

[54] **RECOVERY OF RHENIUM AND MOLYBDENUM VALUES FROM MOLYBDENITE CONCENTRATES**

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[58] Field of Search **75/1, 2, 6, 7, 9, 75/21, 23, 26, 36, 84, 121, 117; 423/592, 22, 53**

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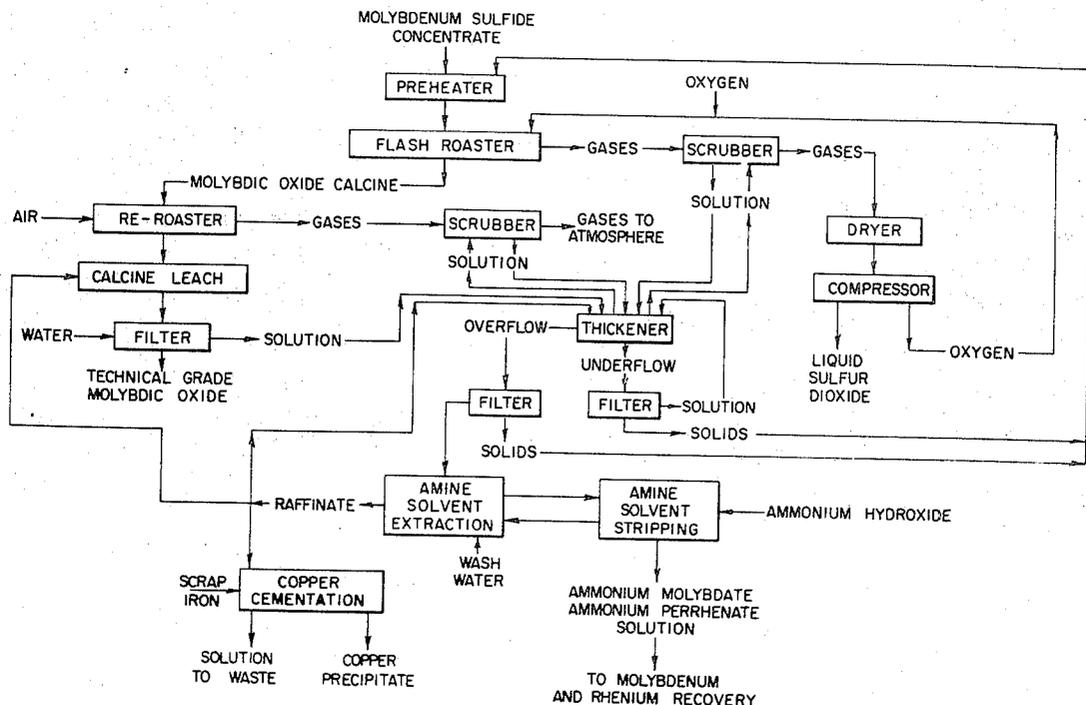
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[57] **ABSTRACT**

An improvement in the recovery of molybdenum and rhenium values by roasting molybdenite which comprises preheating finely divided molybdenite concentrate and passing it downwardly through a vertically oriented reaction zone countercurrent to an upwardly traveling stream of high temperature oxygen, oxygen enriched air or oxygen-sulfur dioxide mixture heated by its passage through a roasting hearth at the bottom of the reaction zone. The rate of oxidation of sulfides is controlled by various means to keep the temperature in the reaction zone below that at which molybdenum oxide volatilizes with resultant inhibition of the volatilization of rhenium oxide. The process is attractive from the standpoint of pollution control as by-product sulfur dioxide gas ordinarily released to the atmosphere is produced in the exhaust gases in concentrations high enough to make its recovery economically feasible.

14 Claims, 2 Drawing Figures



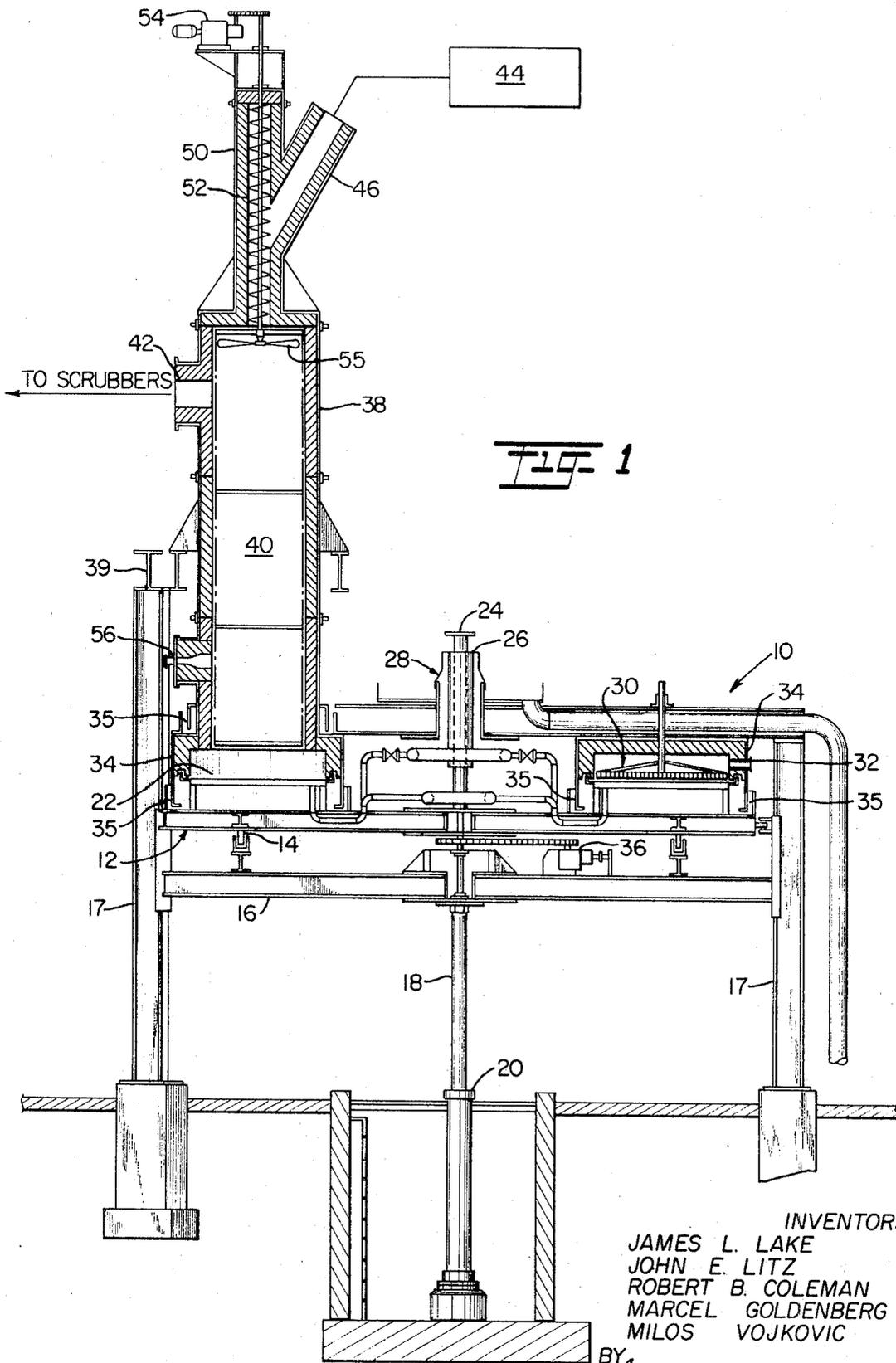


FIG. 1

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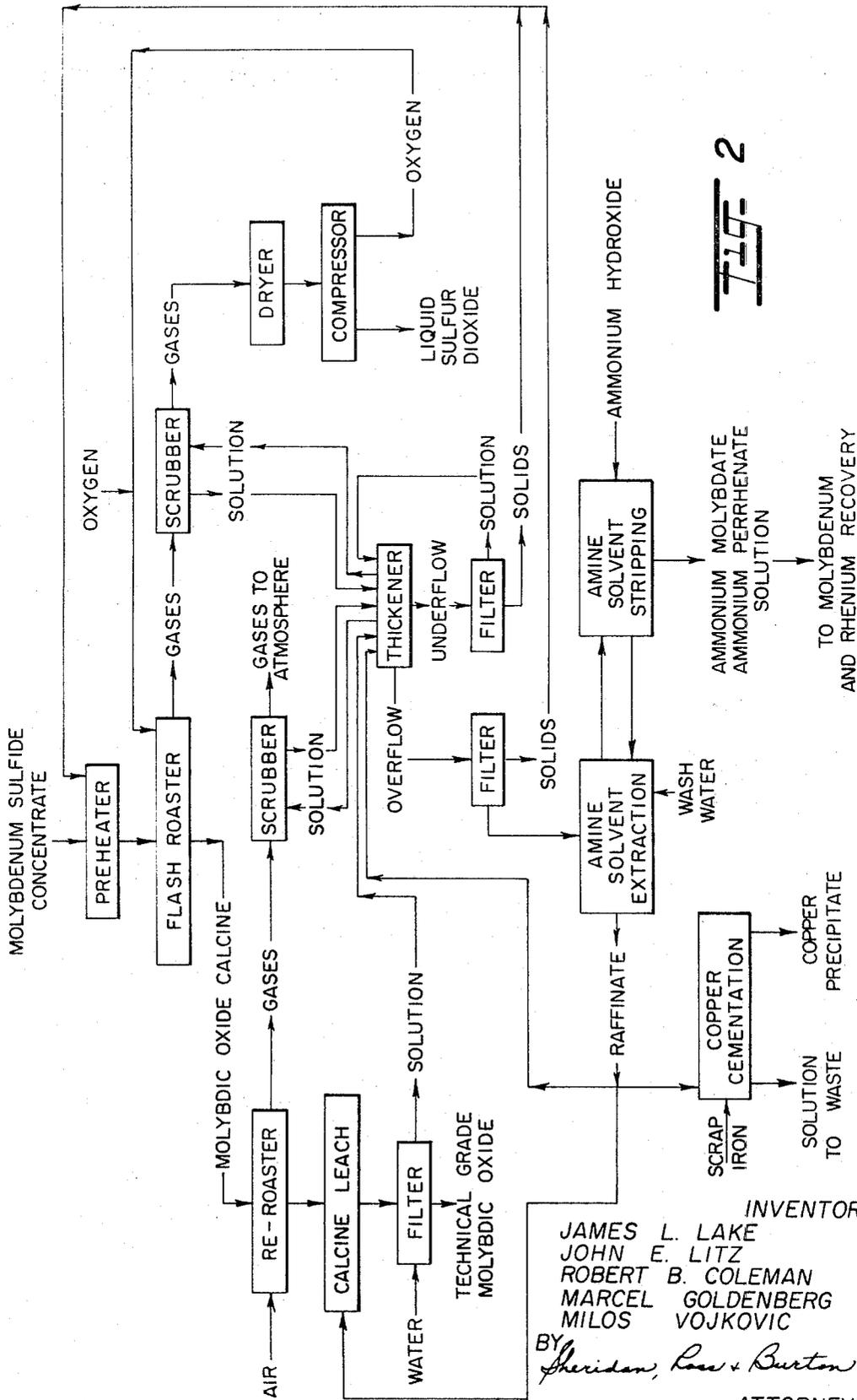


FIG. 2

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BACKGROUND OF THE INVENTION

The scarcity of rhenium in nature and its rapidly increasing importance in industry emphasize the need for a highly efficient and economical process for recovering it from its ores. Molybdenum and rhenium are usually found together in the molybdenite (MoS_2) mineral associated with the so-called "porphyry" copper ore deposits. The molybdenite is usually separated from the bulk of the copper minerals and is recovered as a flotation concentrate containing from 40% to 55% molybdenum. Then the molybdenum sulfide concentrate is roasted to produce an oxide product containing a minimum of sulfur, the chief objective of prior art processes being the ultimate recovery of molybdenum. The rhenium is volatilized during roasting and generally was not recovered.

In presently used processes large volumes of air are passed through the system for temperature control and other reasons resulting in the by-product sulfur dioxide being contained in such large volumes of exhaust gases, mainly air, that its recovery is not economically feasible and it is released to the atmosphere creating serious presentday pollution hazards. Sulfur dioxide gas ordinarily does not occupy much more than 1-2% of the volume of the exhaust gases in these processes.

A process directed to the recovery from molybdenite concentrate of rhenium along with molybdenum is disclosed in U.S. Pat. No. 2,579,107 to Bertolus. The present invention is directed to the recovery from molybdenite of a high yield of rhenium either as a high grade intermediate product or as a high grade metal along with a metallurgical quality molybdic oxide calcine containing a minimum of copper and sulfur impurities, all with an efficient use of heat and materials.

The normal practice for the recovery of rhenium from molybdenite concentrates consists of roasting the concentrate in air utilizing a multiple hearth-type roaster. A portion of the rhenium as rhenium oxide is volatilized and is collected as a fume with the dust in a scrubber where it is dissolved in water. Recoveries of rhenium from the concentrate normally are in the 55% to 65% range. An authoritative opinion by those skilled in the art is that a conventional plant operated primarily for the recovery of rhenium in accordance with prior art procedure could effect a net recovery of 77% of the rhenium.

The small concentration of rhenium oxide in the large volume of exhaust gas resulting from the use of air is an extreme disadvantage.

Accordingly, it is a principal objective of the invention to accomplish a high recovery of the molybdenum and rhenium content of molybdenite concentrates and to produce byproduct sulfur dioxide in the exhaust gas in high enough concentrations to warrant its recovery for use so that it will not pass to the atmosphere as a polluting agent.

SUMMARY OF THE INVENTION

In accordance with the process of the present invention up to 95% of the rhenium in molybdenite is consistently recovered along with a high grade molybdic oxide calcine. A principal feature of the process is the provision of a reaction zone in which finely divided molybdenite is effectively dispersed and moves vertically

and countercurrent to an upwardly traveling stream of pure hot oxygen, oxygen-enriched air or an oxygen-sulfur dioxide mixture emanating from a concentrate roasting furnace, the result being a highly effective oxidation of the sulfur content of the concentrate to sulfur dioxide, of rhenium and molybdenum to their higher oxides, and volatilization of rhenium oxide.

The process begins with roasting a preheated molybdenite concentrate in an oxygen or mixed oxygen-sulfur dioxide atmosphere in a vertical flash roaster. Sulfur dioxide is formed from the oxidation of sulfur and will mix with the oxygen introduced or it may be added with the oxygen to control oxidation rate. The oxidizing gases and the molybdenum sulfide particles pass countercurrently in the vertical section of the flash roaster to provide maximum surface contact between the particles and gases. The length of time of the concentrate particles in the vertical section in countercurrent contact with oxidizing gases is regulated to initiate the oxidation of each of the particles of molybdenum sulfide, such that each of the particles will have a layer of molybdenum trioxide on its outer surface. The particles pass downwardly through the vertical section onto a rotating horizontal hearth where they are annealed for a period of time at approximately 550° to 680°C. in an oxygen or oxygen-sulfur dioxide atmosphere. This annealing step permits complete oxidation of molybdenum to molybdenum trioxide. The major portion of the rhenium is volatilized while the concentrate particles are roasted and annealed, and pass out of the roasting and annealing furnace with the off-gases which contain the excess oxygen, the sulfur dioxide formed and added during roasting, and a small quantity of dust which is incompletely roasted.

An improvement of the invention is the partial control of the rate of oxidation of sulfides in the reaction zone and thereby the temperature of the zone to keep it below that at which molybdic oxide volatilizes or melts with resultant inhibition of the volatilization of rhenium oxide. Part of the heat is due to the oxidation of the sulfides, the rate of this oxidation being controlled by the gas stream composition and the stoichiometric ratio of available oxygen to concentrate in the reaction zone. This oxidation rate and the heat generated thereby are controlled by varying the stoichiometric ratio of oxygen to concentrate using the ratio of sulfur dioxide to oxygen gases in the exhaust gas as a measure of this ratio existing in the reaction area. Other parameters affecting the operation of the process may be varied, these being preheat temperature, height of reactor column and heat dissipation from the column.

In the practice of the process it has been found that less than 10% of the molybdenum and up to 95% of the rhenium report to the off-gas as fumes or dusts and are collected in a suitable scrubber.

BRIEF DESCRIPTION OF THE DRAWINGS

The process will now be described with reference to the accompanying drawings in which:

FIG. 1 is a partial schematic sectional view of the combined roaster and vertical column comprising the flash roaster of the invention.

FIG. 2 is a flow diagram illustrating the operation of the flash roasting process of the invention.

DESCRIPTION OF PREFERRED EMBODIMENT

Referring to FIG. 1, the numeral 10 indicates a con-

ventional rotating hearth furnace used for roasting concentrates. The furnace is illustrative of the type concentrate roasting furnace which is constructed to provide for the introduction and passage of hot gases over the material in the roasting area. Other conventional furnaces of this type are moving horizontal conveyor (sintering machine), circular rabbled hearth (single or multiple), longitudinal rabbled hearth (Edwards style roaster) and horizontal kilns. Beyond this feature of the invention is not limited to any type furnace. A furnace in which a water cooling system is used for temperature control is preferred. If the furnace is air-cooled, the air is not passed through the reaction zone of the flash roaster. The furnace may be operated under negative or positive pressure.

Although the illustrated furnace is of conventional construction and is represented partially in schematic, its principal operating parts will be described. The furnace 10 comprises the rotating hearth 12 rotatably supported by wheels 14 on platform 16 which moves vertically along the interior surfaces of main support legs 17. Central support member 18, which supports platform 16, is mounted for raising and lowering by hydraulic cylinder 20 to correspondingly raise and lower the rotating furnace 12 and the platform 16. The bed of the rotating hearth upon which the concentrate rests is indicated at 22. A water cooling system for the rotating hearth by which water enters the inlet 24 and leaves through the outlet 26 is indicated generally at 28. The furnace is provided with the usual cutter assembly 30 to periodically break crusts which form as the concentrate is roasted. Circumferentially-spaced inlets 32 permit the introduction of gases, such as oxidizing gases, into the hearth area formed by the bed of the hearth and roof 34. The gases may be introduced under positive pressure, or reduced pressure generated at the outlet pipe 42. The hearth 12 rotates in liquid seals indicated at 35 to provide a gastight hearth area. A conventional drive unit 36 is provided for rotating the hearth. The structure just described is well known in the art and forms no part of the invention other than in combination with the structure now to be described.

In order to provide a vertically oriented reaction zone for countercurrent contact of concentrate with gas, a hollow reactor column 38 is mounted vertically on the furnace 10 so that its bottom end opens into the hearth area as shown. The vertical reactor column may be constructed of refractory or insulated material or heat conducting material provided with a cooling or heat transfer media. The reactor column may be made vertically adjustable by constructing it in spool sections or otherwise. For support, it is secured to the top of I-beam 39 by means of a conventional flange and bolt arrangement as shown, the I-beam being attached to support 17. The outer casing of the vertical reactor column 38 forms an inner chamber 40 which is the reaction zone of the vertical column. The reaction zone 40 is provided with an outlet 42 for gases, fumes, dust, etc., including rhenium oxide. Since its bottom end opens into the enclosed area above the rotating hearth 12, gas introduced into inlets 32 passes over the hearth bed 22 and upwardly through the reaction zone 40 and out the outlet 42.

A concentrate preheater unit 44 is mounted above the reaction zone 40 by supports, not shown, and is connected to delivery pipe 46 so that preheated concentrate may be introduced downwardly from the pre-

heater into the reaction chamber 40. A feed screw 50 is vertically mounted in the main passageway 52 of the upper section of the vertical column to aid in introduction of preheated concentrate into the reaction zone 40. The feed screw is driven by conventional drive unit 54 mounted at the top of the vertical column. A feed disperser 55 is mounted on the feed screw 50. A preheat port 56 leads into the bottom of the reaction area 40 for introducing hot gases into the reaction zone during start-up.

The preheater unit 44 is a conventional heater and need not be mounted above the reaction zone as heated concentrate from the preheater located elsewhere can be transferred to the upper end of delivery pipe 46.

The operation of the process of the invention in conjunction with the apparatus just described for a typical operation is as follows.

A finely divided molybdenite concentrate is introduced into the preheater 44 in an inert atmosphere and brought to a minimum temperature in the neighborhood of about 500°C. At the same time, hot gas is introduced into the preheat port 56 and circulated through the reaction zone 40 as a start-up procedure. Oxygen gas may also be introduced at this time through inlet ports 32 and circulated through the area above rotating hearth bed 22 and out the outlet port 42.

When the reaction zone 40 has reached the required temperature, preferably between about 550° and 650°C., the feed screw 50 and the disperser 55 are started up and preheated concentrate is introduced into the reaction zone 40. The feed disperser 55 effectively disperses the small concentrate particles so that maximum surface contact of the particles with countercurrent upwardly traveling hot gas is achieved.

The hearth bed 22 is rotating and the calcine continuously leaves the hearth through an outlet, not shown, preceded by a scraper, where it is collected and subsequently processed to recover metal values from it. The water cooling system 28 is used as necessary to control the temperature of the material on rotating hearth 22.

In the reaction zone 40, sulfur dioxide is formed by oxidation of sulfides present in the molybdenite concentrate. This hot sulfur dioxide gas is mixed with the upwardly traveling hot oxygen and passes out the exit 42 into the scrubbers along with the other gases, fumes and dust where some of it unites with water in the scrubbers to form sulfurous acid and the remainder is collected. The sulfur dioxide produced normally occupies from about 30-50% of the volume of the exhaust gases. Excess oxygen which has not been consumed in the reaction zone passes through the outlet 42 and may be collected for recirculation through the system.

As is well known, the higher the oxide of rhenium the more soluble the oxide is in water, so that maximum oxidation of rhenium is desired for recovery in the scrubbers. The higher oxides are more volatile. As is also well known, rhenium oxide is formed by roasting rhenium sulfide in the presence of oxygen at a temperature between 200° and 300°C.; however, this reaction does not readily proceed in the presence of molybdenum sulfide. After the major part of the sulfur has been driven off as sulfur dioxide in the reaction zone, rhenium and molybdc oxides are formed in the temperature range of about 500° to 650°C. The reaction zone temperature during the oxidation of sulfides must be kept below that at which molybdc oxide volatilizes or melts with resultant inhibition of the volatilization of

rhenum oxide. The rhenum oxide passes to the scrubbers while the molybdic oxide particles fall by gravity to the rotating hearth 22. Some of the unoxidized sulfides will also reach the rotating hearth as well as impurities in the form of compounds of copper, iron, etc. Some of these latter impurities, along with some molybdenum sulfide, also pass to the scrubbers.

The flow diagram of FIG. 1 gives a condensed showing of the process described. After the scrubber solution containing molybdate and perrhenate ions leaves the thickener, the molybdenum and rhenum may be separated and recovered from solution by conventional means. A preferred method is disclosed in co-pending patent application Ser. No. 94,268 filed Dec. 2, 1970, now U.S. Pat. No. 3,681,016.

As shown in the flow diagram, the calcine from the roaster is leached to remove impurities and the leach solution filtered with technical grade molybdic oxide being recovered.

The efficiency of the system in converting a large percentage of the molybdenum and rhenum in the molybdenite to oxides is partially achieved through the high, exposed particle surface area at elevated temperatures which comes in contact with oxygen. This is promoted largely by the efficient dispersion of the vertically traveling sulfide particles and the maximum surface contact of the particles with the countercurrent, upwardly traveling oxygen. Oxygen and preheated concentrate particles are introduced at rates to provide a preferable stoichiometric ratio of oxygen to metal sulfides in the reaction zone of 120% or more. An acceptable ratio was found to be about 170-240%. This ratio can be as low as stoichiometric; however, the process proceeds quite slowly at stoichiometric and a much longer vertical column would be required. Excessive amounts of oxygen beyond the above range could be used as oxygen can be recycled after separation of sulfur dioxide.

An atmosphere free of oxygen is maintained in the preheater at all times. Preferably an atmosphere of nitrogen is used. Preheating of the concentrate before it reaches the reaction chamber greatly accelerates oxidation between the hot sulfides and hot oxygen. It also shortens the required time in the reaction zone for completion of the chemical reactions involved and, accordingly, enables a shorter vertical column to be used. This also reduces the volume of gas necessary in the reaction zone at all times.

Pure oxygen is used as the oxidizing medium; however, oxygen-enriched air can be used but this creates the problem of removing introduced nitrogen from the system. The more available oxygen per volume of gas, the more efficient the system is and the shorter the required height of the vertical column. Accordingly, pure oxygen is the preferred gas for introduction into the furnace.

All of the oxidation reactions do not occur in the reaction zone as they are also occurring on the rotating hearth until the final calcine leaves the furnace. The gases introduced at inlets 43 pass over the concentrate on the rotating hearth and absorb heat before they travel upwardly into the reaction zone. Accordingly, oxidation reactions are occurring continuously through contact of oxygen with the hot calcines on the rotating hearth. The gaseous oxidation products are carried by the oxygen up through the reaction zone and to the

scrubbers. These products are principally sulfur dioxide, rhenum oxides and molybdenum oxides.

Vertical orientation of the reaction zone is preferable in that it makes feasible complete dispersion of the molybdenite concentrate particles above the reaction zone and before the particles enter the reaction zone. The oxygen updraft further disperses the falling particles. As stated previously, the effective dispersion of the hot particles in the hot reaction zone gives maximum surface contact of the particles with the oxygen to provide complete oxidation thereof. This feature is referred to as flash roasting.

A further important feature of the invention is the use of sulfurous acid formed in the scrubbers for leaching of the molybdic oxide concentrate in the recovery of the remaining rhenum from the molybdic oxide calcine. This feature contributes to the economy of the system. Other leaching agents may be used.

The efficiency of the system may be increased by re-roasting the calcine. The molybdenum trioxide produced in the flash roaster may not be completely oxidized and may contain some sulfur in addition to any copper which may have been in the feed. The sulfur is more completely oxidized by re-roasting the calcines in air at 600°C. for thirty minutes. This second roast also insures almost complete oxidation of the copper. It was found most convenient to perform the re-roast in an externally heated kiln using a small air flow to complete the oxidation. An addition portion of rhenum is also volatilized during the re-roast and can be collected by scrubbing the off-gas in a second scrubber.

The process described above consistently provides up to 95% recovery of rhenum from molybdenite concentrate and a molybdic oxide calcine of increased purity.

A refinement in the control of the process will now be described.

It is necessary to maintain proper temperature control for rhenum volatilization while maintaining conditions that will prevent excessive volatilization of molybdic oxide. The most efficient operation of the system is dependent upon the controlled rate of reaction and partial oxidation of each particle of molybdenum sulfide as it descends through the vertical column. This control is required to prevent complete oxidation in a confined zone which would result in high temperature and possible volatilization or fusion of molybdenum oxide. The rhenum volatilization may be depressed because of the formation of a non-volatile oxide or the possible surface sintering or fusion of molybdenum compounds which entrap the rhenum.

The oxidation process in the vertical column is to a degree self-regulating by the variation occurring in the sulfur dioxide to oxygen ratio of the gas stream. As the molybdenum sulfide oxidizes, the sulfur dioxide concentration increases and the oxygen concentration decreases, resulting in a suppression of the reaction rate. Accordingly, the ratio of sulfur dioxide to oxygen in the exhaust gas is, in effect, a measure of the efficiency of the process when the most desirable ratio is known. To demonstrate this, the process was operated at various ratios of sulfur dioxide to oxygen in the exhaust gas, and high volatilization of rhenum oxide with high recovery of molybdenum in the calcine occurred when operating at sulfur dioxide percentages by volume of 30 and 35 in the exhaust gas. These volumes are, of course, related to the ratio of sulfur dioxide to oxygen,

the latter being the only other gaseous component in the exhaust stream pertinent to this control feature. The sulfur dioxide-oxygen ratio in the exhaust stream can be partially controlled to provide the optimum value, if necessary, by the introduction of sulfur dioxide gas with the oxygen. The ratios reflected by 30-35% volume of sulfur dioxide are by no means critical, but its use to provide favorable reaction zone conditions illustrates the effectiveness of this method of control.

There are three other principal parameters affecting the temperature control and/or the oxidation-volatilization process, one or all of which may be used to control these factors in varying degrees. These parameters are: (1) preheat temperature, (2) the height of the reactor column, and (3) heat dissipation from the column. The first of these, like the oxygen-sulfur dioxide ratio, is applied during the operation of the process. The latter two are built-in to the construction of the apparatus.

The preheat temperature is readily controlled by adjusting the heat input to the indirect-fired preheat furnace.

The height of the reactor column determines the dwell time of the sulfide particles in the reaction zone for complete oxidation and for formation and volatilization of rhenium oxide. The optimum height for a given operation is developed by calculations and measurements derived from pilot plant operation. For example, in a continuous pilot plant operation excellent results were obtained using a vertical column 44 inches in height and 6 inches in diameter with a rotating hearth 3 feet in diameter. These dimensional relationships are not critical and would change with change in other variables, such as, concentrate characteristics, composition of feed gases, rate of gas injection, etc.

The heat dissipated from the vertical column is controlled by design, and construction materials used. The construction can be varied from highly insulated construction to high conductivity construction with a cooling media. The radiation and convection loss of heat generated for a metal conducting material and a given feed rate can be readily calculated. Additional heat may be removed from the column by water cooling or other heat exchange media.

The results given below are illustrative of those obtained by application of the above-described process in conjunction with the apparatus described.

Table 1 shows some material balances obtained in roasting tests performed on molybdenite concentrate.

TABLE 1.—ROASTING TEST RESULTS

Preheat temperatures: 650-750°C. range
 Hearth temperature: 550-650°C. range
 Percent stoichiometric oxygen: 170-240

Test	Rhenium balance			Molybdenum balance (percent distribution)		
	Rhenium feed	Product (ppm)	Volatilized (%)	Product	Dust and scrubber	
1.....	567	125	88	94	6	
2.....	707	140	84	94	6	
3.....	736	218	76			
4.....	736	40	95			

The data in Table 1 shows the variability of the rhenium content of the product produced at somewhat

similar conditions. With careful control, a molybdenum product may be produced which contains only 5% of the feed rhenium, demonstrating that the process is effective to provide high yields of both molybdenum and rhenium.

The high sulfur dioxide content of the off-gas rapidly saturated the scrubber solution with sulfur dioxide. As shown in Table 2 below, about 90% of the rhenium reporting to the scrubber was found to be soluble, whereas less than 20% of the molybdenum was soluble (see data in Table 2). Therefore, under normal operating conditions of the process, at least 80% of the rhenium and less than 2% of the molybdenum report to the scrubber solution. The insoluble portion of the dusts, containing the residual molybdenum and rhenium, are separated from the scrubber solution and recycled back to the roaster feed for retreatment.

TABLE 2.—BALANCE OF RHENIUM AND MOLYBDENUM IN SCRUBBER SOLUTION AND SOLIDS

Test	Solution		Solids		Distribution percent			
	Re (ppm)	Mo (g/l)	Re (ppm)	Mo (%)	Re		Mo	
					Soln	Solids	Soln	Solids
1.....	30	1.0	360	54	90	10	15	85
2.....	17	0.2	760	57	92	8	16	84

After the off-gas has been scrubbed of its loading of dust and fume, it consists mainly of sulfur dioxide and oxygen. The gas may be dried and compressed to liquefy the sulfur dioxide. The oxygen remains in the gaseous form and is recycled to the flash roaster.

Table 3 shows the results from re-roasting a number of calcines:

TABLE 3.—RE-ROASTING FLASH ROASTER CALCINES IN AIR AT 600°C.

Sample	Feed calcine		Product calcine		Percent volatilized	
	Re (ppm)	S (%)	Re (ppm)	S (%)	Re	S
1.....	128	1.37	51	1.33	61	6
2.....	218	1.63	86	0.69	61	58
3.....	141	0.49	58	.12	60	76
4.....	192	.72	43	.18	79	78

After re-roasting of the calcine, portions of the copper, the remaining rhenium not collected in the scrubbers, and a portion of the sulfur are soluble in mineral acid solutions. Since the process produces a dilute mineral acid—sulfurous acid—in the scrubbers, it is used to leach the copper and the remaining rhenium from the calcine (Table 4).

TABLE 4.—REMOVAL OF COPPER AND RESIDUAL RHENIUM AND SULFUR FROM RE-ROASTED CALCINES BY LEACHING WITH SULFUROUS ACID

Sample	Feed calcine			Leached residue			Percent solubilized		
	Re (ppm)	Cu (%)	S (%)	Re (ppm)	Cu (%)	S (%)	Re	Cu	S
1.....	86	0.11	0.69	36	0.02	0.28	62	87	63
2.....	51	.12	1.33	28	.01	.25	50	89	83
3.....	58	.75	0.12	17	.02	.10	74	97	26
4.....	43	.90	.18	22	.01	.13	55	99	36

About 7 percent of the molybdenum contained in the calcines is also solubilized in the sulfurous acid leach.

About 7% of the molybdenum contained in the calcines is also solubilized in the sulfurous acid leach.

The leached residue is separated from the leach solution by filtration and after drying is ready for packaging for sale. The leach solution joins the solutions from the scrubbers on the flash roaster and re-roaster.

The effectiveness of the above-described process is graphically illustrated by the high recovery of rhenium and molybdenum achieved. It provides for the recovery of up to 95% of rhenium and high recovery of molybdenum in molybdenite with a minimum of process time and a minimum of oxygen and added heat. The economic advantages of these features are apparent. The process is adaptable to either a batch or continuous operation.

It is an attractive side advantage of the process that a small volume of exhaust gas containing a high percentage by volume of sulfur dioxide is produced. The process is normally operated with an exhaust gas volume discharge rate of 1,350 cubic feet per minute (CFM) with up to 220% excess oxygen and 30-50% by volume of sulfur dioxide in the exhaust gas. This high volume percentage of sulfur dioxide makes its recovery economically feasible for various commercial uses. In contrast, present-day processes utilizing air for cooling and for supplying oxygen are of necessity operated with an exhaust volume discharge rate of 40,000 CFM, 16 volume percent excess oxygen and 1-2 volume percent of sulfur dioxide. This volume percentage of sulfur dioxide in the exhaust gas is so low that its recovery is not economically feasible because it involves processing such large volumes of gas. As a result the sulfur dioxide is exhausted to the atmosphere creating a serious pollution problem in heavily populated areas. The process of this invention eliminates this problem.

The reduced volume of exhaust gas also results in a much higher concentration of rhenium oxide in the exhaust gas than is obtained in conventional processes. As a result, recovery of substantially all of the rhenium is far more feasible and economical than in present processes using air with resultant large volumes of exhaust gas to be processed for recovery of the rhenium oxide.

Reduction of the volume of gas processed through the system by a factor of about 30 results in a drastic reduction in the size of equipment required with significant savings in equipment cost and floor space.

What is claimed is:

1. A method for recovering rhenium and molybdc oxide from molybdenite concentrate which comprises:

a. pre-heating particles of said concentrate in an oxygen-free atmosphere to a temperature not in excess of about 750°C to raise the temperature of the particles to promote flash oxidation of the molybdenite when the particles are introduced into a flash oxidation zone,

b. causing said pre-heated particles to fall through a first oxidizing zone of heated oxygen with said particles and heated oxygen moving countercurrent to each other to disperse said pre-heated molybdenite particles in said heated oxygen to provide maximum particle surface contact with heated oxygen for effective oxidation, said first oxidation zone being heated substantially by the exothermic heat of the reactions occurring in said first oxidation

zone,

c. controlling the temperature in the first oxidation zone during the introduction thereto of said pre-heated particles and thereafter to maintain a temperature therein above the volatilization temperature of rhenium oxide and below the volatilization temperature of molybdc oxide to form rhenium oxide, sulfur dioxide and molybdc oxide, which latter oxide along with other solids passes to a second oxidation zone where any unoxidized molybdenite is completely oxidized, said second oxidation zone being heated by exothermic heat of the reactions occurring therein,

d. passing oxygen through said second oxidation zone to oxidize molybdenite contained therein,

e. passing at least some of the oxygen travelling to said first oxidation zone through said second oxidation zone to heat the oxygen before it reaches the first oxidation zone,

f. recovering rhenium oxide by collecting it in a recovery zone outside the first oxidation zone and dissolving it in water,

g. recovering rhenium from the water solution of rhenium oxide, and

h. recovering insoluble molybdc oxide from the second oxidation zone.

2. The process of claim 1 in which said concentrate is preheated to about 500°C.

3. The process of claim 1 in which molybdenum values are recovered.

4. The process in claim 1 in which rhenium values are recovered.

5. The method of claim 1 in which the temperature of the first oxidation zone resulting from exothermic heat of reaction is controlled by controlling the reaction rate of the oxidation reactions occurring therein.

6. The method of claim 5 in which said reaction rate is controlled by adjusting the relative feed rate of oxygen and molybdenite concentrate to the first oxidation zone to control the stoichiometric ratio of oxygen to metal sulfides introduced therein.

7. The method of claim 6 in which said stoichiometric ratio is at least one.

8. The method of claim 6 in which said stoichiometric ratio is at least 120%.

9. The method of claim 6 in which sulfur dioxide is introduced to the first oxidation zone.

10. The method of claim 6 in which the sulfur dioxide-oxygen ratio in the exhaust gases from the first oxidation zone is used to determine the relative rate of addition of oxygen and concentrate.

11. The method of claim 1 in which the exhaust gas contains up to about 50% by volume of sulfur dioxide.

12. The method of claim 1 in which the dwell time of concentrate particles in the first oxidation zone is controlled by varying the diameter and height of said zone.

13. The process of claim 1 in which oxygen in the exhaust gases is recycled for reuse in the method.

14. The process of claim 1 in which sulfur dioxide in the exhaust gases is dissolved in water to form sulfurous acid and the sulfurous acid used to leach impurities from the molybdc oxide calcine recovered from the second oxidation zone.

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