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PROCESS OF PURIFYING MOLYBDENITE CONCENTRATES

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The present invention relates to a process of purifying molybdenite concentrates, or molybdenite-bearing materials, and more particularly to a process of obtaining molybdenite concentrates substantially free from deleterious impurities without appreciable loss of molybdenum.

In an effort to recover molybdenite from its ores and other sources into commercial concentrates, physical concentration processes, wherein physical separation and selection of minerals were sought, because of certain advantages, have been used extensively heretofore. Concentrates obtained by these means commonly contained contaminants due to the natural limitations of the physical concentration processes. The amount and nature of these contaminants had a direct bearing on the commercial value of these concentrates. Copper, even when present in relatively small amounts, has been found to be particularly deleterious and undesirable, as is reflected in the price structure. Thus the sales price at a recent date of molybdenite concentrates containing about 2.5% copper was 33¢ per pound of contained MoS_2, but was 45¢ per pound for concentrates containing less than about 0.3% copper. The physical separation and rejection of the copper bearing mineral, or minerals, by the so-called physical processes was usually only partially complete, and obtained at the expense of reduced recoveries of the molybdenite. Furthermore, there usually were considerable variations in the degree of completeness of these physical separations, which resulted in varying grades of concentrate and varying over-all recovery of the molybdenite. Such variations were, of course, economically disadvantageous.

I have discovered a process which makes it feasible to avoid the limitations of the physical concentration processes when applied to the production of the desired very high grade commerical molybdenite concentrate, in that physical concentration of the ores or other source of molybdenum sulfide need be carried only so far as to produce a "preliminary" concentrate representing the best economic balance of grade and recovery obtainable by the physical concentration. By the process of the present invention, a molybdenite concentrate, e. g., such a preliminary concentrate, is subjected to a special chemical treatment to produce a final commercial molybdenite concentrate containing substantially no copper.

It is an object of the present invention to provide a process for purifying molybdenite concentrates by freeing them from objectionable impurities, in particular from copper sulfide.

It is another object of the present invention to provide a process for purifying molybdenite concentrates by freeing them from objectionable impurities such as copper sulfide with small or inappreciable loss of molybdenum sulfide.

A further object of the present invention is the provision of a process for purifying molybdenite concentrates by freeing them from objectionable impurities, particularly copper sulfide, which process may be carried out commercially and on an industrial scale.

Other objects and advantages of the present invention will be apparent to those skilled in the art from the following detailed description of the invention.

Generally speaking, the process of the present invention is a chemical one whereby the copper, in particular, and other contaminants rendered soluble, are dissolved without an appreciable loss of molybdenum. This chemical process differs fundamentally from the physical concentration processes in that it is more positive; the completeness of the removal of the copper being under direct control and entirely independent of the molybdenite recovery. In practicing the present process, the specific and selective chemical dissolution of the copper and other contaminants rendered soluble is accomplished without dissolving an appreciable amount of molybdenite.

The process of the present invention comprises bringing an agent containing a compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials, either separately or jointly, into contact with the molybdenite concentrates in the presence of strong mineral acid in dilute form, such as sulfuric acid, hydrochloric acid and mixtures thereof. The chemical reaction, or reactions, thus set up are greatly accelerated by increased temperature, making it desirable to carry them on at, or near, the boiling point of the solution. The liquid portion of the mixture containing the copper and other components, thus dissolved, can then be separated from the insoluble residue containing the undissolved molybdenite by any of the methods familiar to those skilled in the art, such as, filtration and washing, or by decantation and washing. In this manner, molybdenum sulfide concentrates initially containing deleterious amounts of impurities, including copper sulfide, are satisfactorily purified and substantially freed from copper with negligible losses of molybdenum sulfide.

For the purpose of giving those skilled in the art a better understanding of the present invention, the following specific examples are given as illustrative of the mode of carrying out the present invention and of the results obtained from practicing the present invention. The invention contemplates the use of manganese dioxide yielding materials which contain small amounts of iron, as well as the materials set

forth in examples herein given to illustrate the invention.

Example No. I

A molybdenite concentrate assaying about 89.3% molybdenum sulfide (MoS_2) and about 0.96% copper (Cu) was pulped with water to approximately 50% solids and mixed with manganese dioxide (MnO_2) and sulfuric acid (H_2SO_4) in approximately the following ratios:

	Pounds per ton MoS_2 concentrates
MnO_2 (89.3% MnO_2)	56
H_2SO_4 (100% H_2SO_4)	160

The mixture was heated to approximately 200° F. and the reaction allowed to proceed for about 4 hours. After separating the solution from the insoluble material by filtration and washing, the latter assayed approximately 92.7% MoS_2 and only about 0.14% copper. The recovery of molybdenum sulfide was about 99.94% of the original molybdenum sulfide and about 85.5% of the copper had been removed.

Example No. II

A second quantity of the same concentrate used in Example No. I was similarly treated with manganese-iron ore and sulfuric acid in approximately the following ratios:

	Pounds per ton MoS_2 concentrate
Manganese—Iron ore (38% Mn, 12% Fe, chiefly oxides)	70
H_2SO_4 (100% H_2SO_4)	270

The mixture was maintained at about 200° F. for about 4 hours after which the soluble materials were separated from the insoluble materials. The latter assayed about 92% MoS_2 and about 0.04% copper. This was was a recovery of about 99.96% of the original molybdenite from which about 95.8% of the original copper had been removed.

Example No. III

A molybdenite concentrate assaying about 83.2% molybdenum sulfide (MoS_2) and about 4.5% copper (Cu) was similarly treated with manganese dioxide (MnO_2) and sulfuric acid (H_2SO_4) in approximately the following ratios:

	Pounds per ton MoS_2 concentrates
MnO_2 (89.3% MnO_2)	300
H_2SO_4 (100% H_2SO_4)	550

The leached material which was separated from the solution after about 4 hours at a temperature of about 200° F., assayed about 88.5% molybdenum sulfide (MoS_2) and about 0.29% copper. The recovery of the original molybdenum sulfide was about 99.81% and about 93.5% of the original copper was removed.

Example No. IV

A second sample of the same concentrate used in Example No. III was similarly treated with manganese-iron ore and sulfuric acid in approximately the following amounts:

	Pounds per ton MoS_2 concentrates
Manganese—iron ore (38% Mn, 12% Fe, chiefly as oxide)	496
H_2SO_4 (100% H_2SO_4)	620

After thoroughly mixing the materials, the mixture was maintained at about 200° F. for about 4 hours. The insoluble material recovered after separating the soluble constituents therefrom assayed about 83.8% molybdenum sulfide (MoS_2) and about 0.26% copper. About 95.1% of the original copper was removed and about 99.9% of the original molybdenum sulfide (MoS_2) recovered.

Example No. V

From a molybdenite concentrate assaying about 75.9% molybdenum sulfide (MoS_2) and about 1% copper (Cu), two samples were subjected to identical treatments except that hydrochloric acid (HCl) was added to one and sulphuric acid (H_2SO_4) to the other. Each sample was pulped with water to about 50% solids and manganese-iron ore of the type described in Examples Nos. II and IV added in a ratio of about 70 pounds per ton of MoS_2 concentrate. To one sample was added about 268 pounds of HCl and to the other about 360 pounds of H_2SO_4 per ton of concentrate. It will be noted that the two amounts of acid are approximately chemically equivalent. After heating the mixtures and recovering the insoluble material in the same manner as previous examples, the insoluble material assayed about 0.025% copper where HCl had been used and about 0.35% copper where H_2SO_4 had been used. In each case less than 0.05% of the MoS_2 was dissolved.

The generally higher cost of hydrochloric acid makes it economically advantageous to use sulfuric acid in mose cases. However, it will be observed that hydrochloric acid was actually metallurgically superior to sulfuric acid in this instance and might under certain conditions be used in preference to sulfuric acid.

In the foreging examples the acid, although computed on the basis of 100% H_2SO_4 or HCl, was added in commercial concentration. It should be understood that the acid may be added in any desired concentration. Similarly the amount of water used to pulp the concentrate is not critical and may vary from the amounts used in the foregoing specific examples. However, it is clear that through control of the amount of water, not only can the bulk of pulp to be handled be held at a minimum, but also a control over the chemical concentrations of the leach solution can be exercised independent of the amount of reagents added.

The amounts of compound or agent, other than acid, required are more or less dependent primarily upon the impurity content of the molybdenite concentrates, and consequently will vary with varying grades of concentrates. It will be understood that variations in the amount and nature of contaminants that are rendered soluble in addition to the copper contained in the concentrates will cause variations in the ultimate amount of reagents required. For this reason it is not practicable to give a general definition of the amounts of reagents to be added in terms of the copper content alone. As those skilled in the art will readily understand, the amount of reagents required for treating any particular concentrate may be readily determined in the light of the foregoing description by preliminary pilot tests and/or a chemical analysis thereof. I have found it advantageous for the purpose of control of the leach to observe the chemical nature of the leach solution during the progress of the leach and have noted when iron is present in the solution that the degree of oxidation of the iron in solution as indicated by the amount of ferric iron present in the solution after the reactions are substantially complete is oftentimes an excellent guide to the completeness of the copper

removal. I have observed, for example, that a ferric iron content of from four to ten pounds per ton of solution in the final leach solution, or an amount of ferric iron equal to approximately ten to twenty per cent of the total iron in solution, commonly accompanies satisfactory dissolution of the copper. I have, therefore, found it convenient to control the addition of the agent containing the compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials by the concentration of ferric iron, or degree of oxidation of the iron in the final leach solution. The most favorable ferric iron concentration may vary according to the nature of the contaminating minerals in the particular molybdenite concentrates being treated, as one skilled in the art will readily understand. It will also be understood that the iron in solution is derived from dissolution of iron bearing minerals in the concentrates as well as from the compound or agent added when that compound contains iron rendered soluble in the course of the reactions.

The acid requirements vary according to the reagent or reagents used in conjunction with it. I have found that the final acid concentration of the leaching solution: i. e., the excess acid remaining after the reaction or reactions are substantially complete, is a satisfactory guide to the acid addition. For example, in leaches involving manganese dioxide and sulfuric acid I have found a satisfactory final acid concentration to be about 4 to 7% by weight of the liquid portion.

When hydrochloric acid is used, the conditions are similar to those described for sulfuric acid, i. e. final acid concentrations of from about 4 to about 7% by weight of the liquid portion have been found satisfactory.

If nitric acid is used, the acid concentration should be kept below a critical maximum of about 1.25%. The loss of molybdenite by dissolution is greater where nitric acid is employed, but may be kept under about 3% provided the critical concentration is not exceeded. Generally speaking, sulphuric acid and hydrochloric acid are used in preference to nitric acid.

It will be seen from the foregoing illustrative examples that the strong mineral acid (such as sulphuric acid and hydrochloric acid), regardless of the concentration in which it is added, is in dilute form in the mixture during the course of the reactions due to the presence of the water used to pulp the mass.

It is desired to make clear that there is no limitation implied, or intended, in the foregoing disclosure as to the ultimate source of the specific reagents involved. The term "compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials not containing more than a small amount of iron" is used in the specification and the claims to denote these reagents singly and in combination.

It will be understood that the above illustrative examples are offered merely as an aid in the exposition of my invention and that no limitations are imposed on said invention by reason thereof. It will be recognized by those skilled in the art that it might be desirable to deviate from the above specifications according to the individual conditions which might prevail in the application of the invention, but that such deviation, or deviations, would not depart from the spirit of the invention.

From the foregoing it will be observed that the process of the present invention accomplishes the removal of deleterious impurities, particularly copper sulfide, in a very satisfactory manner with inappreciable loss of the valuable molybdenum sulfide. The process is relatively inexpensive and lends itself to commercial application on an industrial scale.

Although the present invention has been described in connection with certain specific and illustrative embodiments thereof, it will be understood by those skilled in the art that variations and modifications thereof may be made without departing from the spirit and scope of the present invention as defined by the appended claims.

I claim:

1. The process of treating molybdenite concentrates to remove copper compounds, including copper sulphide without appreciable loss of molybdenite comprising pulping molybdenite concentrates with water, mixing said pulped concentrate with sulphuric acid and with a compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials, said manganese dioxide yielding materials not containing more than a small amount of iron, heating the mixture for about 4 hours at a temperature of about 200° F. and separating the liquid portion containing the soluble constituents from the insoluble residue whereby a molybdenite concentrate substantially free from copper compounds including copper sulphide is obtained without an appreciable loss of molybdenite by dissolution.

2. The process of treating molybdenite concentrates to remove copper compounds, including copper sulphide without appreciable loss of molybdenite comprising pulping molybdenite concentrates with water, mixing said pulped concentrate with hydrochloric acid and with a compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials, said manganese dioxide yielding materials not containing more than a small amount of iron, heating the mixture for about 4 hours at a temperature of about 200° F. and separating the liquid portion containing the soluble constituents from the insoluble residue whereby a molybdenite concentrate substantially free from copper compounds including copper sulphide is obtained without an appreciable loss of molybdenite by dissolution.

3. The process of treating molybdenite concentrates to remove copper compounds, including copper sulphide without appreciable loss of molybdenite comprising pulping molybdenite concentrate with water, mixing said pulped concentrate with strong mineral acid and with a compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials, said manganese dioxide yielding materials not containing more than a small amount of iron, heating the mixture for about 4 hours at a temperature of about 200° F., and separating the liquid portion containing the soluble constituents from the insoluble residue whereby a molybdenite concentrate substantially free from copper compounds including copper sulphide is obtained without an appreciable loss of molybdenite by dissolution.

4. The process of treating molybdenite bearing materials including molybdenite concentrates to remove undesirable impurities including copper sulphide comprising treating said materials with dilute sulphuric acid in the presence of manganese dioxide containing not more than a small

amount of iron, heating the mass at an elevated temperature until the reactions are substantially complete and separating the liquid portion containing the soluble constituents from the insoluble residue whereby a molybdenite concentrate relatively free from undesirable impurities including copper sulphide is obtained without an appreciable loss of molybdenite.

5. The process of treating molybdenum bearing materials including molybdenite concentrates to remove undesirable impurities including copper sulphide comprising treating said materials with dilute hydrochloric acid in the presence of manganese dioxide containing not more than a small amount of iron, heating the mass at an elevated temperature until the reactions are substantially complete and separating the liquid portion containing the soluble constituents from the insoluble residue whereby a molybdenite concentrate relatively free from undesirable impurities including copper sulphide is obtained without an appreciable loss of molybdenite.

6. The process of treating molybdenite bearing materials including molybdenite concentrates to remove undesirable impurities including copper sulphide comprising treating said materials with a strong mineral acid in dilute form in the presence of a compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials, said manganese dioxide yielding materials not containing more than a small amount of iron, heating the mass at an elevated temperature until the reactions are substantially complete and separating the liquid portion containing the soluble constituents from the insoluble residue whereby a molybdenite concentrate relatively free from undesirable impurities including copper sulphide is obtained without an appreciable loss of molybdenite.

7. The process of removing copper sulphide from molybdenite bearing materials including molybdenite concentrate without an appreciable loss of molybdenite comprising treating the materials with a hot dilute solution of a strong mineral acid and a compound selected from the group consisting of manganese dioxide and material containing predominant amounts of manganese dioxide and containing not more than a small amount of iron and thereafter separating the liquid reaction products from the concentrate to free it substantially from copper compounds.

8. The process of removing copper sulphide from molybdenite bearing material without an appreciable loss of molybdenite comprising transforming the copper sulphide to a compound soluble in water by treating the material with strong mineral acid in dilute form and with a compound selected from the group consisting of manganese dioxide and manganese dioxide yielding materials, said manganese dioxide yielding materials not containing more than a small amount of iron, and washing out the soluble copper compound.

9. The process of removing copper sulphide from molybdenite bearing material without an appreciable loss of molybdenite comprising transforming the copper sulphide to a compound soluble in water by treating the material with manganese dioxide containing not more than a small amount of iron and strong mineral acid in dilute form, and separating the liquid reaction products from the insoluble residue.

10. The process as set forth in claim 9 in which the strong mineral acid is sulphuric acid.

11. The process as set forth in claim 9 in which the strong mineral acid is hydrochloric acid.

12. The process of removing copper sulphide from molybdenite bearing material without an appreciable loss of molybdenite comprising transforming the copper sulphide to a compound soluble in water by treating the material with manganese ore containing not more than a small amount of iron and strong mineral acid in dilute form, and separating the liquid reaction products from the insoluble residue.

13. The process as set forth in claim 12 in which the strong mineral acid is sulphuric acid.

14. The process as set forth in claim 12 in which the strong mineral acid is hydrochloric acid.

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