ferrous ratio, rather than by oxidation of the molybdenum itself, and such oxidation can be effected by either aerating the solution or adding ferric sulfate, although the former is preferred. Even though there is ferric iron present it does not precipitate because the pH is about 1.5. The air does not seem to effect the pH value. It has been found that the small amount of SO_2 originally present in the solution actually aids this oxidation process.

The slurry may then be fed through an organic stripper tank in which any floating oils or other organic materials may be skimmed off. If desired, these materials may be additionally processed for recovery of any of the desired values therein.

The slurry (approximately 47% solids at this point) is now ready for the activated charcoal adsorption operation. It would be advantageous to use a countercurrent flow charcoal adsorption system (the new charcoal and new slurry flowing in opposite directions) so that the freshest charcoal would be in contact with the weakest slurry. However, in order to accomplish this it would be necessary to screen the charcoal from the slurry between each pair of adsorption tanks. Thus if seven tanks are used this would require six additional screens, which would not only require more equipment but would tend to break up the charcoal. This is undesirable because the charcoal must eventually be separated from the ore slurry with a relativel ycoarse screen. On the other hand, a cocurrent flow arrangement, unlike a countercurrent flow system, would be ineffective to build up a high molybdenum loading on the charcoal unless the retention time was greatly increased. A high loading is advantageous since it reduces the quantity of material that must be handled in the stripping operation and the number of stripping operations required for a given quantity of charcoal to extract a given quantity of molybdenum. The present activated charcoal adsorption cycle achieves the advantages of both cocurrent and countercurrent systems with a minimum amount of equipment and without the disadvantages of either.

As can be seen from the flow sheet, in the present cycle the ore slurry and charcoal are cycled in a cocurrent fashion through a first series of charcoal adsorption tanks. The process is continuous and the tanks are at atmospheric pressure. Multiple tanks are used for the adsorption operation since it reduces the chance that some of the ore may short circuit the desired adsorption time period, which is preferably in the order of 8½ hours in this series, and to provide flexibiilty. During this period the ore is gently agitated by an impeller and draft tube arrangement. A small quantity of air may also be introduced into the tanks to maintain proper E.M.F. value, if it is found necessary. The agitation need only be sufficient to keep the solids in suspension since excessive agitation will break the charcoal. Steam is also introduced to the first adsorption tank in the first series to maintain the slurry at approximately 60° C. Generally, the higher the temperature the greater the adsorption efficiency, probably due to the increased mobility of the molybdenum molecules, at least up to approximately 120° C., at which point the molybdenum will start to precipitate. However, 60° C. has been found to be the most economical on the overall. Increased pressures will also increase adsorption efficiency, at least up to the point where they cause the slurry to reach 120° C., but are not economically practical in view of increased equipment and operating costs. Also they tend to cause corrosion problems. For the ore described, approximately 74% of the charcoal and slurry flow is pumped from the first series of adsorption tanks through a first screen (35 mesh) which separates the loaded charcoal, which proceeds on to the stripping operation, from the slurry, which is re-cycled in the charcoal adsorption operation as will now be described.

Approximately 26%, or the balance, of the charcoal-plus-slurry flow from the first series of charcoal adsorption tanks is bypassed from the first screen and fed in a cocurrent fashion through a second series of charcoal adsorption tanks. Also fed into this second series of adsorption tanks is the slurry which was separated from the primary flow by the first screen. Here it is similarly agitated, but for only about 3½ hours. The charcoal-and-slurry flow from the second series of adsorption tanks is then pumped through a second de-watering screen which separates the loaded charcoal from the spent slurry, which is pumped to tailings. The loaded charcoal from the second screen flows back into the first series of charcoal adsorption tanks for recycling. Thus, by virtue of this recycling operation it is possible to build up a molybdenum loading on the charcoal of 8% or more.

It has been found, taking into account flow rate, that adsorption efficiency varies with the number of cubic feet of charcoal per cubic foot of adsorption tank. Based on this it has been found that very satisfactory efficiencies may be obtained using approximately 3 pounds of charcoal per cubic foot of total pulp. It has also been discovered that a charcoal loading of 5 to 15, and preferably 8, pounds of molybdenum per 100 pounds of charcoal will yield a maximum amount of adsorption within a practical period of time. If too long a period is used the charcoal wears, which is undersirable because it then becomes more difficult to separate, and because more equipment is required. Also, a portion of the charcoal is lost, thereby increasing the cost of the new charcoal added. For a given ore this loading may be obtained by regulating the proportion of the charcoal-plus-slurry flow which is bypassed from the first screen to the second series of adsorption tanks. The greater the amount bypassed the greater the charcoal loading. It is undesirable to bypass too much with a given amount of charcoal, within a given period of time, since this will result in a wasteful flow of unadsorbed molybdenum values to tailings. Different degrees of loading may better be achieved by varying the time of absorption.

Although the basic chemistry of the charcoal adsorption process is not well understood, the charcoal does adsorb most (about 96%) of the molybdenum blue and other molydates and only a very small amount of the other impurities. As discussed previously, it has been found that the efficiency of the adsorption operation is substantially affected by the oxidation level of the molybdenum solution. Experiments show that the adsorption process operates satisfactorily when the oxidation potential (E.M.F.) of the molybdenum solution has an E.M.F. value ranging from —220 mv. to —300 mv. but is improved if the E.M.F. value is between —250 mv. and —300 mv., and preferably —270, as measured by a platinum electrode with reference to a saturated calomel electrode. It is also important, for the aforementioned reasons, that the pH of the solution be acidic, in the range of 1.3 to 1.8 and preferably 1.5, at the time it is contacted with the charcoal. Other than for these reasons, the adsorption efficiency does not appear to depend on the pH value within this range. The adjustment of degree of oxidation of the solution is achieved by the aeration step in which air is blown through the leach liquor, and also by the introduction of air directly into the adsorption tanks.

The charcoal used should be of the "activated" type and should have the following characteristics. First, it should preferably be approximately 8 x 20 mesh in size. Second, it must be of a type which will adsorb molybdenum values. Third, it should be sufficiently hard that when it is cycled in the process it will not wear or fracture to a point where it may no longer be separated by the relatively coarse screens used. There are now commercially available several charcoals which meet these

criteria, such as Type CMO, 8 x 20 mesh, supplied by the Pittsburgh Chemical Company. The thicker the pulp treated the more concentrated is the molybdenum to be adsorbed, however, it should not be so thick as to interfere with free circulation of the charcoal and slurry. The present slurry is approximately 47% solids and has a specific gravity ranging from 1.35 to 1.45.

The loaded charcoal from the first screen is washed in water and fed to the charcoal stripping columns. The stripping operation has six stages and is preferably carried out in a semi-continuous cycle operation utilizing six vertical columns of the type employed in ion exchange operations. When the loaded charcoal is loaded into one column it remains there until it is given the six stage treatment and is then removed. The timing of the cycle and staggering of stages is such that charcoal is being loaded and removed continuously, although each column operates on a batch basis. The six stages are as follows:

Stage 1.—The column is filled with loaded charcoal, the process taking about sixty minutes.

Stage 2.—The loaded charcoal is washed for about ten minutes with a downward flow of water.

Stage 3.—The wash water is drained, taking about fifty minutes.

Stage 4.—Ammoniation takes place using a gaseous mixture of from one to two parts of air to one part NH_3 (downward flow). About .8 to 1.2 and preferably .87 to 1.0 pounds of NH_3 are used per pound of molybdenum stripped. As little NH_3 as is necessary should be used because of recovery costs. The air acts as a cooling agent and also assists the stripping operation by providing an oxidizing effect. It is believed that the molybdenum compounds contain thionates, probably as a dithionate ion (S_2O_6—), which will slowly be decomposed in later stages of operation to cause trouble. The air apparently oxidizes them to sulfates, which present no later extraction problems. The air also oxidizes the molybdenum, which aids the stripping process. The amount of air added in excess of a 1:1 ratio with NH_3 will depend on the temperature of the ammoniation reaction, and should be sufficient to prevent this temperature from exceeding the boiling point of the solution. The ammonia reacts with the molybdenum in the solution to form ammonium molybdate. Any iron sulfate carried along will be converted to ferric hydroxide, a slimy substance which is carried out by the wash water.

Stage 5.—Elution takes place with a downward flow of dionized water for about sixty minutes.

Stage 6.—The column is then emptied, which takes about twelve minutes.

Ammonia has been found to be a preferable stripping medium since it is more economical than caustic. In addition, it is relatively easy to recover for re-use. Also, it and its resultant ammonium salts will burn off with calcining to give molybdenum oxide. The pregnant solution which leaves the charcoal stripping columns contains molybdenum as ammonium molybdate (about 70 grams Mo/L), sulfur as ammonium sulfate (about 7 grams S/L), and phosphorus as ammonium phosphate (about .7 grams P/L). The columns are operated at substantially atmospheric pressure and the solution has a temperature of approximately 60° C. as a result of the heat of the ammoniation reaction. The actual temperature of the band of ammoniation occurring in this stage is just below the boiling point and therefore additional heat is not required. Also, it has been found that better stripping efficiencies are obtained if the charcoal is moist, rather than dry. Approximately 98% of the molybdenum is stripped by this process.

In the order of 20 pounds charcoal per ton of dry ore from the charcoal stripping columns is fed to a charcoal regeneration furnace where it is heated to 800° with steam for about one-half hour in the presence of combustion gases (CO_2 and N_2). This amount has been found to keep the charcoal efficiency 90% or greater as compared to virgin charcoal. Otherwise, the charcoal would become poisoned and adsorption would drop off. The charcoal from the regeneration furnace is then mixed with the remaining charcoal flow from the charcoal stripping columns. At this point new charcoal to make up for any losses is also added to the system and the combined charcoal flow is passed through a 1% sulfuric acid wash. H_2SO_4 is preferred because it is cheap and because it is the same as that used in leaching. The acid wash removes any residual NH_3 from the stripping operation which might otherwise react with the iron sulfate in the ore slurry and form iron hydroxide, a slimy precipitate which would clog the charcoal. The acid-washed charcoal is then added to the second series of charcoal adsorption tanks to complete the charcoal cycle. Thus, in this series of adsorption tanks the freshest charcoal will be brought into contact with the weakest slurry to thereby obtain some of the advantages of a counterflow system, but with only one added screen. In addition, the aforedescribed cocurrent recirculation of the slurry permits high loading of the charcoal.

The ammonium molybdate solution from the stripping columns usually contains a small amount of phosphorus (the Mo/P ratio is in the order of 100:1). To remove this the ammonium molybdate solution is cooled to about 20° to 25° C. and is fed to a precipitation tank where it is combined with magnesium sulfate, which causes a precipitation of magnesium ammonium phosphate, thus eliminating any phosphorous compounds picked up in the charcoal from the ore. The pH of the solution should be above 8.6 and is about 9.0 to 9.5. A 25% solution of magnesium sulfate is used in a stoichiometric quantity sufficient to react with the amount of phosphorous present, i.e., about 8 pounds of Epsom salt ($MgSO_4 \cdot 7H_2O$) per pound of phosphorous. The solution is gently agitated for approximately eight hours. This allows time for an analysis of the solution to determine if sufficient magnesium sulfate has been added. Only about 15 to 30 minutes are necessary to actually precipitate. Thereafter, the precipitated phosphorus compound, as well as any precipitated iron and other insoluble hydroxides which precipitated during stripping, are filtered out of the solution. In addition, any other solid material will also be filtered out of the solution. Two tanks may be used alternately so that while one is standing the other is being filled. They operate at atmospheric pressure. The filtered insolubles are then returned to the leach feed repulper at the beginning of the system, i.e., ahead of the leaching operation, for reprocessing to pick up any molybdenum values which may remain in the solution. This is feasible because the charcoal picks up only a minor portion of the phosphorous and therefore the phosphorous will not continue to build up.

The remaining filtrate solution contains ammonium molybdate, ammonium sulfate, and free ammonia. The manner in which the molybdenum values are extracted from the solution does not form a part of the present invention and may be accomplished in any suitable manner. For example, the solution may be passed through a crystallizer in which ammonium paramolybdate crystals will be formed. These crystals may then be filtered out and conveyed to a calciner for conversion to a final product of molybdenum oxide of greater than technical grade. If ammonium paramolybdate is desired as a final product it may be withdrawn from the system prior to the calcining operation.

As will be evident the present invention resides in the provision of a novel hydrometallurgical extraction process, and is not limited to the use of any specific type of apparatus or equipment. Furthermore, in the above example the amounts, ranges and so on are those which are preferable for the extraction of ore of the

type set forth. Ores differing slightly from the ores described herein may also be treated by the present process, the only changes necessary being those which will be readily apparent to one skilled in the art in light of the teachings of the present disclosure.

Thus, there is disclosed in the above description and in the drawing an example embodying the invention which fully and effectively accomplishes the objects thereof, however, it will be apparent that variations in the details set forth may be indulged in without departing from the sphere of the invention herein described or the scope of the appended claims.

What is claimed is:

1. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: leaching the ore with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

2. Process for extracting molybdenum values from an aqueous slurry of ore containing oxidized molybdenum in association with iron, comprising: leaching the ore with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

3. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: leaching the ore with sulfuric acid and sulfur dioxide to form acid colloids of the molybdenum, desorbing the sulfur dioxide, adsorbing the molybdenum acid colloids with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

4. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: leaching the ore with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form an ammonium salt of molybdenum.

5. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: forming an aqueous slurry of the ore having a pulp density of 45% to 50%, leaching the slurry with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

6. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: leaching the ore with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, oxidizing the leach liquor to an EMF level of —220 to —280 m.v. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

7. Process as claimed in claim 6, wherein said oxidizing is performed by aerating the leach liquor.

8. Process for extracting molybdenum values from an aqueous slurry of ore containing oxidized molybdenum in association with iron, comprising: leaching the slurry with sulfuric acid and sulfur dioxide to form acid colloids of molybdenum, desorbing the sulfur dioxide, adsorbing the molybdenum acid colloid with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form an ammonium salt of molybdenum.

9. Process for extracting molybdenum values from an aqueous slurry of ore containing oxidized molybdenum in association with iron, comprising: leaching the slurry with sulfuric acid and sulfur dioxide to form acid colloids of the molybdenum, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of —220 to —380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum acid colloid with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

10. Process for extracting molybdenum values from an aqueous slurry of ore containing oxidized molybdenum in association with iron, comprising: leaching the slurry with sulfuric acid and sulfur dioxide to form acid colloids of the molybdenum, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of —220 to —380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum acid colloid with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form an ammonium salt of the molybdenum.

11. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: forming an aqueous slurry of the ore having a pulp density of 45% to 50%, leaching the slurry with sulfuric acid and sulfur dioxide to form acid colloids of the molybdenum, desorbing the sulfur dioxide, aerating the leach liquor to oxidize it to an E.M.F. level of —220 to —380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum acid colloid with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form an ammonium salt of the molybdenum.

12. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: leaching the ore, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form an ammonium salt of the molybdenum.

13. Process for extracting molybdenum values from an ore containing oxidized molybdenum in association with iron, comprising: leaching the ore, oxidizing the leach liquor to an E.M.F. level of —220 to —380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

14. Process for extracting molybdenum values from an aqueous slurry containing oxidized molybdenum in association with iron, comprising: adding sufficient sulfur dioxide to the slurry to leach the molybdenum, adding sufficient sulfuric acid to the leach liquor to establish and maintain the pH thereof from about 1.0 to 1.3, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about —220 to —380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

15. Process for extracting molybdenum values from an aqueous slurry containing oxidized molybdenum in association with iron, comprising: adding sufficient sulfur dioxide to the slurry to leach the molybdenum, adding sufficient sulfuric acid to the leach liquor to establish and maintain the pH thereof from about 1.0 to 1.3, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about —220 to —380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form ammonium molybdate.

16. Process for extracting molybdenum values from an aqueous slurry containing oxidized molybdenum in association with iron, comprising: adding sufficient sulfur di-

oxide to the slurry to leach the molybdenum, adding sufficient sulfuric acid to the leach liquor to maintain the pH thereof from about 1.0 to 1.3, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about −250 to −300 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

17. Process for extracting molybdenum values from an aqueous slurry containing oxidized molybdenum in association with iron, comprising: adding sufficient sulfur dioxide to the slurry to leach the molybdenum, adding sufficient sulfuric acid to the leach liquor to maintain the pH thereof from about 1.0 to 1.3, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about −250 to −300 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form ammonium molybdate.

18. Process for extracting molybdenum values from an aqueous slurry containing oxidized molybdenum in association with iron, comprising: adding sufficient sulfur dioxide to the slurry to bring the SO_2 ion concentration up to about 10 to 15 grams per liter of solution for leaching the molybdenum, adding sufficient sulfuric acid to the leach liquor to maintain the pH thereof from about 1.0 to 1.3, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about −220 to −380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the loaded charcoal.

19. Process for extracting molybdenum values from an aqueous slurry containing oxidized molybdenum in association with iron, comprising: adding sufficient sulfur dioxide to the slurry to bring the SO_2 ion concentration up to about 10 to 15 grams per liter of solution for leaching the molybdenum, adding sufficient sulfuric acid to the leach liquor to maintain the pH thereof from about 1.0 to 1.3, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about −220 to −380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the loaded charcoal with gaseous ammonia and air to form ammonium molybdate.

20. Process for extracting molybdenum values from ores containing oxidized molybdenum in association with iron, comprising: forming an aqueous slurry of the ore, leaching the slurry with about 53 to 75 pounds of 93% sulfuric acid and about 15 to 30 pounds of 100% sulfur dioxide per ton of ore, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about −220 to −380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

21. Process for extracting molybdenum values from ores containing oxidized molybdenum in association with iron, comprising: forming an aqueous slurry of the ore, leaching the slurry with about 53 to 75 pounds of 93% surfuric acid and about 15 to 30 pounds of 100% sulfur dioxide per ton of ore, desorbing the sulfur dioxide, oxidizing the leach liquor to an E.M.F. level of about −220 to −380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form ammonium molybdate.

22. Process of extracting molybdenum values from ores containing oxidized molybdenum in association with iron, comprising: forming an aqueous slurry of the ore having a pulp density of 45% to 50% solids, leaching the slurry with about 53 to 75 pounds of 93% sulfuric acid and about 15 to 30 pounds of 100% sulfur dioxide per ton of ore to form acid colloids of the molybdenum, desorbing the sulfur dioxide, aerating the leach liquor to oxidize it to an E.M.F. level of about −250 to −300 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, adsorbing the molybdenum acid colloids with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form ammonium molybdate.

23. Process as claimed in claim 22, wherein the stripping air to NH_3 ratio ranges from about 1:1 to 2:1.

24. Process as claimed in claim 23, wherein from about .8 to 1.2 pounds of NH_3 are used per pound of molybdenum stripped.

25. Process for extracting metal values from an aqueous solution thereof in a slurry having a pulp density of from about 45% to 50% solids, comprising: feeding the slurry through a first series of adsorption tanks concurrently with activated charcoal, feeding a fraction of the outflow from the first series of tanks through a second series of adsorption tanks, separating the loaded charcoal from the outflow of the second series of tanks and feeding it again through the first series of tanks, discharging the spent slurry from the second series of tanks out of the adsorption cycle, separating the slurry from the remainder of the outflow from the first series of tanks and feeding it through the second series of tanks, stripping the metal values from the loaded charcoal in the remainder of the outflow from the first series of tanks, regenerating a fraction of the stripped charcoal, and feeding the regenerated fraction of charcoal and the remaining unregenerated stripped charcoal again through the second series of tanks.

26. Process for extracting metal values from an aqueous ore slurry having a pulp density of from about 45% to 50% solids, comprising: leaching the metal values from the ore in the slurry, feeding the slurry through a first series of adsorption tanks concurrently with activated charcoal, feeding a fraction of the outflow from the first series of tanks through a second series of adsorption tanks, separating the loaded charcoal from the outflow of the second series of tanks and feeding it again through the first series of tanks, discharging the spent slurry from the second series of tanks out of the adsorption cycle, separating the slurry from the remainder of the outflow from the first series of tanks and feeding it through the second series of tanks, stripping the metal values from the loaded charcoal in the remainder of the outflow from the first series of tanks, regenerating a fraction of the stripped charcoal, and feeding the regenerated fraction of charcoal and the remaining unregenerated stripped charcoal again through the second series of tanks.

27. Process for extracting metal values from an aqueous ore slurry having a pulp density of from about 45% to 50% solids, comprising: adding sulfur dioxide and sulfuric acid to the slurry to leach the metal values, desorbing the sulfur dioxide, oxidizing the slurry to an E.M.F. oxidization level of about −220 to −380 mv. as measured by a platinum electrode with reference to a saturated calomel electrode, feeding the slurry through a first series of adsorption tanks concurrently with activated charcoal, feeding a fraction of the outflow from the first series of tanks through a second series of adsorption tanks, separating the loaded charcoal from the outflow of the second series of tanks and feeding it again through the first series of tanks, discharging the spent slurry from the second series of tanks out of the adsorption cycle, separating the slurry from the remainder of the outflow from the first series of tanks and feeding it through the second series of tanks, stripping the metal values from the loaded charcoal in the remainder of the outflow from the first series of tanks, regenerating a fraction of the stripped charcoal, and feeding the regenerated

fraction of charcoal and the remaining unregenerated stripped charcoal again through the second series of tanks.

28. Process as claimed in claim 27, wherein stripping is accomplished using ammonia and air.

29. Process for extracting molybdenum values from ores containing oxidized molybdenum in association with iron, comprising: leaching the ore with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, adsorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal with gaseous ammonia and air to form an ammonium salt of the molybdenum, the air to ammonia ratio being from about 1:1 to 2:1.

30. Process as claimed in 29, wherein from about .8 to 1.2 pounds of ammonia are used per pound of metal stripped.

31. Process for extracting molybdenum values from ores containing oxidized molybdenum in association with

iron, comprising: leaching the ore with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, feeding the leach liquor to adsorption tanks where the molybdenum values are extracted by activated charcoal, adding air to the absorption tanks, and stripping the molybdenum values from the loaded charcoal.

32. Process for extracting molybdenum values from the tailings from preliminarily flotation treated natural molybdenum containing ore, comprising: leaching the ore with sulfuric acid and sulfur dioxide, desorbing the sulfur dioxide, absorbing the molybdenum values with activated charcoal, and stripping the molybdenum values from the loaded charcoal.

No references cited.

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