Patented May 28, 1940 2,202,525

UNITED STATES PATENT OFFICE

2,202,525

METHOD OF RECOVERY OF MOLYBDENUM VALUES

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No Drawing. Application September 15, 1937, Serial No. 163,958

12 Claims. (Cl. 23—23)

The present invention relates to the recovery of molybdenum from molybdenum-bearing minerals, more particularly to the recovery of molybdenum by means of solvent extraction.

As is known, the United States has the largest potential supply of molybdenum ores of any country in the world, the largest single domestic source being the deposit at Climax, Colorado. The two important molybdenum-containing minerals are molybdenite (MoS_2) and molybdite (MoO_3). The deposit mentioned, as well as others, contains the molybdenum largely as the sulphide.

These molybdenum-bearing ores seldom carry more than about 1 per cent. of the mineral. However, methods have been developed whereby such ores may be concentrated by flotation so as to produce a concentrate carrying 80 to 90 per cent., or more, of the molybdenum sulphide. In such an operation, however, the oxidized portion of the ore is not floated but appears in the tailings. To date, no profitable commercial use has been made of such oxide, although considerable effort has been expended in an attempt profitably to utilize it. For example, it has been attempted, unsuccessfully, to concentrate the oxide by flotation and by gravity concentration methods. Suggestions have been made as to methods of extracting by means of acid and alkali leaches. Such methods however involve a complicated series of steps, including several precipitations in order to satisfactorily separate the molybdenum from impurities.

It has now been found that effective methods, utilizing the principle of selective solvent extraction by organic solvents, may be developed for the recovery of molybdenum from molybdenum-bearing materials. The novelty and efficacy of the process will be the more apparent from a consideration of its application to the recovery of molybdenum from oxidic ores or compounds, in other words, from those materials which heretofore were considered a commercially impractical source. However, it is clearly to be understood that the principles involved herein may be invoked in any circumstances where it is desired to obtain or extract molybdenum from compounds containing it, a typical example being the recovery of molybdenum from spent catalysts used in the catalytic hydrogenation processes. As will be seen more fully hereinafter, a particularly important feature of the invention is the ability to extract molybdenum in a highly purified form from systems containing it. As will be appreciated by those skilled in the art, the present method or process may be correlated or combined with other steps so as to produce any desired type of molybdenum salts, such for example as calcium molybdate, free from sulphur and hence eminently useful for employment as an addition agent in the manufacture of molybdenum steels.

The present method is based upon the discovery that it is possible, and eminently practical, to extract molybdenum from liquid systems or vehicles containing it by means of suitable selective organic solvents. As will be seen, the major features or steps of the process comprise, solublizing the molybdenum compound, as for example by suitable leaching methods, then preferentially extracting the molybdenum by means of an organic solvent. The solvent phase may then be treated by any suitable method so as to remove the molybdenum therefrom in a state of high concentration and relative purity. The selective solvent or solvents used may be utilized in a cyclic system in which they are separated from the original aqueous system and reemployed in the process. It is found that by utilizing such recycling methods the cost of the treatment is relatively low since the solvent losses involved are very small.

An object of the present invention therefore is to provide a novel method of extracting metal values, such as molybdenum, from systems containing them.

Another object is to provide an improved method of economically utilizing oxidized molybdenum ores.

Yet another object is to provide a method for economically utilizing tailings from a flotation plant operating upon molybdenite.

A further object is to provide an improved method of concentrating metal values by utilizing an organic concentrating medium.

With these and other equally important and related objects in view, the invention comprehends broadly the concept of utilizing the principle of solvent extraction for the recovery of metal values such as molybdenum.

In order to enable a more ready comprehension of the principles of the invention, a preferred type or mode of operation will be indicated hereinafter. It is particularly to be understood however that this is given in an exemplary sense and not as indicating the exclusive method by which the fundamental principles may be embodied in commercial operations. Modifications in operative procedure and the substitution of equivalent solvents will readily suggest themselves to those

skilled in the art and are to be understood as being comprehended herein.

It is to be understood, at this point, that the expressions "solvent" and "selective solubility" are herein used in a general descriptive sense to indicate the ability of the "solvent" to abstract the metal compound from its original phase (acid) and concentrate it in the solvent phase. The phenomenon obtaining, in a strict sense, may not be true solubility, but may possibly involve the formation of an evanescent metallo-organic complex. As will be appreciated, the physico-chemical factors involved are difficult to precisely determine. However, whatever may be the actual mechanism or action, it is found, as a matter of fact, that by contacting organic liquids with aqueous systems containing the metal value, in the manner to be described, abstraction of such values by and concentration in the organic liquid is effected.

As indicated above, a considerable amount of molybdenum occurs naturally in the form of trioxide. In the Climax deposit, the concentration of the molybdenum in the oxidized portion of the ore (calculated as MoS_2) is of the order of from 0.7 per cent. to about 0.1 per cent.

Under the present invention, such oxidized ore may be treated by a simple method to substantially quantitatively separate molybdenum from the other constituents of the ore.

The principles involved in the new treatment will be readily comprehended from a consideration of a typical extraction method. As will be seen, such a method involves essentially the steps of leaching the ore with an acid or otherwise solubilizing the molybdenum; treating the solution to reduce the dissolved metals to the lower valence states and selectively extracting the molybdenum by means of an organic extractant.

To accentuate the feasibility of the present process, a material was advisedly chosen which is a low grade, waste product, namely, the tailings from a concentration cell operating on the molybdenite of the Climax deposit. Obviously, other molybdenum-bearing ores, compounds, and the like, may be utilized as the starting material.

Two hundred grams of such tailings were deposited in a flask and several hundred cc. of water were added. Sulphur dioxide was bubbled into the suspension for a period of several hours. The sulphurous acid which was formed in situ acted upon the ore, dissolving quantities of the molybdenum. During this period, the solution turned blue. After such treatment, the solution was filtered, the insoluble residue washed, and this residue retreated in the same manner, namely, with sulphurous acid. It was found that in this second cycle the solution similarly acquired blue color. This solution was filtered and the filtrates were combined and then concentrated by evaporation. The concentrated solution was then treated to reduce the metal components to a lower valence state by bubbling in sulphur dioxide.

The concentrated solution containing the lower valence metal values was then acidulated with a small amount of hydrochloric acid and then extracted with ethyl acetate. It was found that the ethyl acetate removed the color from the acidic solution. The acetate was allowed to stratify and was separated from the aqueous phase in a separatory funnel. This separated acetate phase was then agitated with distilled water. It was found that the water abstracted the color, leaving the ethyl acetate phase substantially colorless. These two phases were then separated and the ethyl acetate reemployed to again extract the original molybdenum solution. This extraction cycle was repeated several times until the acetate removed no more color from the original acidic solution.

The original acid solution was then further treated to insure reduction of any residual metal constituents to the lower valence state. For this purpose, the original, extracted molybdenum solution was treated with an excess of sodium thiosulphate. It was found that a blue color developed in the solution. The solution was then subjected to the described treatment, namely, to successive extractions with ethyl acetate, the latter, after each extraction being agitated with water to remove the color.

The blue water solutions from the several treatments described above were then combined, concentrated and analyzed for molybdenum. Upon analysis, it was found that the water solution contained 0.25 gram of MoO_3 (equivalent to 0.28 gram of MoS_2). It will be noted that this constituted 0.14 per cent. of the starting material and corresponds to the usual analysis of MoS_2 in the tailings used, thus indicating that the described treatment substantially quantitatively extracted the molybdenum.

It is to be observed that the present method presents a simple and effective system for recovering molybdenum values from even such low grade materials as concentration tailings. As will have been appreciated, the treatment consists essentially in dissolving the molybdenum of the ore or other starting material, treating the solution with an effective reducing agent to reduce the metal values, i. e., molybdenum and impurities such as iron, to lower valence states and then contacting the solution with an organic extractant which selectively abstracts and concentrates the molybdenum value while leaving such impurities as the iron in the aqueous phase.

The extract, i. e., the organic extractant containing the molybdenum values, may then be treated in any suitable manner to recover the molybdenum content, A simple method of accomplishing this is immediately to subject the organic solvent to distillation, thus obtaining the metal value as a residue. For certain types of solvents such a treatment is effective. As explained in our copending application, Serial No. 154,188 filed July 17, 1937, however, certain advantages are secured by displacing the extracted metal value from the extractant by means of water and then recovering the metal value, in the desired form or compound, from the water solution. With this type of treatment, utilizing certain solvents, some small quantity of the solvent may be dissolved in the water but the bulk of the solvent is segregated and recovered for re-use. It is understood that, in commercial procedure, the final aqueous solution which contains the molybdenum values is subjected to concentration so as to recover the molybdenum salt, either in solid form or in a sufficiently high concentration in the water to permit effective precipitation, or reaction, with other reagents, to produce the desired product. For this purpose, the aqueous phase may be concentrated by simple distillation methods. It will be found that the small amount of solvent which was taken up by the water, during its contact with the organic extractant, will come over with about the first 10 per cent. of the distillate. This fraction may be segre-

gated and the solvent recovered therefrom by suitable methods.

As noted above, the distillation may be carried out to the extent desired, that is to say, to obtain a solid residue or aqueous system containing the molybdenum value in any desired degree of concentration. For example, the water may be completely evaporated, the residue converted to the trioxide and then the molybdenum trioxide may be reacted with calcium oxide to produce calcium molybdate. This product, because of its high purity is peculiarly suitable for use in the production of molybdenum alloys.

It will of course be understood that the described method of solublizing the molybdenum content is not the only one that may be employed. Thus, in lieu of sulphurous acid, other acids such as sulphuric, and hydrochloric may be employed. In commercial operations, the molybdenum content may be solublized in any suitable manner such as by straight percolation, upward percolation, pressure digestion and the like. For this purpose, of course, the starting material such as the ore or the compound may be reduced to that degree of fineness which is most effective for the particular leaching agent and installation.

Similarly, while certain reducing agents such as sulphur dioxide and sodium thiosulphate have been mentioned as being effective for reducing metal values to a lower valence state, these are given as illustrative and as equivalents of any other similarly acting reagents.

In the actual solvent extraction, similarly, different types of apparatus may be employed. Thus, the original acid solutions containing the metal values may be subjected to extraction by the organic extractant in a suitable countercurrent system. The optimum conditions of agitation, temperature, velocity of flow, and the like, for the particular type of treatment contemplated, may readily be determined by those skilled in the art.

In carrying out operations under the invention, as already explained, the organic extractant may readily be segregated from the initial acid solution, as well as from the final water wash and recycled in the system.

It is particularly to be observed that the present method provides an excellent means of regenerating spent catalyst. As is known, molybdenum compounds are specialy recommended as catalysts in certain processes, such as catalytic hydrogenation of sulphur bearing organic materials such as oils, coal, and the like. The molybdenum values in such catalyst may readily be reclaimed under the present process, by dissolving the catalyst in suitable acids and then selectively extracting the molybdenum in the manner described.

Under the generic concept of the invention, it will be understood that a large number of specifically different organic extractants may be employed. Thus, the ester, ethyl acetate, mentioned in the particular test herein described, is given merely as an example of other equivalent organic extractants. Thus, in lieu of ethyl acetate, other esters may be employed, such as; butyl, amyl and sec. hexyl acetates, amyl formate, butyl butyrate, butyl propionate, as well as aromatic esters such as ethyl benzoate and tri-cresyl phosphate. Again, aliphatic alcohols such as butyl and amyl alcohol, methyl n.-butyl carbinol, and the like, may be employed. Other inexpensive solvents such as the aliphatic ethers, of the type of ethyl, isopropyl, butyl, dibutyl, amyl and diamyl ethers, and aromatic ethers such as phenetol may be used. Likewise, the ketones comprise a group of relatively effective and inexpensive solvents contemplated under the present invention, such for example as isobutyl ketone, methyl ketone, mixed ketones like methyl amyl ketone, methyl isobutyl ketone, as well as ketonic condensation products like mesityl oxide. Alkyl cyanides such as proprionitrile may also be used with good results. Any such organic compound which possesses the ability to selectively extract the molybdenum from the aqueous system may be employed.

It will thus be observed that the described system of recovering metal values presents marked advantages. The preliminary step of bringing the desired values into solution may be effected by employing inexpensive reagents and standard equipment. Since the organic extractant substantially quantitatively removes the desired metal value, and since it may be segregated from the molybdenum-containing solution and recycled with minimal losses, the system is eminently economical.

While preferred modifications of the invention have been described, it is to be understood that these are given to illustrate the fundamental principles involved and to indicate the wide permissive operative technique as well as the broad range of extractants and reagents which are available for effectuating these principles.

We claim:

1. A method of recovering molybdenum from acid solutions which comprises, treating the solution with a reducing agent to reduce the molybdenum to a lower valence state, then extracting the solution with an organic solvent capable of selectively extracting the contained molybdenum value from the solution and recovering the molybdenum from the organic solvent.

2. A method of recovering molybdenum values from acid solutions containing such values in a high valence state which comprises, reducing the metal value to a lower valence state, selectively extracting such metal value with a water-immiscible, selective, organic solvent and separating the molybdenum from the solvent.

3. A method of recovering molybdenum values from compounds containing such values which comprises, dissolving the compound in a suitable acid, converting the metal value to a low valence state, selectively extracting the value with a water-immiscible, selective, organic solvent and recovering the molybdenum from the solvent.

4. A method of recovering molybdenum values from compounds containing such values, which comprises, dissolving the compound in a suitable inorganic solvent, having an acid reaction, reducing the metal value to a low valence state, selectively extracting such value with a water-immiscible, selective, organic extractant and recovering the molybdenum from the organic extractant.

5. A method of recovering molybdenum values from compounds containing such values which comprises dissolving the compound in sulphurous acid, and thereby reducing the metal value to a lower valence state, selectively extracting such value with a water-immiscible, selective, organic solvent and separating the molybdenum from the solvent.

6. A method of recovering molybdenum from molybdite which comprises, dissolving the molybdenum oxide in an acid, converting the molybdenum to a lower valence state by adding a

reducing agent thereto, then extracting the molybdenum with a water-immiscible, selective, organic solvent and recovering the molybdenum from the solvent.

7. In the treatment of molybdenite containing molybdite in which the ore is concentrated by flotation to produce a concentrate of molybdenum sulphide and tailings containing molybdenum oxide that improvement which comprises, treating the tailings to dissolve the molybdenum content and reducing the molybdenum to a lower valence state, selectively extracting the molybdenum from the acid solution with a water-immiscible, selective, organic solvent and recovering the molybdenum from the solvent.

8. A method of treating molybdenite ore containing molybdite to recover the molybdenum content thereof which comprises separating the molybdenum sulphide from the molybdenum oxide; dissolving the oxide in a suitable mineral acid reducing the molybdenum to a lower valence state, extracting the molybdenum from the solution with a water-immiscible, selective, organic solvent and recovering the molybdenum from the organic solvent.

9. A method of recovering molybdenum from molybdite which comprises, leaching the ore with a leaching agent having an acid reaction and capable of dissolving the molybdenum oxide, reducing the molybdenum to a low valence state, selectively extracting the molybdenum content of the resulting solution with a water-immiscible, selective, organic solvent and separating the molybdenum from the organic solvent.

10. A method of recovering molybdenum values from acid solutions containing such values, which comprises, converting the value to a low valence state in which it is selectively extractable by a water-immiscible, selective, organic solvent, intimately contacting the organic solvent with the solution for a period of time sufficiently prolonged to insure extraction of the molybdenum value, separating the organic solvent from the solution and recovering such value from the organic solvent.

11. A method of recovering molybdenum from acid solutions which comprises, treating the solution with a reducing agent to convert the molybdenum to a low valence state, contacting the solution with a water-immiscible, selective, organic solvent which selectively extracts the molybdenum content; separating the solvent phase from the acid phase; recovering the molybdenum from the solvent phase and recycling such solvent for reuse.

12. A method of recovering molybdenum from molybdenum-containing materials which comprises dissolving the material in a suitable acid, treating the solution with a reducing agent to convert the molybdenum to a low valence state, selectively extracting the molybdenum content with a water-immiscible, selective, organic solvent; separating the solvent from the solution, contacting the separated solvent with water to extract the molybdenum from the solvent phase and recovering the molybdenum from the water extract.

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