PROCESS FOR RECOVERY OF MOLYBDENUM AND RHENIUM VALUES FROM MOLYBDENITE CONCENTRATE

MOLYBDENITE CONCENTRATE

\[ \text{H}_2\text{O}, \text{HNO}_3 \]

MOLYBDENITE OXIDATION

\[ \text{O}_2 \]

COUNTERCURRENT FILTRATION

\[ \text{H}_2\text{O} \]

HYDRATED MOLYBDENUM TRIOXIDE

COMBINED SOLVENT EXTRACTION

RECOVERY OF MOLYBDENUM AND RHENIUM

SULFURIC ACID SOLUTION CONTAINING ACID SOLUBLE METALS: CU, ZN, Fe, etc.

RHENIUM SOLVENT EXTRACTION

TO AMMONIUM MOLYBDATE RECOVERY

TO RE METAL PRODUCTION

FIG. 1

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16 Claims

ABSTRACT OF THE DISCLOSURE

Process for the recovery of molybdenum and rhenium from molybdenite which comprises: oxidizing the molybdenite in the molybdenite concentrate slurry to the hexavalent form with oxygen or oxygen containing gases and less than a stoichiometric amount of nitric acid for the sulfide sulfur present, recovering molybdenum and rhenium values from the resulting solution when it contains up to 600 g./L of sulfuric acid with an amine or quaternary ammonium type extractant, removing the molybdenum and rhenium values from the extractant with ammonium hydroxide, selectively recovering rhenium values from the resulting alkaline solution with a quaternary ammonium type extractant, recovering the remainder of the molybdenum values from the eluate, stripping rhenium from the extractant with perchloric acid or perchlorate salt and recovering rhenium from the stripping solution.

SUMMARY OF THE INVENTION

Conventional processes for the recovery of molybdenum from molybdenite involve roasting the molybdenite concentrate in air or otherwise processing it at high temperatures with the consequent release to the atmosphere of polluting gases, such as oxides of sulfur. The molybdc oxide product produced by these processes requires extensive purification. In view of the stringent regulations now being promulgated by the states and federal government regulating the amounts of polluting gases, such as sulfur dioxide, which can be emitted to the atmosphere, processes for the recovery of metals from sulfide ores without release of sulfur-containing gases are in demand. Another requirement for new processes is that they produce a higher purity molybdc oxide product.

Rhenium, which occurs largely in molybdenite, has now become a valuable metal for use in catalytic applications and others. Prior processes for the recovery of molybdenum from molybdenite have generally not been designed for the recovery of rhenium along with the molybdenum. Substantial recovery of rhenium along with molybdenum would enhance the commercial feasibility of any molybdenum recovery process.

Recovery of molybdenum as molybdc oxide from molybdenite concentrates using an oxidizing leach catalyzed by nitric acid is disclosed in the article entitled "Oxidizing Leach of Sulfide Concentrates and Other Materials Catalyzed by Nitric Acid" by C. Bjerling and G. A. Kolta, p. 135, of "Results of Papers Published From the International Mineral Congress, Technical Papers, 7th Meeting, New York, N.Y. 1964, Published 1965." The application of the same type process to other nonferrous metals is disclosed in U.S. Pat. 2,805,936.

In accordance with the process disclosed in the article, a relatively high concentration of nitric acid is required. Further, in order to perform the leaching necessary to recover 99% molybdc oxide as disclosed, it is necessary to at least partially neutralize the sulfuric acid formed in the oxidizing leach. The article also refers to performing the oxidizing leach in two steps.

Reduction of the amount of nitric acid used is an important economic consideration. Reduction of nitric acid is a saving in itself and it necessarily results in lesser amounts of nitrogen oxide gases being formed, with less oxygen being required to oxidize these gases to prevent their release to the atmosphere and reform nitric acid.

Neutralization of the sulfuric acid formed in the oxidizing leach before recovery of dissolved molybdenum is time consuming and the neutralization agent adds to the expense of the process. Neutralization of the sulfuric acid eliminates the possibility of cost reduction through sale of the acid. Further, the presence of contaminant metals or metalloids complicates the recovery of molybdenum by leaching and makes it more difficult to obtain a high purity product.

Although rhenium has been recovered from the flue gases resulting from the roasting of molybdenite as a calcined molybdc oxide product is recovered, no successful wet process for the simultaneous recovery of molybdenum and rhenium from molybdenite in substantial amounts is known. So far as is known, there are no oxidation leach processes utilizing nitric acid for the recovery of both molybdenum and rhenium from sulfide ores.

Accordingly, the principal object of this invention is to provide a process for the recovery in high yields of high purity molybdenum and rhenium from sulfide ores or concentrates by an oxidizing leach process utilizing nitric acid, which requires a minimum amount of nitric acid, eliminates the necessity for neutralizing the sulfuric acid formed during the oxidizing leach, and is effective in the presence of other metal or metalloid contaminants.

The process of the invention comprises subjecting finely divided molybdenite concentrate to an oxidizing leach in the presence of nitric acid to form insoluble molybdenum compounds and a solution having dissolved therein the rhenium values and some of the molybdenum values, recovering from the solution the molybdenum and rhenium values with an amine or quaternary ammonium type extractant, stripping molybdenum and rhenium values from the solvent with ammonium hydroxide, separating the rhenium from the molybdenum in the stripping solution with a quaternary ammonium type extractant, followed by final recovery of molybdenum and rhenium by conventional techniques.

It has been found that the process of this invention surprisingly requires about one-tenth the amount of nitric acid required in the prior process. By the use of an ion exchange system peculiarly applicable to the molybdenite oxidation leach solution for recovering molybdenum and rhenium values in the solution, the necessity of a further molybdenum recovery leaching step is avoided with consequent elimination of the necessity for neutralizing the sulfuric acid formed in the oxidation leach. This leaves the sulfuric acid available for sale. The extraction step recovers rhenium from this oxidation leach solution along with molybdenum. Further, the extraction step selectively recovers molybdenum and rhenium in the presence of the particular contaminant metals and metalloids present in the oxidation leach solution.

The process requires about 10-25 grams of nitric acid per liter of solution in contrast to the prior process which required about 100 grams per liter. The amount of nitric acid required is about 1/10 of the theoretical stoichiometric amount for the reaction involved in the oxidation leach step, i.e.,

\[ \text{MoS}_2 + 9\text{HNO}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{MoO}_4 + 9\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \]

Substantial recovery of the molybdenum and rhenium values in the oxidation leach solution has been effected
by use of an amine type ion exchange resin in the presence of up to 600 grams of sulfuric acid per liter of solution. So far as is known, this has never been done at acid concentrations approaching those used in this process. The lower limit of the amount of sulfuric acid present is determined by the speed of the process necessary for economic feasibility. The process is most advantageously performed in an autoclave to prevent escape of gases and to effectively enable independent control of pressure and temperature. It was found that the process can be conducted within acceptable temperature and oxygen pressure ranges.

As to the particle size of the concentrate, a very small particle size is preferable to provide the maximum feasible contact surface area.

The sulfuric acid formed in the process can be marketed without processing the leach solution or it can be readily purified before marketing.

The process is readily performed within a period of one hour. Process time is an important economic consideration.

The principal contaminant metals are iron and copper. The amine type and quaternary ammonium ion exchange resins used selectively recover molybdenum and rhenium in the presence of these metals.

The amine type resins which are operative to extract molybdenum and rhenium values from the oxidation leach solution are conventional long chain primary, secondary and tertiary amines used in the industry as metal ion extractants. Quaternary ammonium compounds may also be used. A preferred amine is a tertiary amine with a mixture of C₅₋C₉ carbon chains sold under the trade name of Alamine 336. Other preferred amines are those sold under the names Amberlite LA–1 (secondary amine), Alamine 304 (tri-alkyl amine) and Amberlite XLA–3 (primary amine). These amines are of the type disclosed in U.S. Pat. 3,052,516 and 3,156,524 and are referred to herein as amine type resins or amine extractants. The quaternary ammonium extractants are operative for separating rhenium and molybdenum from the alkaline strip solution containing these metals as ammonium molybdate and ammonium permanganate.

Conventional aromatic hydrocarbon diluents are used with the amine and quaternary ammonium resin extractants.

The quaternary ammonium extractants which are suitable are of the type disclosed in U.S. Pat. 3,083,085 and 3,575,687. A preferred agent is one being sold under the trade name of Aliglate 336.

The amine or quaternary ammonium extractant is highly effective to selectively extract rhenium and molybdenum from the oxidation leach solution which contains metal ion contaminants occurring in molybdate. The solution also contains sulfates and nitrates among other sols resulting from the catalytic oxidation leach.

Some of the molybdenum from the molybdic acid goes in solution during the oxidation leach step and the remainder is recovered mainly as an insoluble hydrated molybdate oxide, which is calcined to a high purity oxide.

The degree of conversion of the molybdenum to the insoluble compound, and consequently the amount to be recovered from solution by the extraction agent, can be controlled. The extraction step, or a second leach step accompanied by neutralization of sulfuric acid as in the prior art, is necessary to recover the molybdenum in solution. The extraction step is necessary to recover the rhenium from the oxidation leach solution. It is an obvious advantage of this invention, resulting in a reduction of required nitric acid, among other advantageous features, that the molybdenum in solution can be recovered in the extraction step necessary for the recovery of rhenium with an extractant peculiarly adaptable for this purpose to the nitric acid treated oxidation leach solution.

The oxidizing agent, nitric acid, can be supplied as aqueous nitric acid, nitrates, or by the addition of nitrous oxide gases which are oxidized to nitric acid during the reaction. Oxygen is introduced into the autoclave under pressure as required. The autoclave used was of the conventional type equipped with pressure and temperature-indicating devices.

The process of the invention is outlined in FIG. 1 of the accompanying drawings depicting a flow diagram of the process.

In practicing the process of the invention, the molybdene concentrate is introduced to the pressure reactor vessel as a wet slurry. Use of the wet slurry is an advantage of the present invention, since in the roasting processes the concentrate used must be dried. After the wet slurry is added to the reactor, water is added as necessary. The slurry may contain as high as 25% solids.

Nitric acid is then added to the slurry in the reactor in an amount varying from 0.037 to 0.37 pound of nitric acid per pound of molybdenum in the reactor, depending on the purity of the concentrate employed.

The temperature of the slurry containing the nitric acid is raised to about 100° C. at which temperature the oxygen gas is introduced into the autoclave under pressure and the reaction proceeds as in the beginning. These reactions are proceeding simultaneously at the total molybdene oxidation reaction is complete at times in no more than one hour, depending on the amount of molybdene present in the system.

The pressure reactor is then discharged, substantially all of the rhenium being dissolved and at least 85% of the molybdenum values being present as an insoluble hydrated hexavalent molybdenum oxide compound.

After the solids and liquid have been separated, the solid hexavalent molybdenum oxide can either be dried and marketed or subjected to conventional ammonium disulfonation techniques and finally recovered as ammonium molybdate or calcined to produce a high purity molybdenum trioxide.

The solution containing the rhenium values and less than 15% of the molybdenum values is subjected to solvent extraction with an amine type or quaternary ammonium solvent to separate the rhenium and molybdenum values from the sulfuric acid and other metal impurities, such as copper, zinc and iron. The molybdenum and rhenium barren sulfuric acid solution can be further processed for recovery of other metal values, such as copper, prior to utilization or discarding to waste.

The amine or quaternary ammonium extractant is diluted in either an aliphatic or aromatic hydrocarbon diluent and mixed with the strong sulfuric acid solution resulting from the oxidation and the result that the molybdenum and rhenium values are transferred to the solvent phase. These metal values are then re-extracted from the solvent phase by mixing with a strip solution containing ammonium hydroxide or other alkali stripping agent, such as other alkali hydroxides, carbonates, etc. The beneficial effects of staging in a countercurrent manner can be taken advantage of, if desired, to increase the yield.

The ammonia strip solution containing ammonium molybdate and ammonium permanganate is further processed with a quaternary ammonium type extractant or solid ion exchange resin to separate the rhenium from the molybdenum, the rhenium reporting to the solvent phase. This procedure is disclosed in U.S. Bureau of Mines Report of Investigations 6246, 1963, by P. E. Churchward and J. B. Rosenbaum. The ammonium molybdate is recovered from the aqueous rhenium-barren phase using conventional techniques. Rhenium values are recovered from
the solvent by stripping with perchloric acid or perchlorate salt followed by recovery of rhenium as ammonium perrenate in accordance with conventional procedures.

It has been found that the rate of oxidation leach is much faster if heat of reaction is removed from the pressure vessel wall during the reaction. The removal of heat prevents pressure build-up which in turn prevents introduction of oxygen under the existing conditions. The net effect is that more oxygen is available for the oxidation of the oxides of nitrogen back to nitric acid and the oxidation of molybdenum to the insoluble hydrated molybdc oxide. Experimentation has shown that during the reaction there is a large temperature differential between the dome gases and the slurry in the bottom of the reactor with the latter being much lower, the high temperature of the dome gases being due to the exothermic oxidation of the nitrogen oxide gases to nitric acid. Accordingly, it is preferred to locate cooling elements in the top of the reactor to remove heat as fast as possible. To accomplish the favorable heat removal the specially designed reaction vessel of FIG. 2 of the drawings was constructed.

Referring to FIG. 2, the numeral 10 identifies the wall of the pressure vessel which is provided with cooling jacket 12. The upper body of the vessel 10 terminates in a neck portion 14 terminating in a circular flange 16 defining the top opening of the vessel which is closed by the top 18 secured to flange 16 by bolts and nuts 20. A drain pipe 22 in the bottom of the vessel provided with valve 24 is for draining slurry from the vessel. The vessel is mounted on legs 25.

A neck 38 having a flange 30 with a top 32 bolted thereto with bolts and nuts 34 is seated in the top 18 of the vessel. A rotating mechanical seal 36 is mounted in top 32 and a turbine shroud 38 extends into the vessel 10 from the bottom of top 32 and is constructed integral therewith. The shroud is provided with gas inlet orifices 40 on opposite sides. The bottom of the shroud 38 terminates in a flat circular flange 42 which is provided with slurry inlet orifices 44. A motor 46 is mounted on the top 32 for driving turbine shaft 48 to rotate turbine blades 50.

A feed inlet pipe 52 provided with valve 54 is mounted in vessel top 18. A pressure gage 58 is also mounted in the top 18 for measuring the internal pressure of the vessel. For removing heat from the upper section or dome of the reactor, cooling coils 60 are mounted in the dome section with inlet 62 and outlet 64 extending through the upper wall of the vessel 10. Similar coils 60' are shown schematically in the bottom of the vessel for removing heat from slurry. These coils are optional. They may be mounted with inlet and outlet pipes through the vessel wall-like coils 60.

A thermowell 68 for liquid temperature and a thermowell 70 for gas phase temperatures are mounted in the vessel wall as shown with the former extending into the slurry area and the latter extending into the gas area.

During the entire period for the oxidation leach, cooling fluid is circulated through the coils 60 and also the coils 60' if the latter are used. Other cooling means to remove heat from the reaction area may be used.

The following examples are illustrative of the invention but not limiting thereof. In the examples, concentrations are given in weight percentages. Unless otherwise indicated the samples used in the examples had approximately the following composition:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Wt. percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>53.9–56.5</td>
</tr>
<tr>
<td>Re</td>
<td>0.081–0.089</td>
</tr>
<tr>
<td>Cu</td>
<td>1.05–1.15</td>
</tr>
<tr>
<td>Fe</td>
<td>1.33–1.45</td>
</tr>
</tbody>
</table>

**EXAMPLE 1**

The purpose of this example was to illustrate the conversion of MoS₂ to MoO₃ in a typical nitric acid oxidation of molybdenite.

Four hundred grams of molybdenite concentrate was transferred to a pressure autoclave reactor to which 25 grams of nitric acid were added along with one liter of water. The apparatus was sealed and heated to 125° C. at which point oxygen was introduced to keep a pressure of 150 p.s.i.g. The temperature reached a maximum of 170° C. The oxidation of molybdenite was substantially complete in a period from 1–2 hours and was complete in 4 hours. The results are given in Table 1.

**TABLE 1**

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. percent</th>
<th>t.g.</th>
<th>Mo₂S₃ conversion to MoO₃ percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo in solution</td>
<td>8.8</td>
<td></td>
<td>99+</td>
</tr>
<tr>
<td>Re in solution</td>
<td></td>
<td>96.0</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ concentration of filtrate</td>
<td>459</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results show that almost 100% conversion of MoS₂ to MoO₃ is obtained by the nitric acid oxidation process.

**EXAMPLE 2**

The purpose of this experiment was to determine the range of nitric acid necessary to dissolve rhenium values in molybdenite and oxidize the quadravalent molybdenum in molybdenite to the hexavalent form.

Various quantities of nitric acid were introduced into a pressure autoclave containing 100 grams of molybdenite concentrate and one liter of water. The entire contents were reacted for one hour at 125°–170° C. and 150 p.s.i.g.

Following the reaction, the entire contents were filtered for solids and solution recovery with the solution being analyzed for Mo, Re, and Cu. The filter cake, believed to be a hydrated molybdenum oxide compound, was leached with an ammonia solution, followed by leaching with dilute hydrochloric acid to determine the amount of unreacted sulfide material remaining. The results are presented in Table 2.

**TABLE 2—EFFECT OF NITRIC ACID**

<table>
<thead>
<tr>
<th>MoO₃ added to system, lb, Ab, Mo</th>
<th>Cu in solution, percent</th>
<th>Mo in solution, percent</th>
<th>Re in solution, percent</th>
<th>H₂SO₄ concentration, g/l</th>
<th>MoS₂ to MoO₃ conversion, remission, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.3</td>
<td>0.3</td>
<td>3.7</td>
<td>1.39</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>0.037</td>
<td>88.6</td>
<td>12.4</td>
<td>81.4</td>
<td>102.0</td>
<td>77.1</td>
</tr>
<tr>
<td>0.008</td>
<td>83.9</td>
<td>23.7</td>
<td>85.3</td>
<td>167.0</td>
<td>68.3</td>
</tr>
<tr>
<td>0.016</td>
<td>82.9</td>
<td>14.4</td>
<td>95.0</td>
<td>187.0</td>
<td>94.5</td>
</tr>
<tr>
<td>0.023</td>
<td>82.9</td>
<td>14.0</td>
<td>92.9</td>
<td>210.4</td>
<td>67.7</td>
</tr>
<tr>
<td>0.051</td>
<td>87.6</td>
<td>16.3</td>
<td>96.3</td>
<td>230.0</td>
<td>68.9</td>
</tr>
</tbody>
</table>

The results show that about 0.037 wt. percent of nitric acid based on molybdenum is required to initiate the oxidation reaction, and that at about 0.371 wt. percent substantially all of the MoS₂ has been converted to MoO₃.

**EXAMPLE 3**

The purpose of this example was to determine the effect of sulfuric acid on bringing rhenium, molybdenum, and copper into solution during pressure oxidation of a molybdenite concentrate and on the conversion of MoS₂.
to MoO₃. Sulfuric acid was added in measured amounts to the concentrate mixture as necessary to control the sulfuric acid concentration. The amount of nitric acid used was 0.21 pound of nitric acid per pound of molybdenum. The experiment was performed under conditions similar to those for Example 2. The results are reported in Table 3.

### TABLE 3.—EFFECT OF SULFURIC ACID CONCENTRATION

<table>
<thead>
<tr>
<th>H₂SO₄ added to system, g/l. Mo</th>
<th>Cu in solution, percent</th>
<th>Mo in solution, percent</th>
<th>Re in solution, percent</th>
<th>H₂SO₄ concent., g/l.</th>
<th>MoS₂ to MoO₃ conversion, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75.5</td>
<td>13.7</td>
<td>96.6</td>
<td>112.5</td>
<td>94.7</td>
</tr>
<tr>
<td>75</td>
<td>82.8</td>
<td>14.0</td>
<td>91.1</td>
<td>170.7</td>
<td>58.8</td>
</tr>
<tr>
<td>125</td>
<td>81.6</td>
<td>25.1</td>
<td>95.6</td>
<td>260.0</td>
<td>56.8</td>
</tr>
<tr>
<td>175</td>
<td>81.8</td>
<td>20.1</td>
<td>97.6</td>
<td>300.7</td>
<td>97.3</td>
</tr>
<tr>
<td>400</td>
<td>80.5</td>
<td>20.2</td>
<td>97.8</td>
<td>400.1</td>
<td>99.0</td>
</tr>
</tbody>
</table>

The data in Table 3 indicate that the presence of sulfuric acid up to a concentration of 466 g/l. has very little effect on the conversion of MoS₂ to molybdenite to MoO₃. The presence of sulfuric acid has little or no effect on reducing rhenium to solution and only a slight effect on molybdenum reduced to solution.

### EXAMPLE 4

The purpose of this experiment was to determine the effect of oxygen overpressure on oxidation of MoS₂ to MoO₃ over a narrow temperature range. Various oxygen overpressures were used. The temperature varied between 100 to 110°C. The amount of nitric acid used was 0.28 pound per pound of quadrivalent molybdenum to be oxidized and the reaction was allowed to proceed for one hour. The results are given in Table 4.

### TABLE 4.—EFFECT OF OXYGEN OVERPRESSURE

<table>
<thead>
<tr>
<th>Oxygen overpressure, p.s.i.g.</th>
<th>Mo in solution, percent</th>
<th>Re in solution, percent</th>
<th>MoS₂ to MoO₃ conversion, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>14.1</td>
<td>37.0</td>
<td>28.0</td>
</tr>
<tr>
<td>100</td>
<td>13.2</td>
<td>35.3</td>
<td>29.3</td>
</tr>
<tr>
<td>150</td>
<td>11.6</td>
<td>36.8</td>
<td>24.5</td>
</tr>
<tr>
<td>200</td>
<td>14.9</td>
<td>40.2</td>
<td>35.9</td>
</tr>
</tbody>
</table>

The results of Table 4 indicate that the oxygen overpressure at the 100–110°C. operating temperature does not have any great effect on the oxidation rate of the molybdenite. A small decrease in conversion rate can be noted as the oxygen overpressure is increased.

### EXAMPLE 5

In order to determine the effect of temperature on molybdenite oxidation, three experiments were performed on 100 gram samples of the concentrate. The nitric acid added to each system was 0.28 pound per pound of quadrivalent molybdenum to be oxidized. A pressure of about 150 p.s.i. was used. The reaction period at a given temperature was held constant at one hour. The results are presented in Table 5.

### TABLE 5.—EFFECT OF TEMPERATURE

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Mo in solution, percent</th>
<th>Re in solution, percent</th>
<th>MoS₂ to MoO₃ conversion, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>70</td>
<td>14.5</td>
<td>37.1</td>
</tr>
<tr>
<td>125</td>
<td>70</td>
<td>14.7</td>
<td>39.9</td>
</tr>
<tr>
<td>175</td>
<td>200</td>
<td>11.9</td>
<td>94.8</td>
</tr>
</tbody>
</table>

The results of Table 5 indicate that temperature does affect the reaction rate with a large increase in reaction rate occurring from 105°–125°C.

### EXAMPLE 6

The purpose of this experiment was to investigate various solvents for extraction of molybdenum and rhenium values from the solution obtained after filtering the slurry obtained by the molybdenite oxidation reaction described in the foregoing examples. The following solvents were used in this test. All were diluted in an aromatic hydrocarbon having a flash point of 117°F.

5 volume percent Aliquat 336 (quaternary ammonium compound)

3,739,057

The aqueous feed solution analyzed as follows:

- Mo
- Re

The results are reported in Table 6.

### TABLE 6.—EFFECT OF SOLVENTS

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Phase ratio O/A</th>
<th>Phase separation time, sec.</th>
<th>Solvent loading, g/l. Mo</th>
<th>Mo extracted, percent</th>
<th>Re extracted, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliquat 336</td>
<td>2</td>
<td>59</td>
<td>10.3</td>
<td>60.6</td>
<td>94+</td>
</tr>
<tr>
<td>XLA-3</td>
<td>2</td>
<td>297</td>
<td>7.9</td>
<td>46.2</td>
<td>99+</td>
</tr>
<tr>
<td>XLA-9</td>
<td>2</td>
<td>58</td>
<td>7.4</td>
<td>43.3</td>
<td>99+</td>
</tr>
</tbody>
</table>

All three reagents extracted some molybdenum and all of the rhenium values in a very short time from the strong sulfuric acid solution. Additional staging would have recovered more than 90% of the molybdenum values on the solvent.

### EXAMPLE 7

Another extractant was investigated and involved a mixture of 5% Alamine 336 (a mixture of C₈ and C₁₀ carbon chains having a molecular weight of 392) and 95% Cyclosol 53 (an aromatic hydrocarbon having a flash point of 117°F), which was mixed with the same solution used in Example 6 to determine the amount of molybdenum which could be extracted. The organic to aqueous phase ratios were varied. The retention time during mixing in separatory funnels was two minutes. The results are reported in Table 7.

### TABLE 7.—MOYLDENUM EXTRACTION USING ALAMINE 336

<table>
<thead>
<tr>
<th>Phase ratio O/A</th>
<th>Aqueous phase analysis after mixing, g/l. Mo</th>
<th>Mo extracted, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>25.5</td>
<td>24.9</td>
</tr>
<tr>
<td>0.5</td>
<td>24.2</td>
<td>28.6</td>
</tr>
<tr>
<td>1.0</td>
<td>21.1</td>
<td>27.9</td>
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<td>17.8</td>
<td>47.8</td>
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<td>3.0</td>
<td>19.1</td>
<td>79.5</td>
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<td>4.0</td>
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<td>77.1</td>
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<tr>
<td>5.0</td>
<td>6.6</td>
<td>89.9</td>
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</tbody>
</table>

1 The aqueous from the phase ratio of O/A=5 was mixed with fresh solvent.

### EXAMPLE 8

This experiment was performed to investigate the range of sulfuric acid concentration within which suitable molybdenum and rhenium extraction can be made. The sulfuric acid concentration of the solution resulting from the oxidation step was adjusted with distilled water or concentrated sulfuric acid. Analysis of the solution indicated that 8.0 g/l. Mo and 0.05 g/l. Re were present in solution. The extractant used for this experiment con-
The results of Table 8 indicate that molybdenum extraction is affected by high sulfuric acid concentrations with only 14.0% of molybdenum present being extracted at a sulfuric acid concentration of 600 g./l. At some point, between a concentration of 300-600 g./l. of sulfuric acid, molybdenum extraction appears to be markedly affected and sulfuric acid concentration below about 100 g./l. apparently has no effect on molybdenum extraction. The presence of sulfuric acid in concentrations up to 600 g./l. has no effect on the extraction of rhenium with the solvent extraction system used.

**EXAMPLE 9**

This experiment was performed to investigate the effectiveness of an aliphatic hydrocarbon diluent with tertiary and secondary amine solvents when extracting molybdenum from the solution resulting from the oxidation process. The tertiary amine was the Alamine 336 used in the previous example. The concentration used was 10 volume percent in a kerosene having a flash point of 175° F. The secondary amine is marketed by Rohm and Haas Company under the name of Amberlite LA-1, has a molecular weight of 351 to 393 and is mixed with kerosene to result in a solvent containing 10 volume percent Amberlite LA-1. The feed liquor used for this experiment contained 14.58 g./l. Mo and 350 g./l. H2SO4. Several contacts were made at an organic to aqueous phase ratio of 1. The data is presented in Table 9.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Alamine 336 aqueous analysis, g./l.</th>
<th>Ambralite LA-1 aqueous analysis, g./l.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>5.29</td>
<td>5.23</td>
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<tr>
<td>2</td>
<td>4.69</td>
<td>2.18</td>
</tr>
<tr>
<td>3</td>
<td>3.09</td>
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<tr>
<td>4</td>
<td>1.48</td>
<td>1.27</td>
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<tr>
<td>5</td>
<td>0.89</td>
<td>0.86</td>
</tr>
<tr>
<td>6</td>
<td>0.61</td>
<td>0.84</td>
</tr>
<tr>
<td>7</td>
<td>0.44</td>
<td>0.61</td>
</tr>
</tbody>
</table>

The data indicate that greater than 90% of the molybdenum values can be extracted with the solvents employed, as shown by the aqueous analysis following each contact.

**EXAMPLE 10**

This experiment was performed to investigate the effectiveness of the process of this invention on a pilot plant scale. A 100-gallon autoclave reactor was charged with 83.0 pounds of molybdenite concentrate containing 67.2 pounds of MoO3 and 50 gallons of water. The rhenium content was 0.056% (0.0498 pounds). The temperature of the slurry was raised to 310° F., and 2.2 pounds of nitric acid were added. Sufficient oxygen was added intermittently to keep the pressure at 140 p.s.i.g. Another 1.1 pounds of nitric acid were added at the end of 20, 40, 60, and 68 minutes of reaction time. Oxygen was fed to the system until the reaction was complete as indicated by the oxygen consumption, which was negligible at the end of 2.0 hours. The temperature measured in the top of the reactor never exceeded 380° F. The slurry was cooled to 200° F., at which time the reactor was discharged. Analysis of the solids and solution indicated that 99.8% of the quadrivalent molybdenum had been oxidized to the hexavalent state.

Analysis of the solution after oxidation indicated the presence of 24.5 g./l. Mo and 0.118 g./l. Re. The H2SO4 concentration as determined by base titration to phenolphthalein end point was 247 g./l. H2SO4.

The solution was fed to a continuous solvent extraction circuit where the molybdenum and rhenium values were separated from most of the sulfuric acid and metallic cations such as iron, copper, and zinc. An aqueous ammonium solution (5 N) was used to strip the metal values from the solvent to result in a solution containing 192 g./l. Mo and 0.855 g./l. Re. The solvent employed was 5% Alamine 336 and 95% Cyclosol 53 diluent. The purified strip solution was further contacted with a solvent containing 5% quaternary ammonium compound (Aliquat 336) in 95% Cyclosol 53 diluent to separate the rhenium values from the molybdenum values. The raffinate solution containing the molybdenum values was fed to a spray dryer to recover 15.2 pounds of MoO3 or 22.6% of the molybdenum introduced to the autoclave reactor. The solvent was stripped of its rhenium values using 1 M perchloric acid to result in a purified rhenium solution containing 97% of the rhenium values or 0.0483 pound of Re in the perchloric acid solution. The rhenium solution was further purified by conventional techniques to produce an ammonium permanganate product of 99.9% purity.

The solid hydrated molybdenum oxide was leached with an ammonium solution to dissolve the molybdenum values as ammonium molybdate. The ammonium insoluble material was filtered and the ammonium molybdate solution spray dried to produce a high purity molybdenum trioxide. Ammonium molybdate can be produced, if desired. 50.7 pounds of MoO3 were recovered during this step of the process, making a total of 65.9 pounds of MoO3 recovered by the oxidation and solvent extraction steps.

The process can be effectively and economically conducted at temperatures from about 100° C. to 200° C. at pressures up to about 300 p.s.i.g. and in a time of not more than about 1–2 hours.

The percentage of hexavalent molybdenum which is solubilized in the oxidation leach step can be controlled and it is believed that this percentage has a bearing on the amount of nitric acid used and the overall efficiency of the process. To convert the last 15–20 percent of molybdenum present to the insoluble hydrated molybdate oxide would probably require an unproportionate excess of nitric acid.

The invention provides a process by which substantially all of the molybdenum and rhenium values in molybdenite can be recovered in one overall operation. It has the advantage that dissolved rhenium and molybdenum values from the oxidation step can be simultaneously recovered in the presence of other metal impurities and large amounts of formed sulfuric acid by the quaternary ammonium or amine type solvent which is peculiarly applicable to the solution resulting from the nitric acid oxidation step. This eliminates the necessity for neutralization of the solvent which was necessary in prior processes for the recovery of dissolved molybdenum with a leaching step. The process has the further advantage that substantially all of the rhenium is dissolved in the oxidation leach step so that it can be recovered along with molybdenum.

What is claimed is:

1. A process for recovering molybdenum and rhenium values from molybdenite which comprises:
(a) introducing a water slurry of particulate molybdenite into a pressure vessel,
(b) introducing nitric acid into the pressure vessel to form a slurry with the molybdenite, in an amount from about 0.037–0.37 pound of nitric acid per pound of quadrivalent molybdenum in the molybdenite to be oxidized to hexavalent molybdenum,
(c) raising the temperature of the slurry inside the pressure vessel to about 100°C. to start the reaction,
(d) introducing oxygen under pressure into the pressure vessel to provide an oxidizing medium with the nitric acid to oxidize the sulfides of molybdenum and rhenium to the oxides,
(e) maintaining the temperature within the gas phase reaction zone in the vessel as the oxidation proceeds at substantially that at which nitrogen oxide gases formed during the oxidation are oxidized to nitrogen dioxide for regeneration of nitric acid by the reaction of formed nitrogen dioxide with water,
(f) recovering the insoluble solid molybdenic oxide formed by oxidation from the pressure vessel, and
(g) contacting the liquid component of the slurry containing up to 600 grams per liter of sulfuric acid with an extractant selected from the group consisting of an amine extractant and a quaternary ammonium extractant to recover dissolved molybdenum and rhenium values on the extractant.

2. The process of claim 1 in which the temperature of the slurry varies from about 100°C.–200°C. C, the pressure in the pressure vessel is maintained up to about 300 p.s.i.g., and vapor from the gas phase reaction zone is continuously circulated through the slurry to aid in temperature control of said zone.

3. A process for the recovery of molybdenic oxide and rhenium from molybdenite which comprises:
(a) introducing a water slurry of particulate molybdenite into a pressure vessel,
(b) introducing nitric acid into the pressure vessel in an amount from about 0.037–0.37 pound per pound of molybdenum,
(c) raising the temperature of the slurry inside the pressure vessel to at least about 100°C. C. to start the reaction,
(d) introducing oxygen under pressure into the pressure vessel to provide an oxidizing medium with the nitric acid to oxidize the sulfides of molybdenum and rhenium to the oxides,
(e) removing heat from the gas phase reaction zone in the pressure vessel and continuously circulating vapor from the gas phase reaction zone through the slurry to maintain the temperature in the gas phase reaction zone as the oxidation proceeds to that at which nitrogen oxide gases formed during the oxidation are oxidized to nitrogen dioxide for regeneration of nitric acid by the reaction of nitrogen dioxide with water,
(f) recovering the solid molybdenic oxide formed by oxidation from the pressure vessel, and
(g) contacting the liquid component of the slurry remaining in the pressure vessel and containing up to 600 grams per liter of sulfuric acid with an extractant selected from the group consisting of an amine extractant and a quaternary ammonium extractant to recover dissolved molybdenum and rhenium values on the extractant.

4. The process of claim 3 in which the slurry temperature inside the pressure vessel is maintained between about 100°C.–200°C. C. during oxidation and the pressure is maintained in the pressure vessel up to about 300°C.

5. A process for recovering molybdenic oxide from molybdenite by oxidation of the molybdenite which comprises:
(a) introducing a water slurry of molybdenite particles into a pressure vessel and sealing the pressure vessel,
from the pressure vessel heat of reaction generated by the oxidation reactions occurring therein to prevent pressure build-up inside the pressure vessel and thereby permit rapid introduction of oxygen therein to accelerate the oxidation reactions occurring inside the pressure vessel; whereby molybdenum sulfide is rapidly oxidized to insoluble molybdic oxide, and (g) recovering insoluble molybdic oxide from the slurry in the pressure vessel.

14. The process of claim 13 in which gases from the gas phase reaction zone in the pressure vessel are continuously circulated through the slurry.

15. The process of claim 13 in which rhenium and molybdenum solubilized during the oxidation are recovered from the slurry.

16. The process of claim 5 in which solubilized rhenium and molybdenum are recovered from the slurry after oxidation by contacting the slurry with an amine extractant.

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HERBERT T. CARTER, Primary Examiner

U.S. Cl. X.R.

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