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M. M. BERTOLUS

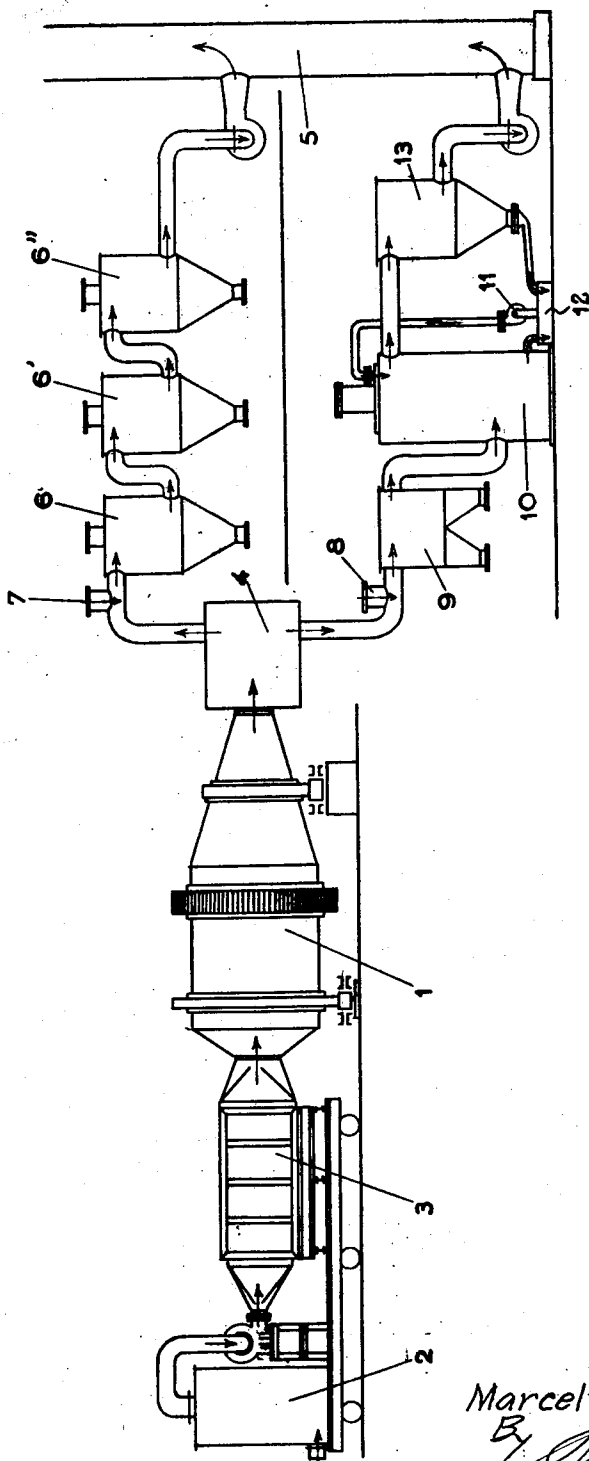
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INDUSTRIAL PROCESS FOR EXTRACTING RHENIUM

Filed March 27, 1948

2 SHEETS—SHEET 1

Fig 1



Inventor
Marcel Michel Bertolus
By *Robert Burns*
Attorney

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M. M. BERTOLUS

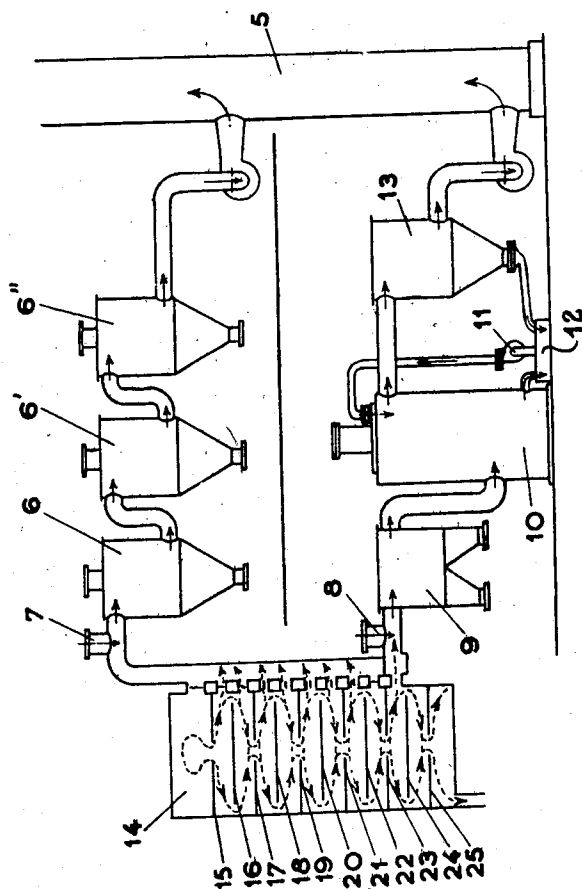
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2 SHEETS—SHEET 2

Fig 2



Inventor
Marcel Michel Bertolus
By *Robert E. Burns*
Attorney

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INDUSTRIAL PROCESS FOR EXTRACTING RHENIUM

Marcel M. Bertolus, Paris, France

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The present invention relates to an industrial process for the recovery of rhenium which exists in nature in very small quantities in certain ores where it is associated in the form of rhenium sulfide with natural molybdenum sulfide (molybdenite). It is known that the volatile oxide Re_2O_7 can be produced by roasting pure rhenium sulfide at a temperature as low as 200–300° C. in the presence of air or oxygen, i. e. at a temperature lower than that of volatilization of the molybdenum oxide which is known to be 700° C. It has been accordingly suggested to produce rhenium oxide by heating molybdenite in the presence of air or oxygen at a temperature comprised between 200° and 300° C.

I have discovered however that, contrary to what might be expected, the rhenium sulfide does not behave in the manner stated above in the presence of molybdenum sulfide and that oxidation of rhenium sulfide does not take place in the presence of molybdenum sulfide at temperatures even above those which would start the reaction in the absence of the molybdenum sulfide. Furthermore, if the temperature is raised sufficiently to start the reaction, production of SO_2 takes place first, causing a mechanical entrainment of molybdenum compounds, particularly of MoS_2 dust which contaminates the rhenium oxide Re_2O_7 . If the temperature is too high, volatilization of molybdenum trioxide MoO_3 is produced simultaneously.

The object of the present invention is a selective extraction of rhenium oxide by roasting molybdenite containing traces of rhenium sulfide.

Another object of the invention is to avoid, when thus roasting molybdenite, a large dilution of rhenium caused by an important flow of SO_2 which would contaminate the rhenium oxide by MoS_2 entrained in the form of a fine dust.

A further object of the invention is to maintain the rhenium content as high as possible at all steps of the extraction process in order to make the production of rhenium industrially and commercially workable. Still another object of the invention is the extraction of rhenium from copper-molybdenum sulfide ores which are first subjected to selective flotation for producing a molybdenite concentrate.

With these and other objects in view, the process according to the invention comprises, as a first phase, the heating of the molybdenite in an oxidizing atmosphere to a temperature above 500°, maintaining this temperature by combustion of the combined sulfur until substantially

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all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during the first phase of treatment, separating molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550° C. but below the temperature of volatilization of molybdenum oxide, and supplying oxygen, whereby the rhenium compounds are oxidized to Re_2O_7 and the latter volatilized, while entrainment of the molybdenum oxide in the evolved gases is precluded by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process, and separating the rhenium oxide therefrom.

Applicant has discovered that:

(1.) The volatilization of rhenium oxide only starts after the sulfur of the molybdenite has been substantially eliminated as sulfur dioxide.

(2.) It is necessary to raise the temperature above 500° C. in order to cause the volatilization of Re_2O_7 .

(3.) The temperature has to be raised to at least 550° C. (but below 700° which is the volatilization point of molybdenum oxide) because at 550° C. the crystals of the molybdenum oxide begin to sinter, thus forming a porous permeable mass allowing the rhenium heptoxide to escape freely but preventing mechanical entrainment of molybdenum oxide dust.

Accordingly, the rhenium oxide may be obtained as the by-product of the manufacture of molybdic acid without altering this latter.

As to the selective flotation to which the copper-molybdenum sulfide ore is first subjected before the roasting, in order to eliminate the major part of its gangue and to separate copper from molybdenite, it allows molybdenite concentrates to be obtained containing rhenium in a ratio of $1/3000$ to $1/5000$, whereas the raw materials utilized so far for the extraction of rhenium according to other methods, show a rhenium content varying from $1/300,000$ to $1/500,000$.

Furthermore the two-step treatment according to the invention permits to render extraction much quicker and simpler owing to the fact that the volume of gas subjected to the extraction of rhenium oxide is reduced in a very considerable proportion and that furthermore the said gases are, as stated above, free of molybdenite dust, free of fluorhydric acid and free of oil vapour (oil used in the flotation treatment) which are developed at the beginning of the roasting treatment.

By way of example, a detailed embodiment for carrying out the process according to the invention has been described below and illustrated in the attached drawing as well as two embodiments of the apparatuses required for its operation.

Fig. 1 shows diagrammatically an elevation of an extraction installation comprising a rotary kiln for roasting.

Fig. 2 shows a corresponding view of an installation provided with a continuous roasting kiln.

As shown on Fig. 1, this installation comprises a rotary kiln 1 in which a load of molybdenite is introduced, the said molybdenite having been preferably separated from its copper sulphide and which is supplied with hot air from a hot-air drier 2 and a preheater 3, for instance an electrical preheater. At the outlet of the kiln a dust chamber 4 is provided on which are branched two distinct circuits for the evacuation of the gases developed by roasting through the chimney 5, the said circuits being put separately in service according to requirement. The first of those circuits is branched on chamber 4 during the first period of the roasting treatment and comprises several dust extractors, for instance three cyclones 6, 6', 6'' in which molybdenite dust sucked by gases is precipitated, the said cyclones being preceded by an air inlet 7 for cooling.

The second evacuation circuit is branched on chamber 4 during the second period of the roasting treatment and is arranged for the extraction of rhenium oxide. It comprises an air inlet 8 for cooling, a separator, for instance a multicyclone 9 kept at a sufficiently high temperature so that the rhenium oxide vapors cannot condense in it, for instance from 250° to 300° C., a scrubber tower 10, preferably provided with a sprayer for the injection of the solvent intended to dissolve the rhenium oxide. The said solvent is preferably water or a highly diluted base and circulates along a closed circuit in which it is discharged by a pump 11 in order to obtain in tank 12 as high a concentrated solution as possible of rhenium oxide which facilitates the extraction of the latter by a known process. Following the scrubber tower 10, a second cyclone 13 is provided for the purpose of recuperating the liquid drops sucked into the said scrubber tower by the draft of gases. According to an alternative not shown on the drawing the scrubber tower may be followed by a Cottrell separator in which the separation of the rhenium oxide is obtained electrostatically by imparting electric charges to the said rhenium oxide, the said charges causing its deposit in the apparatus.

This installation operates as follows:

Assuming the kiln to be loaded with molybdenite, the whole of the electrical energy available is put on the electrical air preheater in order to carry the mass in the kiln to the temperature at which the reaction is starting.

As soon as the oxidation of molybdenite has begun and when temperature rises on account of the heat developed by the reaction, the electrical power on the preheater is lowered. Also the air supply is adjusted so that the temperature in the kiln does not exceed 600° C. During that period of the process, the gases developed by roasting are evacuated through circuit 6, 6', 6''.

At the end of the treatment, when most of the sulphur has been eliminated the temperature drops in the kiln. Then the electrical power supplied to the preheater is raised again in order to bring that temperature back to about 600° C. in order to obtain a complete oxidation of rhenium and a complete sublimation of its oxide Re_2O_7 .

To collect the latter product the first gas circuit is closed and the exhaust circuit 8—9—10—13 is opened.

The installation shown on Fig. 2 differs from that described above in that it comprises a continuous roasting kiln 14 instead of a discontinuous rotary kiln, for instance a kiln of the Nichols-Herreshoff type comprising a number of hearth plates 15 to 25 heated by electrical devices or by gas or fuel oil distributors not shown on the drawing. The molybdenite loaded on those plates is mixed during roasting by scrapers which make it come down from one sole to another (according to the path shown on the drawing in dotted lines) as roasting is progressing, the molybdic acid being finally evacuated through the outlet provided at the bottom of the kiln. A few last soles of that furnace, for instance the two lower soles 24, 25 upon which molybdenite falls at the end of the roasting treatment are kept at a temperature of 550° C. to 600° C. and the gases which are developed by the roasting of the mass on the two latter soles are sucked in the exhaust circuit 8—9—10—13 which is strictly the same as above, while the gases developed on the upper soles are sucked in the exhaust circuit 7—6—6'—6''.

In both cases, the molybdenite dust which deposits in the cyclones 6, 6', 6'' are recuperated and turned back to the kiln 1 or 14 with at the same time a certain quantity of rhenium oxide which may escape from the kiln in the earlier period of the roasting treatment. To this end, temperature is lowered in the multicyclones for obtaining the condensation of Re_2O_7 at the same time as the deposit of the molybdenite dust.

What I claim is:

1. Industrial process for the extraction of rhenium from molybdenite concentrate containing traces of rhenium sulfide comprising, as a first phase, the heating of the concentrate in an oxidizing atmosphere to a temperature above 500° C., maintaining this temperature by combustion of the combined sulfur until substantially all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during the first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550° C. but below the temperature of volatilization of molybdenum oxide, and supplying oxygen whereby the rhenium compounds are oxidized to Re_2O_7 and the latter volatilized, while entrainment of the molybdenum oxide in the evolved gases is precluded by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process, and separating the rhenium oxide therefrom.

2. Industrial process for the extraction of rhenium from molybdenite concentrate containing traces of rhenium sulfide comprising, as a first phase, heating the concentrate in an oxidizing atmosphere by combustion of the combined sulfur to a temperature between 500° C. and 600° C. and maintaining this temperature until substantially all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during this first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550° C. but below the temperature of

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volatilization of the molybdenum oxide and supplying oxygen-containing gas whereby the rhenium compounds are oxidized to Re_2O_7 and the latter is volatilized, while entrainment of the molybdenum oxide in the evolved gases is precluded by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process and separating the rhenium oxide therefrom.

3. Industrial process for the extraction of rhenium from molybdenite concentrate containing traces of rhenium sulfide comprising, as a first phase, heating the concentrate in an oxidizing atmosphere by combustion of the combined sulfur to a temperature between 550°C . and 600°C . and maintaining this temperature until substantially all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during this first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550°C . but below the temperature of volatilization of the molybdenum oxide and supplying oxygen-containing gas whereby the rhenium compounds are oxidized to Re_2O_7 and the latter is volatilized, while entrainment of the molybdenum oxide in the evolved gases is inhibited by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process and scrubbing said gases with a highly diluted base to dissolve the rhenium oxide.

4. Industrial process for the extraction of rhenium from molybdenite concentrate containing traces of rhenium sulfide comprising, as a first phase, heating the concentrate in an oxidizing atmosphere by combustion of the combined sulfur to a temperature between 550°C . and 600°C . and maintaining this temperature until substantially all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during this first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550°C . but below the temperature of volatilization of the molybdenum oxide and supplying oxygen-containing gas whereby the rhenium compounds are oxidized to Re_2O_7 and the latter is volatilized, while entrainment of the molybdenum oxide in the evolved gases is inhibited by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process and scrubbing said gases with water to dissolve the rhenium oxide.

5. Industrial process for the extraction of rhenium from molybdenite concentrate containing traces of rhenium sulfide comprising, as a first phase, heating the concentrate in an oxidizing atmosphere to a temperature between 550°C . and 600°C . by combustion of the combined sulfur and maintaining this temperature until substantially all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during this first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550°C . but below the temperature of volatilization of the molybdenum oxide and supplying oxygen-containing gas whereby the rhenium

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compounds are oxidized to Re_2O_7 and the latter is volatilized, while entrainment of the molybdenum oxide in the evolved gases is precluded by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process, bringing them into intimate contact with a finely divided and highly diluted base dissolving the rhenium oxide and separating the droplets of the solution thus obtained from the insoluble residual gaseous phase.

6. Industrial process for the extraction of rhenium from molybdenite concentrate containing traces of rhenium sulfide comprising, as a first phase, heating the concentrate in an oxidizing atmosphere to a temperature between 550°C . and 600°C . and maintaining this temperature by combustion of the combined sulfur until substantially all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during this first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550°C . but below the temperature of volatilization of the molybdenum oxide and supplying oxygen-containing gas whereby the rhenium compounds are oxidized to Re_2O_7 and the latter is volatilized, while entrainment of the molybdenum oxide in the evolved gases is precluded by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process, cooling said separately collected gases, bringing them into intimate contact with a finely divided and highly diluted base dissolving the rhenium oxide, imparting electric charges to the droplets of the solution thus obtained and separating same from the insoluble gaseous phase by electrostatic separation.

7. Industrial process for the extraction of rhenium from copper-molybdenum sulfide ores, comprising a preliminary step consisting in the production of a molybdenite concentrate containing traces of rhenium sulfide by selective flotation of said ore, then, as a first phase, heating said concentrate in an oxidizing atmosphere to a temperature above 500°C . and maintaining this temperature until substantially all the sulfur has been oxidized to sulfur dioxide, collecting the gases evolved during this first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying heat to maintain the material at a temperature above approximately 550°C . but below the temperature of volatilization of the molybdenum oxide and supplying oxygen-containing gas whereby the rhenium compounds are oxidized to Re_2O_7 and the latter is volatilized, while entrainment of the molybdenum oxide in the evolved gases is inhibited by a fusing together of the molybdenum oxide particles, collecting separately the gases evolved during this second phase of the process and separating the rhenium oxide therefrom.

8. Industrial process for the extraction of rhenium from copper-molybdenum sulfide ore containing traces of rhenium sulfide, comprising a preliminary step consisting in the concentrating of molybdenite by a selective flotation of said ore, said traces of rhenium sulfide being contained in the concentrates, heating of the molybdenite concentrates during a first phase of treatment in an oxidizing atmosphere to a tem-

perature between 550° C. and 600° C. and maintaining this temperature by combustion of the combined sulfur until substantially all the sulfur has been eliminated as sulfur dioxide, collecting the gases evolved during this first phase of treatment, separating the molybdenite dust contained therein and returning same into the process, then, as a second phase, supplying external heat to maintain the material at a temperature above approximately 550° C. but below the temperature of volatilization of the molybdenum oxide and supplying oxygen-containing gas whereby the rhenium compounds are oxidized to Re_2O_7 and the latter is volatilized, while entrainment of the molybdenum oxide in the evolved gases is inhibited by a fusing together of the molybdenum oxide particles into a porous and permeable, nondusting mass, collecting separately the gases evolved during this second phase of the process, cooling said separately collected gases, bringing them into intimate contact with a finely divided and highly diluted base, imparting electric charges to the droplets of the solution thus obtained and separating same from the insoluble gaseous phase by electrostatic separation.

MARCEL M. BERTOLUS.

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