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EXTRACTION OF RHENIUM INCIDENTAL TO MANUFACTURE OF MOLYBDENUM OXIDE

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FIG. 1.

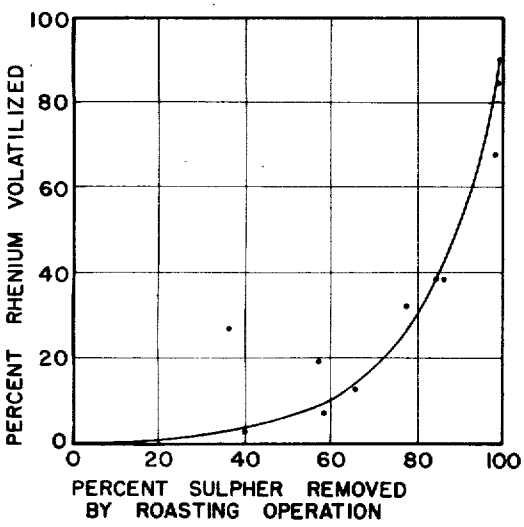
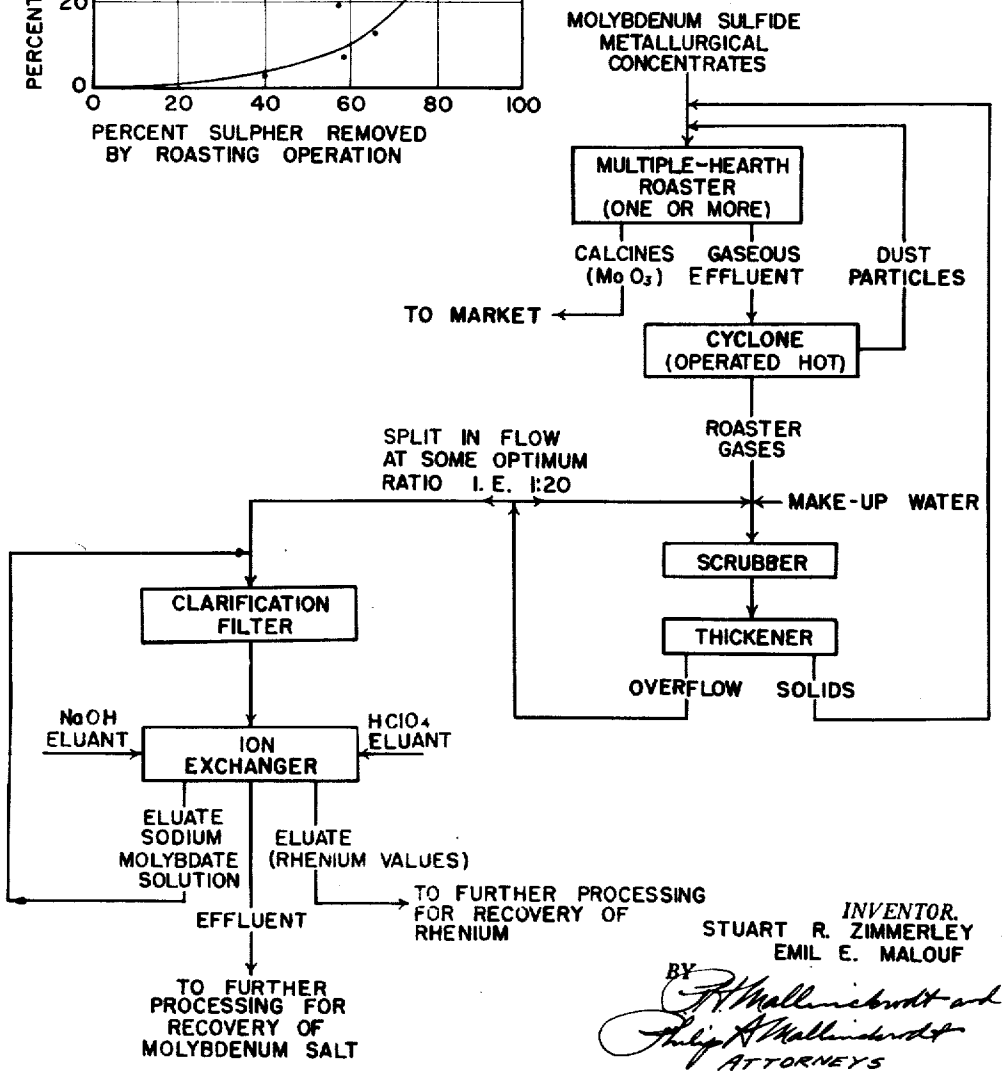


FIG. 2.



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EXTRACTION OF RHENIUM INCIDENTAL TO MANUFACTURE OF MOLYBDENUM OXIDE

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7 Claims. (Cl. 23—23)

This invention relates to the extraction of the rare metal rhenium from materials with which it occurs, and is concerned particularly with rhenium extraction on an industrial basis as an incident to the manufacture of molybdenum oxide from molybdenum sulfide metallurgical concentrates.

Molybdenum sulfides in the form of metallurgical concentrates, derived as a by-product of the milling of various low grade copper sulfide ores for their copper content, are commonly utilized for the commercial production of molybdenum oxide. They are subjected to a roasting operation for the oxidation of their sulfur content.

It has been known for some time that rhenium occurs in minute quantity in certain low grade copper sulfide ores, and is collected in the molybdenum sulfide concentrates resulting from the metallurgical milling of such ores.

In United States Patent No. 2,579,107 issued to Marcel M. Bertolus on December 18, 1951 and entitled "Industrial Process for Extracting Rhenium," there is disclosed a process whereby both the roasting of molybdenite metallurgical concentrates containing rhenium and treatment of the gaseous effluent therefrom are carried out in two separate stages. The first stage involves burning off most of the sulfur and collecting and recycling dust entrained in the gaseous products of sulfur combustion. The second requires application of roasting heat from an external source, and involves dissolving and recovering volatilized rhenium oxide. It is said by the patentee that volatilization of rhenium oxide starts only after the sulfur has been substantially eliminated as sulfur dioxide during the first stage of the roasting.

We have now discovered that, contrary to the teaching of this patent, a very sizable proportion of the total rhenium content is actually volatilized as rhenium oxide during the burning of sulfur in the roasting operation, and that it is lost if it is not recovered from the roaster gases during that stage.

We have also discovered that an ion-exchange tcehnique can be employed on a commercial basis to great advantage with respect to the rhenium-bearing solution obtained from scrubbing the roaster gases with a solvent for rhenium oxide, whether that solution be acidic or basic in character and regardless of sulfates, chlorides, and other contaminants picked up during the scrubbing procedure.

As a result, we are able to accomplish an exceptionally high recovery of rhenium values from molybdenum sulfide metallurgical concentrates on an industrial basis and as an incident of standard roasting operations.

We have developed a process wherein:

(1) A much greater recovery of rhenium is possible than has been obtainable heretofore.

(2) It is unnecessary to conduct the roasting operation or to treat the gaseous effluent therefrom in more

than a single stage, thereby rendering the process applicable to standard roasting practice and equipment and effecting considerable economies in initial plant cost, in space occupied, and in operating expense.

(3) Existing roasting operations for the production of molybdenum oxide may be converted to by-product recovery of rhenium very simply and at minimum expense.

(4) The ultimate production of rhenium metal is considerably facilitated by reason of the high purity of the rhenium compounds obtained.

From one standpoint, the present invention may be regarded as an improvement on the so-called two-step rhenium recovery process of the afore-mentioned Bertolus patent, in that all of the roaster gases given off by the roasting of the metallurgical concentrates at and above the temperature at which rhenium oxide volatilizes are treated with a solvent for such rhenium oxide. Inasmuch as the volatilization temperature of rhenium oxide under normal conditions is approximately 450 degrees centigrade, all roaster gases given off by the charged material at approximately that temperature and above are treated with a solvent for the dissolution of rhenium.

From another standpoint, the invention may be regarded as contributing a new process to the art, involving the steps of roasting molybdenum sulfide metallurgical concentrates containing rhenium, subjecting all gaseous effluent from the roasting operation at and above the temperature at which rhenium oxide volatilizes to treatment with a liquid solvent for rhenium oxide, clarifying the resulting solution, and treating such clarified, rhenium-bearing solution for the separation and recovery of rhenium values.

In the accompanying drawing:

Fig. 1 constitutes a graph based upon numerous tests and showing that rhenium oxide does volatilize to a considerable extent along with the burning of sulfur during the roasting of molybdenum sulfide metallurgical concentrates containing rhenium; and

Fig. 2, a flow sheet illustrating a typical application of our process in practice.

Many laboratory tests conducted by us have proven that a very large part of the rhenium content of molybdenum sulfide metallurgical concentrates is volatilized during the time that sulfur is being burned, and is not normally caught with the flue dusts. Data obtained from standard roasting operations of a large industrial producer of molybdenum oxide shows that this holds true to an even greater extent in actual commercial practice. The graph of Fig. 1, wherein rhenium oxide volatilization is plotted against sulfur oxidation during the roasting of molybdenum sulfide metallurgical concentrates, is based upon and substantiated by the results of these tests.

While it can be seen from the graph that rhenium oxide volatilization does get off to a relatively slow start, the rate increases rapidly over a significant period of time prior to the substantially complete oxidation of sulfur.

The following tests substantiate the graph:

TEST 1

Ten pounds of molybdenite metallurgical concentrates from the Nevada Consolidated Division of Kennecott Copper Corporation were subjected to a roasting operation in a single hearth laboratory roasting furnace equipped with several rabble arms and operated under natural draft. The furnace was preheated, and the charge of concentrates assaying 34 percent sulfur by weight was introduced after the furnace had attained a roasting temperature of between 500 and 600 degrees C. The calcines were sampled during the roasting procedure, and the

samples analyzed for both rhenium and sulfur content, with the following results:

Percent of Total Re Fumed Off	Percent of Total S Roasted Off	Percent of Total S Remaining in Calcines
26.50	36.05	63.95
38.50	83.87	16.13
68.00	98.27	1.73
85.50	99.00	1.00
90.70	99.77	0.23

The same procedure was repeated with respect to many different batches of concentrates from the same source and having substantially the same sulfur content, a single sampling from each being taken at respectively different stages of sulfur elimination for the purpose of substantiating the results of Test No. 1. Results from a representative number of these additional tests follow:

Percent of Total Re Fumed Off	Percent of Total S Roasted Off	Percent of Total S Remaining in Calcines
TEST 2		
38.80	85.46	14.54
TEST 3		
38.80	84.65	15.35
TEST 4		
32.50	78.27	21.72
TEST 5		
19.80	71.61	28.39
TEST 6		
12.10	65.46	34.54

The other similar tests provided merely cumulative evidence.

Copper sulfide ore from the Nevada Consolidated Division of Kennecott Copper Corporation is exceptionally high in rhenium content. For that reason, laboratory tests were centered largely upon molybdenite metallurgical concentrates derived from that ore.

A similar test involving less frequent samplings was carried out, however, on molybdenite metallurgical concentrates assaying 33.50 percent sulfur by weight from the Chino Division of Kennecott Copper Corporation, which in general contain approximately one-half the rhenium of the concentrates of the foregoing tests. The following results bear out the proposition that a large proportion of the rhenium is fumed off during the burning of sulfur:

TEST 7

Percent of Total Re Fumed Off	Percent of Total S Roasted Off	Percent of Total S Remaining in Calcines
3.85	38.60	61.40
19.23	57.01	42.99

To supplement the laboratory findings, data was obtained from a large scale industrial producer of molybdenum oxide in connection with its standard roasting operations, wherein molybdenum sulfide metallurgical concentrates from various sources are fed to multiple hearth roasting furnaces on a continuous basis, and are subjected to roasting temperatures of between 550 and 650 degrees C. for approximately eight hours.

In an instance where concentrates from the Utah Copper Division of Kennecott Copper Corporation assaying 36.22 percent sulfur by weight were fed to the roaster, it was found that 51.3 percent of the total rhenium content was fumed off during the burning of the sulfur content to the point where 21.3 percent of the original sulfur remained in the calcine. Throughout the remainder of the roasting period, during which the sulfur content was reduced to 1.70 percent of the original, the amount of rhenium fumed off increased to 76.3 percent of that present in the concentrates as initially charged.

In a similar instance, with the feed assaying 35.62 percent sulfur by weight, 63.1 percent of the rhenium was volatilized up to the point where 7.30 percent of the original sulfur remained in the calcined concentrates. By the time the remaining sulfur was reduced to 1.40 percent of the original, a total of 71.9 percent of the rhenium was fumed off.

In an instance where concentrates from the Nevada Consolidated Division of Kennecott Copper Corporation assaying 36.14 percent sulfur by weight were fed to the roaster, 62 percent of the total rhenium content fumed off during the burning of the sulfur content to the point where 15.00 percent of the original sulfur remained in the calcines, while, throughout the remainder of the roasting period during which the sulfur content was reduced to 2.00 percent of the original, the amount of rhenium fumed off increased to 91 percent of that present in the concentrates as initially charged.

In this commercial operation, having due regard to the quantity of concentrates treated, analysis of flue dusts showed that by far the larger part of the rhenium volatilized was carried off in the flue gases. In the last instance cited above, where concentrates from Nevada Consolidated were being roasted, less than 10 percent of the rhenium was found in the flue dusts.

Our process is based largely upon the foregoing discoveries, and, in its essentials, involves treating with a solvent for rhenium oxide all roaster gases given off by the concentrates at and above the volatilization temperature of rhenium oxide, followed by the recovering of rhenium values from the solution so obtained.

In its application to the extraction of rhenium incidental to the industrial roasting of molybdenum sulfide metallurgical concentrates for the production of molybdenum oxide, nothing need be altered in the roasting equipment or procedure. No auxiliary roasting stage need be introduced.

It is normal practice in such an industrial operation to pass the gaseous effluent from the roaster through dust collecting equipment such as cyclones, multiclones, rotoclones, and the like for the elimination of solid particles contained by the roaster gases. Accordingly, it is only necessary to install, first, gas scrubbing equipment, so that the volatilized rhenium oxide may be extracted from the roaster gases prior to passing such gases into the atmosphere as waste, and, second, equipment for the recovery of rhenium from the scrubber solution.

With respect to the gas scrubbing equipment, it is particularly advantageous to provide for recirculation of the scrubber solution in order to build up the concentration of rhenium therein prior to the rhenium recovery stage.

One aspect of our invention resides in the specific manner of separating the rhenium from molybdenum, sulfates, chlorides, and other impurities with which it is intimately associated in the scrubber solution.

We have found that the rhenium ions in the scrubber solution may be easily and almost completely freed from contaminants by a known adsorption and elution technique utilizing an anionic exchange material.

A preferred procedure conforming to our process is set forth in the flow sheet of Fig. 2.

The roasting of molybdenum sulfide metallurgical concentrates for the production of molybdenum oxide is customarily carried out in one or more multiple hearth furnaces of conventional construction. Whether a single furnace is operated to accomplish substantially complete oxidation of sulfur, or whether several are utilized for the purpose depends upon various factors in any given instance.

Regardless of how the roasting is carried out, however, all roaster gases given off by the roasting of charged material at and above the temperature at which rhenium oxide volatilizes will, in accordance with the present process, be treated with a solvent for the dissolution of rhenium oxide.

The metallurgical concentrates are preheated prior to being fed to the first hearth of the furnace, and do not ordinarily reach the volatilization temperature of rhenium oxide (450 degrees C.) until at least the second hearth of the furnace. Nevertheless, as a matter of convenience, all roaster gases may be commingled and treated together.

Thus, it can be seen that the roasting procedure normally employed industrially for the production of molybdenum oxide need not be altered in any respect. The calcines are discharged from the furnace in the usual manner as MoO_3.

It is preferred to remove as many of the solids as possible from the gaseous effluent discharged from the furnace, and, for this purpose, a conventional cyclone type of dust collector may be used. It is desirable that it be operated hot, so as to minimize condensation of volatilized rhenium oxide. The collected dust is recycled to the roaster.

Following removal of solids in this manner, the gases are scrubbed with a solvent for the rhenium oxide. This is best accomplished by passing them through conventional gas scrubber equipment, for example, a scrubber tower utilizing water as the scrubbing agent and having provision for recirculation of the washings.

It is known that water effects a very satisfactory dissolution of rhenium oxide. While weak caustic or acidic solutions may also be employed for the purpose, there is normally no reason for preferring such solutions to ordinary water.

The recirculation circuit for the scrubber washings includes means, advantageously a thickener, for removing from the rhenium-bearing solution solids carried over with the gases from the cyclone. The removed solids are recycled to the furnace.

The recirculating flow of such rhenium-bearing solution is split at some optimum ratio, say one to twenty, prior to its re-entry into the scrubber, the minor portion being passed to a clarification stage, usually filtration, and then to a rhenium recovery stage. The major portion of the flow is supplemented by make-up water prior to repassage through the scrubber.

By recirculation in this manner, rhenium concentration is built up in the solution to such an extent as to greatly facilitate recovery of the rhenium values on a commercial basis.

Rhenium values may be recovered from the clarified rhenium-bearing solution by the generally accepted chemical precipitation procedure utilizing a potassium compound as disclosed by U. S. Patent No. 2,414,965 to Melaven et al. Because of the difficulties caused by impurities, however, this and other similar procedures are not favored. Rather, we have found that a known ion-exchange procedure developed as an analytical method utilizing laboratory materials and reagents, may be readily applied commercially to the impure rhenium-bearing solutions derived on an industrial basis by our procedure above-described, whether such solutions remain in their normal acid condition or be converted to basic condition by treatment with an alkali.

In accordance with this aspect of our process, the clarified rhenium-bearing solution is passed through ion-exchange equipment of conventional type in intimate exchange relationship with an anionic exchange material, for example, a strongly basic alkyl amine type of synthetic resin. The rhenium ions along with some molybdenum ions will be adsorbed by the exchange material. The effluent contains some molybdenum, and may be treated for its recovery in the form of a molybdenum salt.

When it is apparent by breakthrough of rhenium in the effluent that the exchange material is saturated, the exchange column is first eluted with a basic eluant, preferably sodium hydroxide, for the removal of molybdenum, and is then eluted with a weak solution of a strong acid which is highly ionized in aqueous solution, for removal of the rhenium ions. A 0.5 molar solution of perchloric acid is preferred for the purpose. As is customary practice in ion-exchange techniques, the column is washed with water following passage therethrough of any of the solutions mentioned above.

The basic eluate is preferably added to the normal rhenium-bearing influent solution for recycling through the exchange column.

The acidic eluate solution contains the rhenium values, and represents a rhenium-bearing solution of high purity.

Whereas this process is here illustrated and described with respect to a particular preferred specific practice thereof, it should be realized that changes may be made within the scope of the following claims, without departing from the essential contributions which we have made to the art.

We claim:

1. An industrial process for the recovery of rhenium values from molybdenum sulfide metallurgical concentrates containing rhenium, comprising extracting rhenium from said concentrates in the form of rhenium oxide by roasting said concentrates at temperatures effective to produce a molybdenum oxide calcine; obtaining a rhenium-bearing solution by treating with a liquid solvent for rhenium oxide all gases given off by the roasting of said concentrates at and above the temperature at which the sulfur begins to burn; clarifying the rhenium-bearing solution so obtained; and treating the clarified solution for the separation and recovery of rhenium values.

2. An industrial process for the recovery of rhenium values from molybdenum sulfide metallurgical concentrates containing rhenium, comprising extracting rhenium from said concentrates in the form of rhenium oxide by roasting said concentrates at temperatures effective to produce a molybdenum oxide calcine; obtaining a rhenium-bearing solution by treating with a liquid solvent for rhenium oxide all gases given off by the roasting of said concentrates at and above the temperature at which the sulfur begins to burn; building up the rhenium content of said rhenium-bearing solution by repeated treating of fresh quantities of said gases therewith; clarifying the rhenium-bearing solution so obtained; and treating the clarified solution for the separation and recovery of rhenium values.

3. An industrial process for the recovery of rhenium values from molybdenum sulfide metallurgical concentrates containing rhenium, comprising extracting rhenium from said concentrates in the form of rhenium oxide by roasting said concentrates at temperatures effective to produce a molybdenum oxide calcine; obtaining a rhenium-bearing solution by treating with a liquid solvent for rhenium oxide all gases given off by the roasting of said concentrates at and above the temperature at which the sulfur begins to burn; clarifying the rhenium-bearing solution so obtained; separating rhenium ions from molybdenum ions and other impurities by adsorption on an anionic exchange material; and forming a relatively pure rhenium-bearing solution by elution of said exchange material.

4. An industrial process for the recovery of rhenium

values from molybdenum sulfide metallurgical concentrates containing rhenium, comprising extracting rhenium from said concentrates in the form of rhenium oxide by roasting said concentrates at temperatures effective to produce a molybdenum oxide calcine; obtaining a rhenium-bearing solution by treating with a liquid solvent for rhenium oxide all gases given off by the roasting of said concentrates at and above the temperature at which the sulfur begins to burn; building up the rhenium content of said rhenium-bearing solution by repeated treating of fresh quantities of said gases therewith; clarifying the rhenium-bearing solution so obtained; separating rhenium ions from molybdenum ions and other impurities by adsorption on an anionic exchange material; and forming a relatively pure rhenium-bearing solution by elution of said exchange material.

5. In an industrial process for the extraction of rhenium from molybdenum sulfide metallurgical concentrates, wherein said concentrates are roasted at a temperature above 500 degrees centigrade for the burning of sulfur but below the temperature of volatilization of molybdenum oxide, and a rhenium-bearing solution is produced by treating roaster gases with a solvent for rhenium oxide, the improvement which comprises treating with the solvent for rhenium oxide all roaster gases given off during the roasting of said concentrates at and above said temperature.

6. An industrial process for the recovery of rhenium values from molybdenum sulfide metallurgical concentrates containing rhenium, comprising extracting rhenium from said concentrates in the form of rhenium oxide by roasting said concentrates at temperatures effective to produce a molybdenum oxide calcine; scrubbing with a liquid solvent for rhenium oxide all gases given off by the

roasting of said metallurgical concentrates at and above the temperature at which the sulfur begins to burn; recovering the washings produced by such scrubbing operation; removing solids from said washings; directing the resulting washings back to the gas scrubbing operation; diverting a minor portion of said resulting washings to a rhenium recovery stage; and recovering rhenium values at said rhenium recovery stage.

7. In an industrial process for the production of a molybdenum oxide calcine by roasting a molybdenum sulfide concentrate containing rhenium sulfide at a temperature above 500 degrees centigrade but below the temperature at which molybdenum oxide volatilizes, said roasting resulting in a calcine substantially free of molybdenum sulfide and from which the major portion of the rhenium has been removed, the improvement which comprises subjecting the entire volume of gases from the roasting operation, which gases contain sulfur dioxide and a major portion of the rhenium originally present in the concentrate, to scrubbing with an aqueous solution to recover the rhenium in solution.

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