

UNITED STATES PATENT OFFICE.

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EXTRACTION OF METALS FROM THEIR ORES.

1,399,554.

Specification of Letters Patent.

Patented Dec. 6, 1921.

No Drawing. Original application filed March 14, 1917, Serial No. 154,848. Divided and this application filed June 7, 1917. Serial No. 173,308.

To all whom it may concern:

Be it known that I, EDWARD M. HAMILTON, a subject of the King of Great Britain, residing at the city and county of San Francisco and State of California, have invented new and useful Improvements in the Extraction of Metals from Their Ores, of which the following is a specification.

This invention relates to the recovery of certain metals from their ores and concentrates and pertains especially to a method for the extraction of molybdenum.

The usual method of dealing with molybdenum ores is in the case of the sulfid to roast and extract the oxid with ammonia, the resulting liquor being evaporated to dryness resulting in ammonium molybdate. In the case of the ore wulfenite $PbMoO_4$ a high grade concentrate is first made and this concentrate is fused with soda ash forming lead carbonate and sodium molybdate. The latter being soluble in water is dissolved out and the liquor evaporated or molybdic acid may be precipitated by addition of an acid to the liquor but this method is not satisfactory because precipitation is usually incomplete and the least excess of acid tends to redissolve the precipitate already formed.

It happens in the case of certain ores that it is impossible to obtain a concentrate high in molybdenum, and at the same time make a high percentage recovery of the metal in question from the ore; for instance, where molybdenum occurs in small quantities in ore containing a large proportion of sulfids of iron together with copper, gold and other heavy minerals, it is possible to recover by mechanical means as high as 90% of the molybdenum together with most of the heavy sulfids present resulting in a concentrate containing only a few per cent. (say from 1 to 10 per cent.) of molybdenum, the remainder being almost entirely sulfids or other heavy minerals. Such a product is unsuitable for treatment to recover the molybdenum by any of the commercial methods now in use on the ground of expense. On the other hand, if it is desired to make a concentrate containing a high per-

centage of molybdenum (say from 10% to 50%) suitable for the present commercial processes of molybdenum recovery, the loss of molybdenum in the process of concentration is so high as to constitute a serious source of loss of the metal.

In addition to the above difficulties the presence of copper renders the ammonia process inapplicable since the copper being soluble in the ammonia is extracted with the molybdenum and it is found very difficult to separate it.

The object of the present invention is to devise a process whereby a concentrate high in heavy minerals and containing a low molybdenum content such as that already described, can be treated successfully and at an expense within the limits demanded for a commercial process.

Preparation of the ore for treatment.— My process consists of first grinding the material to be treated to a suitable degree of fineness or otherwise preparing it so that it becomes amenable to the subsequent reactions by chemical treatment necessary. In the case of molybdenum, except where the same occurs as sulfids, I usually grind the ore to pass a 200 mesh standard sieve, although it may not be necessary in every case to grind as fine as this. Where the ore is in the form of a sulfid, as is commonly the case with molybdenum ores, it may be necessary to roast the ore. Where the ore is to be roasted it is only necessary ordinarily to grind the sulfid ore to about 20 mesh which size it yields readily to treatment and generally requires no further grinding after roasting. I have found it advisable in the case of a roasted ore to give a thorough water-wash to remove soluble salts of copper and iron before proceeding to digest the pulp in the soda solution.

Such a washing may be done either by percolation or by agitation, the pulp in the latter case being of course filtered before going to the digesting tank.

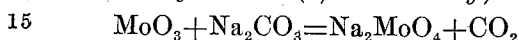
Reagent.—The ore, having been suitably pulverized and roasted if necessary, is made into a pulp with water to which has been added, or to which there is later added, a

suitable amount of carbonate, bi-carbonate or hydroxid of one of the alkali metals; the amount being determined by the molybdenum content of the material; it being usually advisable to have present an excess of the re-agent over the amount actually called for by the equation.

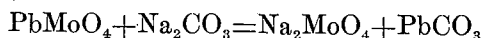
The reagent I prefer is commercial sodium carbonate, (soda ash) on account of its cheapness.

The reaction may be represented by the following equations:

Molybdenite (after roasting).



Wulfenite.



Ratio of solution.—The ratio of solution to ore in the mixture is not vital to the reaction but with low grade material it is advisable to keep it low, say between 1:1 and 2:1, both to reduce the quantity of liquor to be handled subsequently and also to obtain a higher degree of concentration of the dissolving reagent, but in the treatment of products rich in molybdenum it is usually better to increase the dilution since otherwise there may be a formation of large crystals of sodium molybdate which may be troublesome to dissolve during the washing out process.

Heating.—The pulp so formed is heated up to or above the boiling point of the solution.

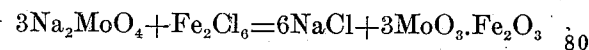
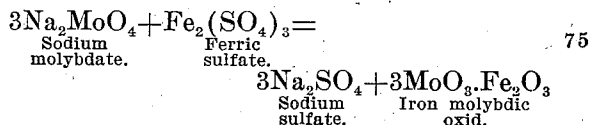
In the case of molybdenite when the ore is roasted to oxid the reaction usually takes place rapidly and completely at the atmospheric boiling point so in most cases I do not find it necessary to raise the temperature above that point. In treating wulfenite, however, the higher temperature obtained by heating under pressure is of great assistance.

The higher the temperature rises above the atmospheric boiling point of water the more rapid and complete is the reaction, and I find a useful point to work at is one hundred (100) pounds pressure within the receptacle equal to a temperature of 327.9 degrees F. When this temperature has been maintained long enough to complete the reaction, which may take from one to three hours the pressure is lowered and the charge withdrawn, or what is preferable for a working plant a series of such receptacles may be used, so arranged that the pulp is pumped from one to the other and continuously discharges at the end of the series, the speed of flow being determined by the time it is found necessary to keep the ore under the influence of the heat and reagent.

Filtering and washing.—The pulp after being subjected to the heating process is

filtered and the residue well washed with water, the resulting liquor containing the molybdenum in the form of sodium molybdate.

I treat the sodium molybdate with a solution of a salt of a metal, preferably a ferric salt, which precipitates the molybdenum as a double oxid of iron and molybdenum.



Neutralizing.—Before treating the molybdate solution with the iron solution I find it advantageous first to neutralize with an acid any free sodium carbonate that may be present so as to avoid precipitating hydroxid of iron and raising the iron content of the precipitate. In this way it is possible to obtain a product whose iron content conforms very closely with the proportions called for by the chemical formula.

By this precipitation method I have been able to obtain a practically complete recovery of the molybdenum from its solution.

The formation of an iron compound of molybdenum is no drawback when this metal is to be used for the manufacture of special steels as it is customary to add such ingredients in the form of ferro-alloys of the said metal. The precipitate obtained by my process after being dried and pulverized may be reduced to a ferro-alloy powder by igniting with carbon or to a ferro-alloy pig by fusion with carbon in the electric furnace, in either of which forms it is suitable for addition to steel in the manufacture of special steels.

To sum up the advantages of my process:

- (1) It is applicable to products of concentration low in molybdenum such as it is unavoidable to make in many instances if a high recovery is to be obtained from the ore, and such as could not be profitably treated by processes at present in use.
- (2) It solves the problem of the association of copper with molybdenum ore.
- (3) It provides an efficient and inexpensive method of recovering molybdenum from its alkaline solutions.

This application is a division of my original application, filed March 14, 1917, Serial Number 154,848.

Having thus described my invention, what I claim and desire to secure by Letters Patent is—

1. The process of recovering molybdenum from its ores and concentrates which comprises reducing the ore or concentrate to a suitable condition of fineness for further chemical treatment, mixing the pulverized material with water and with a non-volatile

alkali-metal compound the aqueous solution of which is alkaline to form a pulp, heating the pulp to convert the molybdenum into a soluble compound, filtering, and re-

5 covering the values from the filtrate.

2. The process of recovering molybdenum from its molybdate ores and concentrates which comprises reducing the ore or concentrate to a suitable condition of fineness
10 for further chemical treatment, mixing the pulverized material with water and with an alkali-metal salt of carbonic acid to form a pulp, heating the pulp at a temperature above 212° F. to convert the molybdenum
15 into a soluble compound, filtering, and recovering the values from the filtrate.

3. The process of recovering molybdenum from its ores and concentrates which comprises reducing the ore or concentrate to a
20 suitable condition of fineness for further chemical treatment, mixing the pulverized material with water and with sodium carbonate to form a pulp, heating the pulp to convert the molybdenum into a soluble compound, filtering, and recovering the values
25 from the filtrate.

4. The process of recovering molybdenum from its molybdate ores and concentrates which comprises reducing said ore or concentrate to a suitable condition of fineness
30 for further chemical treatment, mixing the pulverized material with water and with sodium carbonate to form a pulp, heating the pulp at a temperature above 212° F. until a soluble molybdate is formed, filtering, neutralizing the filtrate and recovering values from the neutralized filtrate.

5. The process of recovering molybdenum from its molybdate ores and concentrates which comprises reducing said ore or con-

centrate to a suitable condition of fineness for further chemical treatment, mixing the pulverized material with water and with a non-volatile alkaline metal compound, the aqueous solution of which is alkaline to
45 form a pulp, heating the pulp at a temperature above 212° F. until a soluble molybdate is formed, filtering, neutralizing the filtrate, adding a soluble ferric salt of iron to the neutralized filtrate to precipitate a
50 double oxid of iron and molybdenum, removing said precipitate and reducing it to ferro-molybdenum.

6. In a process of recovering molybdenum from ores or concentrates thereof,
55 the step which comprises leaching the molybdenum-bearing material with a suitable solvent comprising an alkaline sodium compound in sufficient proportion to secure a commercially complete extraction of the
60 molybdenum, as molybdate while leaving undissolved a substantial proportion of the impurities of the ore.

7. In a process of recovering molybdenum from ores or concentrates thereof, the step
65 which comprises leaching the molybdenum-bearing material with a sodium carbonate solution in sufficient proportion to secure a commercially complete extraction of the molybdenum, while leaving undissolved a
70 substantial proportion of the impurities of the ore.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

EDWARD M. HAMILTON.

Witnesses:

H. E. WEST,

S. E. WOODWORTH.