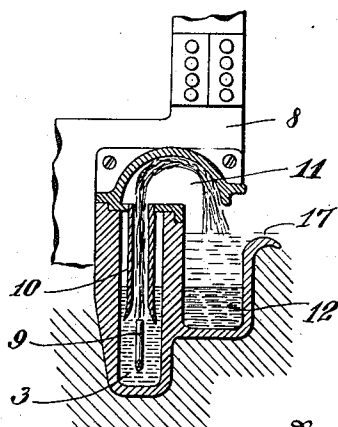
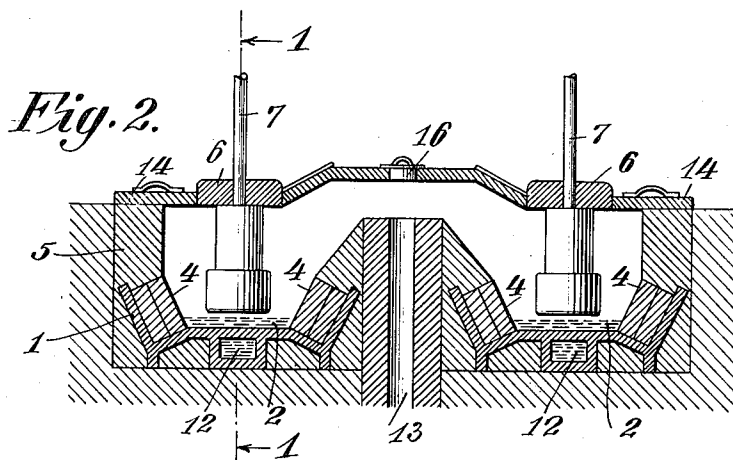
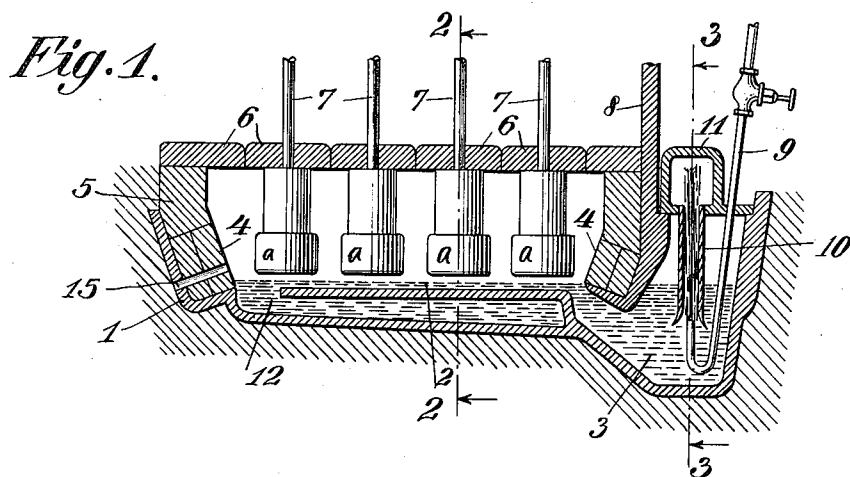


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METHOD OF EXTRACTING AND RECOVERING MOLYBDENUM FROM ITS ORES AND CONCENTRATES.
APPLICATION FILED JAN. 18, 1917.

1,299,559.

Patented Apr. 8, 1919.



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UNITED STATES PATENT OFFICE.

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METHOD OF EXTRACTING AND RECOVERING MOLYBDENUM FROM ITS ORES AND CONCENTRATES.

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Specification of Letters Patent.

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To all whom it may concern:

Be it known that I, HENRY ALFRED DOERNER, a citizen of the United States, residing in Denver, county of Denver, and State of Colorado, have invented certain new and useful Improvements in Methods of Extracting and Recovering Molybdenum from Its Ores and Concentrates; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to a method for the extraction and recovery of molybdenum from its ores and concentrates; and more particularly to the recovery of molybdenum oxid of commercial purity from ores or concentrates; and especially from those ores and concentrates which contain copper or other deleterious elements which are not separated by the usual methods of treatment.

I have found that when molybdenum ores or concentrates or other appropriate molybdenum-containing materials are heated with a suitable chlorid to a sufficient temperature to fuse the same and under proper conditions the molybdenum will distil off in the form of volatile chlorids or oxychlorids; and that from the distilled product molybdenum oxid can be readily obtained by the action of water or steam, hydrochloric acid being at the same time set free.

In the practice of the invention, the molybdenum-containing material, such as the molybdenum sulfid ore, molybdenite, mixed with a suitable chlorid such as ordinary salt (sodium chlorid), is heated to a sufficient temperature to form a fused bath and under appropriate conditions for combining the molybdenum with the chlorin of the chlorid and for distilling off the resulting chlorids or oxychlorids thus formed. The action is promoted by carrying out the operation in an oxidizing atmosphere.

In the preferred practice of the invention, I use a fusible chlorid, such as sodium chlorid, and electrolyze a fused bath containing the chlorid and the molybdenum

ore; and I will describe my invention more particularly in connection with such preferred embodiment.

In the accompanying drawings I have illustrated a suitable type of apparatus for effecting the extraction and recovery of the molybdenum by the use of a fused bath containing the molybdenum ore and a chlorid such as sodium chlorid.

In these drawings, Figure 1 shows a longitudinal vertical section of a suitable furnace for the practice of the invention. Fig. 2 is a transverse vertical section of a double furnace taken on the line 2—2 of Fig. 1; and Fig. 3 is a sectional view taken on the line 3—3 of Fig. 1.

The electric furnace shown comprises a cast iron or steel box 1 divided into three compartments. The hearth 2, where the fused salt is decomposed by the electric current, has its floor covered with a layer of a fluid metal such as molten lead which is adapted to combine with an alkali metal such as sodium to form an amalgam. The molten lead flows continuously to the well 3 from which it is ejected by means of steam introduced through the pipe 9, through the pipe 10 and into the chamber 11, from where it flows back through the channel 12 to the hearth 2.

The hearth is lined with magnesite bricks 4 and is held in the fire-clay setting 5. Over the hearth are the carbon or graphite anodes *a* suspended by the terminal rods 7, which pass through the fire-clay cover 6. The molten lead forms the cathode and is connected with the terminal 8.

The gaseous products are drawn off from the furnace through the flue 13 to suitable condensing chambers (not shown). The furnace is provided with covers 14 to close the openings through which the material is introduced into the furnace; and with a tap-hole 15 to enable the molten contents of the furnace to be drawn off as desired.

In the preferred practice of the invention, a mixture of salt and molybdenum ore is fed to the furnace and a direct current of suitable voltage and amperage is passed

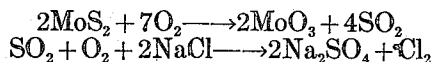
through the molten bath, liberating chlorin at the anodes α . This chlorin thereupon reacts with the molybdenum to form volatile molybdenum chlorids which are drawn off as gaseous products to the condensing chambers by means of slight suction.

Molybdenum forms a number of volatile chlorids and oxychlorids which are difficult to distinguish and identify; and moreover the principal chlorids or mixtures of chlorids may vary with the conditions under which the reaction is carried out.

The molybdenum chlorids or oxychlorids which pass off to the condensing chamber are decomposed therein into molybdenum oxid and hydrochloric acid by the action of steam or water. This decomposition of the molybdenum chlorids and the formation of the oxids and hydrochloric acid may with advantage be carried on in the condensing chamber itself. The hydrochloric acid can be separated by evaporation or distillation and recovered, leaving behind the molybdenum oxid.

Inasmuch as molybdenum also forms a number of oxids, as well as a number of chlorids, the final product will vary according to the variations in the chlorid distillate.

With ores containing sulfids, such as molybdenite, air may be admitted to oxidize the sulfur and thereby assist the action of the chlorin with resulting economy in the use of the chlorid. Thus, where, under non-oxidizing conditions the sulfur of the molybdenum sulfid may combine with the chlorin to form sulfur chlorid, under oxidizing conditions it may be oxidized to sulfur dioxid so that less chlorin is required for the reaction. The oxidization of the molybdenum sulfid, and the action of the sulfur dioxid in setting free chlorin, which may supplement or replace the electrolytically formed chlorin, may be illustrated by the following equations:



The chlorin is moreover set free within the reacting mass where it can combine with the molybdenum to form volatile compounds. Molybdenum can thus be removed which, if no such chlorin were set free, would tend to remain in the slag in soluble form.

The setting free of the chlorin at the anode is accompanied by liberation of sodium at the cathode, and this sodium amalgamates with the molten lead to form an amalgam which flows to the well 3 from which it is ejected by the jet of steam into the chamber 11, being decomposed by the steam into molten lead and into sodium hydroxid, which, at the high temperatures used, is obtained in a fused and anhydrous state. The

decomposition of the steam by the metallic sodium to form the sodium hydroxid is accompanied by the formation of hydrogen which may be drawn off and allowed to escape or utilized in an auxiliary heater or for other purposes.

The fused caustic soda accumulates in the chamber 11 above the molten lead and overflows the lip 17 into a suitable receiver (not shown). The impoverished amalgam consisting mainly of molten lead which has been further heated by the reaction of the steam and sodium, flows back to the hearth 2 through the channel 12. The molten lead cathode is thus circulated from the hearth to the well 3 and back to the hearth, combining with the sodium set free from the bath and giving up the sodium on treatment with the steam.

The heating of the fused bath can be effected by the resistance of the current passed through it, and the bath can thus be kept at the proper temperature by proper regulation of the current; but the heating action of the current may be supplemented by an auxiliary heater, and particularly by the use of such an auxiliary heater to preheat the salt and ore mixture which is fed to the furnace.

Fusion of the salt and ore takes place at a temperature slightly above 800°C ., and I have found a temperature of about 900°C . a satisfactory operating temperature for the molten bath.

While I have described a type of furnace particularly adapted to the practice of the invention. I do not desire to limit myself to the use of any particular type of furnace or even to the electrolytic decomposition of the chlorid in a fused bath; although such an electrolytic procedure, using a molten or liquid metal cathode, I consider to be a particularly valuable embodiment of my invention and one having many advantages.

When the invention is practised without the electrolysis of a fused bath, a mixture of molybdenite and salt, for example, can be heated to the proper temperature in any suitable manner and subjected to an oxidizing atmosphere so that the chlorids or oxychlorids of molybdenum will distil off in a manner similar to that which I have already described. Thus, for example, where the mixture of molybdenite and salt is heated to fusion, and subjected to the oxidizing atmosphere by injecting air into the fused bath, the sulfur dioxid formed by the oxidizing atmosphere and the sulfur of the sulfid (molybdenite) reacts with more oxygen and with the salt to form chlorin, which combines with the molybdenum to form volatile compounds that distil off in a manner similar to that already described. In this case the reaction of the sulfur, oxygen (from the oxidizing atmosphere) and salt, furnishes

or sets free chlorin which reacts in much the same manner as the chlorin set free by electrolysis.

When the electric current is used, its action, aside from its other advantages and functions, assists the distillation and is a convenient method of maintaining the desired temperature. It has the further important function, when used with a fused bath, of decomposing the chlorid and supplying active chlorin to the molybdenum of the ore, as well as of furnishing metallic sodium and caustic soda.

While I have described my invention more particularly with the use of sodium chlorid, it will be understood that other suitable chlorids, fusible or unfusible, are adapted for use in the process.

I claim:

1. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which comprises heating the material to a sufficient temperature to form a fused bath and subjecting the fused bath to the action of free chlorin under proper conditions to combine with and to volatilize the molybdenum as chlorid or oxychlorid; substantially as described.

2. The method of recovering molybdenum from its sulfid ores, concentrates and other molybdenum-sulfid-containing materials, which comprises heating such materials in the presence of a chlorid to a sufficient temperature to form a fused bath and under oxidizing conditions to set free chlorin and to volatilize the molybdenum in the form of chlorids or oxychlorids; substantially as described.

3. The method of recovering molybdenum from its sulfid ores, concentrates and other molybdenum-sulfid-containing materials, which comprises heating such materials in the presence of a source of chlorin to a sufficient temperature to fuse the same, and to set free chlorin and under proper conditions to volatilize the molybdenum in the form of chlorids or oxychlorids and recovering molybdenum oxid therefrom by the action of steam or water; substantially as described.

4. The method of recovering molybdenum from its sulfid ores, concentrates and other molybdenum-sulfid-containing materials, which comprises heating the material with a chlorid to a sufficient temperature to fuse the same and under proper oxidizing conditions to set free chlorin and to volatilize the molybdenum as chlorid or oxychlorid and recovering molybdenum oxid therefrom by the action of steam or water; substantially as described.

5. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which com-

prises heating the material with a chlorid by means of an electric current to a sufficient temperature to form a fused bath, and under proper conditions to set free chlorin from said chlorid within said bath to combine with and to volatilize the molybdenum as chlorid or oxychlorid; substantially as described.

6. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which comprises electrolyzing the fused bath containing such material and a chlorid to volatilize the molybdenum as chlorid or oxychlorid; substantially as described.

7. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which comprises electrolyzing a fused bath containing such material and a chlorid to volatilize the molybdenum as chlorid or oxychlorid and recovering molybdenum oxid from the volatilized product by the action of steam or water; substantially as described.

8. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which comprises electrolyzing a fused alkali chlorid bath containing such material, using a fluid metal cathode adapted to form an amalgam with the alkali metal, and thereby combining the molybdenum with chlorin and volatilizing the molybdenum chlorid or oxychlorid thus formed, and at the same time forming an amalgam with the cathode, decomposing the amalgam to form caustic alkali, and returning the impoverished cathode metal for the formation of further amounts of amalgam; substantially as described.

9. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which comprises electrolyzing a fused alkali chlorid bath containing such material and thereby volatilizing the molybdenum as chlorid or oxychlorid, combining the alkali metal set free with a fluid metal cathode in the form of an amalgam, and recovering molybdenum oxid from the volatilized chlorids by the action of steam or water; substantially as described.

10. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which comprises electrolyzing a fused sodium chlorid bath containing such material, under oxidizing conditions, and thereby decomposing the sodium chlorid and combining the chlorin with the molybdenum in the form of volatile chlorids, separating such volatilized chlorids and recovering molybdenum oxid therefrom by the action of steam or water, combining the sodium set free with a molten lead cathode in the form of an amalgam, de-

composing the amalgam with steam to form caustic alkali and to recover the molten lead in an impoverished condition, and returning the impoverished metal for combination with
5 further amounts of metallic sodium; substantially as described.

11. The method of recovering molybdenum from its ores, concentrates and other molybdenum-containing materials, which com-

prises heating the material to a sufficient 10 temperature to form a fused bath and setting free chlorine within said bath to combine with and to volatilize the molybdenum as chlorid or oxychlorid; substantially as described. 15

In testimony whereof I affix my signature.

HENRY ALFRED DOERNER.