This invention relates to the treatment of the ores of molybdenum.

Molybdenum occurs in nature most commonly in the form of ores containing the mineral molybdenite, MoS₂. Such ores may be concentrated by flotation methods which are effective and economical and yield high grade products. Under proper operation the concentrate will contain 90% to 95% of MoS₂.

The largest use for molybdenum at present is in the preparation of alloy steel which has many excellent properties. The molybdenum usually is added either as ferro-molybdenum or as calcium molybdate. The molybdenite concentrate is entirely unsuited for addition to steel, since its sulphur content would have an extremely deleterious effect.

The sulphide ore of molybdenum is moreover quite generally associated with sulphides of iron and copper. In treating such ores by flotation the iron and copper sulphides will enter the molybdenite concentrate unless special conditions are adhered to and a differential flotation operation is conducted. A fairly good separation of the molybdenum and copper can be made, but only at the expense of losing an important amount of the molybdenum. Copper is considered to be a very detrimental impurity in any molybdenum product used for steel alloying and commercial custom places a maximum limit of 0.3% copper content in molybdenite concentrates.

This invention provides a method for cheaply, economically and conveniently treating molybdenite concentrates which contain copper, producing molybdates suitably free of iron and sulphur, and also recovering the copper in a marketable form, which constitutes a valuable by-product.

By the process of this invention molybdenite concentrates can be successfully treated no matter how much copper is present. We have successfully treated concentrates which contained 60% chalcopyrite equivalent to about 20% copper. Such ability to treat copper bearing materials is one of the salient features of the invention and one of its chief sources of economy, since it not only permits a greater recovery of molybdenite in the flotation operation, but the copper is recovered as a valuable by-product.

In the manufacture of molybdenum steel alloy there are various impurities other than sulphur and copper which are very deleterious. Phosphorus and arsenic especially are very harmful.

By the process of this invention these impurities and certain others as well are completely eliminated from the final product or at the worst reduced to scarcely detectable traces.

Numerous processes for converting molybdenite concentrates to calcium molybdate or ferromolybdenum are described in the technical literature. A process which is commonly employed comprises carefully roasting the ore or concentrate at a low temperature and with liberal access of air, whereby the molybdenum sulphide is converted to molybdenum oxide, according to the following equation:

\[2\text{MoS}_2 + 7\text{O}_2 \rightarrow 2\text{MoO}_3 + 4\text{SO}_2\]

Care must be taken to carry the roasting to the ultimate point so as to be certain no unroasted MoS₂ remains. Care must also be exercised not to raise the temperature too high, since the molybdenum trioxide is appreciably volatile and loss would result. Also fusion or sintering will occur at too high a temperature which prevents complete elimination of the sulphur. When the roasting operation has been completed lime is added to the charge while still in the furnace.

The lime combines with the molybdenum trioxide to form calcium molybdate, according to the following equation:

\[\text{CaO} + \text{MoO}_3 \rightarrow \text{CaMoO}_4\]

This is the finished product of this process. It will be observed that the only possibility for eliminating impurities by this process is by volatilization. Copper, iron, silica and most of the arsenic and phosphorus are non-volatile under the conditions of the roasting and entering the finished product.

The chemical principles upon which the present invention functions will now be described. The practical application of these principles will be explained by description of the various steps in the process. It is understood that the invention is not limited to the exact procedure described, but the scope of the invention is defined in the claims.

The principal steps of the process are shown in the flow sheet of the accompanying drawing.

The first step in the process consists in thoroughly roasting the molybdenite concentrate which, as stated above, need not be free of copper. This may be done in any suitable roasting furnace, such as a muffle, or in a hand operated reverberatory or in a mechanical furnace such as the MacDougall or Herrerosch. The chemical reaction, ordinarily stated as representing the roasting of molybdenite has already been given. We have found that this reaction does not com-
pletely describe the conditions, but that, instead, the reaction proceeds in two distinct stages, represented by the equations:

\[
\begin{align*}
5 \text{MoS}_2 + 3 \text{O}_2 & \rightarrow \text{MoO}_3 + 2 \text{SO}_2 \\
2 \text{MoO}_3 + 4 \text{O}_2 & \rightarrow 2 \text{MoO}_5 
\end{align*}
\]

The second reaction is more difficult to effect, particularly if any sintering occurs. We have observed a wide difference in behavior of molybdenite concentrates from different sources, particularly with respect to the tendency to form molybdenum dioxide. Since the presence of molybdenum dioxide in the roasted product introduces difficulties in the subsequent steps of the process, the roasting operation is controlled so as to produce as small an amount as possible. We have found that best results are obtained by a prolonged roast at low temperature and with free access of air. We prefer to maintain the temperature at approximately 500° C. during the first two hours and increase to 600° C. at the end of the third hour. It is not necessary to roast out all of the sulphur in order to prevent the introduction of sulphur into the finished product, but any molybdenum sulphide which is not roasted at least to the dioxide will not be recovered in the subsequent operations. Sulphides of iron and copper are simultaneously roasted, being converted largely to the corresponding molybdates, but partly to the sulphates, as shown by the equations typifying the behavior of pyrite—

\[
\begin{align*}
4 \text{FeS}_2 + 11 \text{O}_2 & = 2 \text{Fe}_2 \text{O}_3 + 8 \text{SO}_2 \\
6 \text{Fe}_2 \text{O}_3 + 3 \text{MnO}_2 & = 4 \text{Fe}_3 \text{O}_4 + 3 \text{MnO}_2 \\
5 \text{Fe}_2 \text{O}_3 + 3 \text{SO}_2 & = 2 \text{Fe}_2 \text{SO}_4 
\end{align*}
\]

Copper exhibits a marked tendency to form the sulphate, whereas iron tends largely to form the molybdate. So far as possible it is desirable to decompose the copper and iron sulphates during the roasting operation in the interest of reducing the consumption of reagents in the subsequent operations. Sulphates which are not so decomposed do not exert any other unfavorable effect than consumption of reagent and are not especially harmful. We have found little difficulty in reducing the content of sulphates to 1.2% SO₃ calculated on the weight of roasted material. During the roasting a volatilization of minor impurities occurs, but this effect is unimportant.

We have found that molybdenite concentrates from some sources are peculiarly difficult to roast. Marked sintering occurs and the content of molybdenum dioxide is unusually high. This may be corrected in certain cases by roasting until almost all of the sulphur is eliminated, removing from the furnace, cooling, grinding and returning to the furnace for a short roast, for example one-half hour at 500° C. As an alternative and preferable method we mix with the concentrates, before roasting, some material which will assist in the roast. Such an inert material as finely ground silica will have some beneficial effect. Sulphides of iron and copper may be employed to advantage and these may usually be obtained merely by changing the conditions of the flotation operation by which the molybdenum is originally recovered. When copper or iron or both are used to aid the roasting it is advantageous to employ an amount chemically equivalent to the molybdenum content of the concentrate to form the molybdates of said metals. The most advantageous method, and the method we preferably employ, is to return part of the leach residue which consists largely of silica and iron and copper oxides. This has the added advantage of subjecting the material to more than one treatment.

The second step in our process consists of leaching the roasted product with a fairly strong solution in which the active ingredient is a caustic alkali, hereinafter exemplified by caustic soda. Since the process is cyclic in nature, this solution is derived from a later step of a previous cycle of operations and contains other compounds than sodium hydroxide in solution.

For the purpose of explanation only the sodium hydroxide content will be considered at this point, since it is the only material taking part in the reactions. The molybdenum trioxide of the roasted material is rapidly dissolved by the sodium hydroxide, forming sodium molybdate, according to the equation:

\[
2\text{NaOH} + \text{MoO}_3 \rightarrow \text{Na}_2\text{MoO}_4 + \text{H}_2\text{O}
\]

Ferric oxide and copper oxide are unaffected and remain insoluble. Ferric sulphate and copper sulphate react with the sodium hydroxide, forming the respective insoluble hydroxides and soluble sodium sulphate, according to the equations:

\[
\begin{align*}
\text{Fe}_2(\text{SO}_4)_3 + 6\text{NaOH} & = 2\text{Fe(OH)}_3 + 3\text{Na}_2\text{SO}_4 \\
\text{CuSO}_4 + 2\text{NaOH} & = \text{Cu(OH)}_2 + 2\text{Na}_2\text{SO}_4
\end{align*}
\]

The resulting sodium molybdate solution is accordingly completely free of iron and copper, but will contain all the sulphur trioxide in the roasted ore in the form of sodium sulphate. Iron and copper molybdates, formed in the roasting, are completely decomposed by the caustic solutions according to the equations:

\[
\begin{align*}
\text{Fe}_2(\text{MoO}_4)_3 + 6\text{NaOH} & = 2\text{Fe(OH)}_3 + 3\text{Na}_2\text{MoO}_4 \\
\text{CuMoO}_4 + 2\text{NaOH} & = \text{Cu(OH)}_2 + \text{Na}_2\text{MoO}_4 + \text{H}_2\text{O}
\end{align*}
\]

We have found that if there is a deficiency of caustic soda during the leaching operation the solutions will become acid due to solution of molybdate oxide and formation of molybic acid. We have further found that when this occurs insoluble molybdates of copper and iron are formed. We believe the reactions involved are as follows:

\[
\begin{align*}
\text{Fe(OH)}_2 + \text{Na}_2\text{MoO}_4 & = \text{Fe(OH)}_3 + \text{Na}_2\text{MoO}_4 \\
\text{Cu(OH)}_2 + \text{Na}_2\text{MoO}_4 & = \text{CuMoO}_4 + 2\text{NaOH}
\end{align*}
\]

For this reason we prefer to operate our process under such controlled conditions that there is always an excess of caustic soda present. We preferably maintain this excess alkalinity at a minimum of 1.0 gram NaOH per liter, as determined by titrating with standardized hydrochloric acid, using phenol phthalein as the indicator. We have found that at this alkalinity no insoluble iron or copper molybdates are formed. We have also found that in case the proportions of the leach have been improperly adjusted and the solution becomes acid, with simultaneous precipitation of copper and iron molybdates, the situation may be corrected by increasing the alkalinity to the preferred minimum value, for example, by adding caustic solution. When this is done the insoluble molybdates are decomposed in accordance with the reactions previously given.

Alkalinity corresponding to about 0.5 gram and even less of NaOH per liter has been found to be sufficient to prevent precipitation of the insoluble molybdates or to dissolve them if they have been formed.

As previously pointed out, the caustic soda solution has little or no power to dissolve any molybdenum dioxide which may be present. One of the novel features of our invention is the provision of means to recover the molybdenum di-
oxide. When the content of molybdenum dioxide in the leached residue is low, we preferably introduce an additional step into the leaching operation. This step consists of the addition of a reagent which is capable of acting as an oxidizing agent in alkaline solution. We preferably employ a relatively strong solution of sodium hypochlorite which oxidizes the molybdenum dioxide to the trioxide, in which form it is readily soluble in the caustic solution. The sodium chloride which results from the sodium hypochlorite does not interfere with the determination of the amount of molybdenum dioxide present in the leaching residue. Other oxidizing agents may be employed, such as, for example, gaseous chlorine. In extreme cases, where the content of molybdenum dioxide is unusually high, and the expense of providing oxidizing reagents during the leach would be burdensome, we preferably conduct the leaching operation without any such added oxidizing agent, and subject the residue from the leaching to a second roasting operation and a separate leach, in which the proportion of solution to solids is reduced to correspond with the former content of the residue in such material. We have also found that the various methods for overcoming the difficulty which is introduced by the tendency to form molybdenum dioxide during the roasting may be advantageously combined in certain cases. For example, part of the residue may be mixed with the molybdenite concentrates being roasted, and so reduce the production of molybdenum dioxide that the method of treating with an oxidizing agent will be entirely effective and economical. Since it is essential in one of the subsequent steps, the process to maintain the volume at nearly the boiling point, we preferably carry out all steps of the process in hot solutions. This avoids the expense of cooling and heating the solution and also assists the other steps of the process, since the reactions in heated solutions are more rapid and complete and filtrations are also more rapid. The use of hot solutions is not, however, essential for obtaining satisfactory leaching. We have carried out the leaching operation at normal atmospheric temperatures and obtained the same results as at higher temperatures, except that a longer time was required. Although we preferably operate the process at an elevated temperature in all steps, we do not limit the scope of our invention to any particular temperature at which the leaching operation is to be conducted. The leaching operation is conducted in tanks of suitable size and provided with means for agitation, such as a propeller. The tanks may be made of wood, which conserves the heat, or of iron, since the caustic solutions do not exert any corrosive action on iron.

As will be discussed in connection with one of the steps of the process, the strength of the cycling solution may be varied within rather wide limits. We have found that generally satisfactory results are obtained by having the return caustic solution which goes to the leaching operation have a content of 25 grams from each liter of the fresh material, as determined by titration with standardized hydrochloric acid, using phenol-pthalein indicator. A solution of this strength will dissolve 28 grams of MoO₃ per liter while being reduced to the minimum of 1.0 gram NaOH per liter, provided the sulphate content of the fresh material does not exceed about 1.2% SO₃. This is equivalent to 0.243 pound of MoO₃ per gallon of solution, or 4.32 gallons per pound of MoO₃. Concentrates with about 5% copper will yield a roasted product with about 85% MoO₃. With such material the dissolving capacity of the leaching solution is about 0.286 pound of calcine per gallon. Stronger solutions may be used, but cause rapid deterioration of filter cloths and the strength of solution here specified is sufficiently concentrated to give economical operations without handling undue volumes.

We have found that the reaction is quite rapid, and with the heated solutions which we preferably employ, a leaching time of about an hour is satisfactory. The extraction of the molybdenum is excellent, recoveries realized being regularly in excess of 99% on roasted material which is substantially free of MoO₂ when the leaching is performed with the aid of an oxidizing agent. At the completion of the leaching operation the mixture is filtered. We preferably employ a filter press for this operation since the hot solutions make vacuum filtration impractical. The residue is granular and filters readily. The cake in the filter press is then washed with several volumes of fresh water. When the original molybdenite concentrate contains over 3% copper and only a small amount of insoluble matter, such as silica, we have found the residue will analyze about 20% copper. This material is admirably adapted for sale to a copper smelter as it is free of sulphur and has a high iron content which is of value as flux. Any gold or silver in the original concentrate will also be saved in this residue, but usually there is only a small amount. The filtered solution from the leach will contain not only the sodium molybdate, but the small intentional excess of free caustic soda and the sodium sulphate derived from the iron and copper sulphates produced in the roasting operation.

Most molybdenite concentrates contain small amounts of phosphorus, arsenic, and vanadium. There is probably a certain minor volatilization of these impurities during roasting, particularly of the arsenic. The filtered leaching solutions usually contains a small amount of phosphoric or arsenate radicals, or some of both. The leaching solution being at all times alkaline absorbs carbon dioxide from the atmosphere with formation of sodium carbonate which must also be considered as an impurity.

The third step of the process consists in the removal of all these impurities from the filtered leaching solution except the free caustic soda and the sodium sulphate by precipitating them as the respective salts of the alkaline earth metals calcium, strontium, or barium, exemplified hereinafter by the salts of calcium, according to the following equations:

\[
\begin{align*}
2\text{Na}_2\text{PO}_4 + 3\text{Ca}_3\text{MoO}_4 & = 2\text{Ca}_3(\text{PO}_4)_2 + 3\text{Na}_2\text{MoO}_4 \\
2\text{Na}_2\text{AsO}_4 + 3\text{Ca}_3\text{MoO}_4 & = 2\text{Ca}_3(\text{AsO}_4)_2 + 3\text{Na}_2\text{MoO}_4 \\
\text{Na}_2\text{CO}_3 + \text{Ca}_3\text{MoO}_4 & = \text{CaCO}_3 + 3\text{Na}_2\text{MoO}_4 \\
\text{Na}_2\text{VO}_4 + 2\text{Ca}_3\text{MoO}_4 + \text{H}_2\text{O} & = 2\text{Ca}_3\text{V}_2\text{O}_5 + 2\text{Na}_2\text{MoO}_4 + 2\text{NaOH}
\end{align*}
\]

The reactions are rather slow and we preferably employ a considerable excess of calcium molybdate, assisting the reaction by agitation and heating. We find it convenient to carry out the purification reaction in a tank especially reserved for this purpose. This tank should be of such size as to contain the total volume of filtrate from one cycle of the leaching operation. The tank is preferably provided with a steam jacket which is particularly useful in case the plant has been shut down for sufficient time to permit the solutions to cool off. Since it is this oper-
ation which removes the carbonates and since the carbonates are derived almost entirely by absorption of carbon dioxide from the atmosphere, this purification operation should be carried out immediately before the final precipitation of the molybdenum and the solution, after purification, should be immediately precipitated to avoid new contamination of the final calcium molybdate by calcium carbonate. We preferably employ calcium molybdate equivalent to roughly ten times the impurities to be precipitated and agitate for one hour at a temperature near the boiling point. At the completion of the operation the mixture is given ample time to settle and the clear liquid decanted off and passed through a filter press to clarify it. The thickened residue is allowed to remain in the tank and is used for successive purification operations until its content of calcium molybdate is practically consumed. It is then removed, filtered and washed and discarded, or further treated for the recovery of its molybdenum and vanadium contents. The calcium salts are almost crystalline and granular and settle rapidly in a small bulk. A wide variety of reagents may be used in the purification of the molybdate solution. For instance, other compounds of calcium, barium, and strontium, such as the chlorides, hydroxides, sulfates, etc., may be used. Also compounds of other metals such as magnesium, zinc, manganese, iron, aluminum and copper may be used, but these compounds generally must be used in large excess and give precipitates which are difficult to filter.

The filtered solution will contain about 5% Na2MoO4, a little excess caustic soda, and a small amount of sodium sulphate. The next, i.e. fourth, step in the process is the precipitation of the molybdenum as calcium, barium, or strontium molybdate, preferably by boiling with milk of lime, according to the equation:

\[
\text{Na}_2\text{MoO}_4 + \text{Ca(OH)}_2 \rightarrow \text{CaMoO}_4 + 2\text{NaOH}
\]

This reaction is surprisingly rapid, considering the very low solubility of the solid phases. For efficient operation, i.e. substantial completion of the reaction in a reasonable time (1 to 2 hours), the temperature of the reaction mixture must be at least about 95° C. At 85° C, the reaction proceeds very slowly. At 90° C, the reaction is substantial, but still quite slow.

When employing Ca(OH)2 as the precipitant the reaction reaches an equilibrium depending upon the concentration of caustic alkali. The proportion of the total quantity of molybdenum in solution, precipitated, will vary from about 75% at a caustic soda concentration of about 60 grams per liter to an apparent maximum of about 90%. The molybdenum not precipitated is not lost due to the caustic use of the solution. When employing the caustic soda concentration of 20 grams per liter above referred to, in the leaching step, the precipitation will proceed to the extent of about 85% of the molybdenum content of the solution.

When using strontium and barium hydroxides the reaction goes to practical completion throughout the normal range of caustic alkali concentration and heating of the reaction mixture is not necessary as it is in the case of calcium hydroxide.

As previously stated the filtered solution from the leach contains a small amount of sodium sulphate. At the causticity at which the precipitation of calcium molybdate is carried out, no calcium sulphate is precipitated, the reaction

\[
\text{CaSO}_4 + 2\text{NaOH} = \text{Ca(OH)}_2 + \text{Na}_2\text{SO}_4
\]

being predominately in favor of precipitation of Ca(OH)2. We have precipitated calcium molybdate from solutions which contained 5% Na2SO4 and found that the product contained only the smallest trace of sulphate, probably due to poor washing. The sulphate produced in roasting tends to build up in the solution, but this is counteracted by mechanical loss of solution in washes and by periodic removal of solution. The washes and removed solution are stripped of molybdenum before discarding in a subsequent step of the process.

In the preferred form in which we practice our invention the precipitation with lime is carried out in two stages. In the first stage the filtered leaching solution contained in a steam jacketed iron tank provided with an agitator, is treated with a mixture of CaMoO4 and Ca(OH)2 resulting from the second stage of the preceding cycle, and which was left in the tank. This mixture contains only enough Ca(OH)2 to precipitate roughly half of the 85% of the molybdate which will be precipitated in the two stages. The solution is heated and agitated to contact with this material for about 2 hours and then allowed to settle. The clear liquor is decanted off to a second tank exactly similar to the first one and without filtering, any small amount of calcium molybdate remaining suspended being of no importance. The thickened calcium molybdate is then filtered in a filter press and the filtrate added to the main bulk of the decanted solution in the other tank. In this first stage of the precipitation there is a considerable excess of Na2MoO4 which tends to consume all the Ca(OH)2 and gives a precipitate which is essentially CaMoO4. This is the finished product of the process, and after washing is dried in any suitable manner. We have consistently produced CaMoO4 containing 43-45% molybdenum, compared to a theoretical content of 48%.

In the second stage of the precipitation the solution is treated with an amount of Ca(OH)2 equivalent to 85% of the total molybdate in the solution prior to the first stage. This gives a considerable excess of calcium hydroxide which tends to carry the reaction to the maximum possible point as rapidly as possible. We preferably agitate the solution and heat it for another two hours, then allow to settle. The clear solution is decanted off and passed through a filter press to remove any suspended CaMoO4, which would otherwise be lost and the filtrate is returned to the leaching cycle. The thickened mixture of CaMoO4 and Ca(OH)2 is left in the tank and the next batch of solution from the leach is run in on top of it to become the first stage in the precipitation. The resulting filtered and regenerated solution will analyze, under the conditions of leaching, etc., previously described as the preferred conditions, approximately as follows:

- Free NaOH: 20.0 grams/liter
- Na2MoO4: 8.0 grams/liter
- Ca(OH)2: 0.93 grams/liter

plus an additional and variable content of Na2SO4.

In any cyclic process such as this the volume of the solution must be kept constant. It is necessary to add fresh water in order to wash the residue from the leaching and also the calcium molybdate. This tends to increase the volume...
of the solution in the cycle. The tendency to increase is partly compensated by the water which is contained in the leach residue and in the final calcium molybdate as they leave the process and also by the water lost by evaporation from the hot solutions. If these two tendencies were made to balance each other, for example, by limiting the volume of wash water, the volume could be kept constant. However, if this were done, the sodium sulphate content would increase after each cycle and ultimately introduce difficulties. We preferably control the volume of the cycle solution in the same time as the concentration of sodium sulphate by the following two expedients: When washing the two filter cakes from the process only the first and strongest washes are returned to the main volume of solution of the process. The final and weaker wash waters are treated in a special operation for recovery of the molybdenum content. Also after each cycle of operations we remove a small portion of the filtrate from the final precipitation of the calcium molybdate. This serves to control the building up of the sodium sulphate. We have found that 5% of the volume of the solution is a practical proportion to remove.

The molybdenum is recovered from the combined weak washes and the portion of the main solution discarded, by precipitation with finely ground gypsum according to the following equation:

\[
\text{Na}_2\text{MoO}_4 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{CaMoO}_4 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}
\]

The reaction proceeds as indicated only when there is present an excess of caustic soda, which is, of course, present in large amount in the portion of the main solution removed. This excess caustic soda reacts with the gypsum to produce calcium hydroxide, according to the equation:

\[
2\text{NaOH} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca(OH)}_2 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}
\]

The reaction serves to completely precipitate the molybdenum and leave only sodium sulphate in solution.

We preferably perform this operation in a small tank provided with an agitator. We have found it necessary to heat the mixture. The reaction is fairly slow and we preferably continue the agitation for about two hours, employing a slight excess only of gypsum. The mixture is then transferred to a filter and washed. The filtrate and washings are discarded since they contain only the sodium sulphate which it was desired to eliminate. The mixed precipitate of \(\text{CaMoO}_4\) and \(\text{Ca(OH)}_2\) is employed in the operation of precipitating the calcium molybdate in the main cycle of operations. Any un consumed gypsum which it contains is converted to calcium molybdate and sodium sulphate in this operation. We are aware that various other reagents might be employed for this operation, such as the strong mineral acid salts of the alkaline earth and heavy metals, but we preferably employ gypsum because it is readily obtainable in Irish purity, is very cheap and serves the double purpose of binding much of the other elementary substances and at the same time neutralizing the caustic soda and permits the reaction to proceed to completion.

As a result of the removal of a portion of the main cycling solution, there is a loss of caustic soda which it is necessary to make up by addition of caustic soda to the process. It is necessary to add at each cycle an amount of caustic soda equivalent to 5% of the sodium content in the whole volume of cycling liquid. In practice we have found the consumption of caustic soda to be equal to 0.025 NaOH per pound of \(\text{CaMoO}_4\) produced. This is only 50 pounds of NaOH per ton of \(\text{CaMoO}_4\) and is not a very important item of cost. The consumption of gypsum and hydrated lime is about 10% in excess of the theoretically calculated requirements based on the \(\text{CaMoO}_4\) produced and without correcting for impurities in the commercial qualities of the gypsum and hydrated lime. It will therefore be obvious that our process is extremely economical as regards consumption of reagents and the cost thereof.

The invention has been described with particular reference to the use of sodium hydroxide as the dissolving agent for the molybdenum oxide and the use of calcium molybdate as the agent for purifying the resulting solution and the use of lime or calcium hydroxide as the precipitating agent for the molybdenum in solution. It is to be understood, however, that the other caustic alkalis, particularly caustic potash, may be used in place of caustic soda in the leaching step; that oxides, hydroxides, molybdates or other suitable salts of metals of the group consisting of Ca, Ba, Sr, Mg, Zn, Mn, Fe, Al, Cu, etc., may be used in the purification, and that the hydroxides of barium or strontium may be used in place of calcium hydroxide in the precipitating step.

We claim:

1. Process which comprises roasting a molybdenum sulphide containing material to the conversion of at least a part of the molybdenum sulphide content thereof to molybdenum trioxide, leaching the roasted material with a solution containing caustic alkali, separating the resulting solution containing alkali metal molybdate from undissolved residue, purifying the solution by agitating it in the presence of alkaline earth metal molybdate, separating the so-purified solution from solid matter, reacting the purified solution with an hydroxide of an alkaline earth metal and recovering the so-precipitated alkaline earth metal molybdate from the resulting caustic alkali-containing mother liquor.

2. Process which comprises leaching a material containing iron molybdate associated with impurities with a solution containing caustic alkali, separating the resulting solution containing alkali metal molybdate from undissolved residue, purifying the solution by agitating it in the presence of an alkaline earth metal molybdate, separating the so-purified solution from solid matter, reacting the purified solution with an hydroxide of an alkaline earth metal and recovering the so-precipitated alkaline earth metal molybdate from the resulting caustic alkali-containing mother liquor.

3. Process which comprises agitating a solution containing alkali metal molybdate, caustic alkali and impurities in the presence of an alkaline earth metal molybdate, separating the so-purified solution from solid matter, reacting the purified solution with an hydroxide of an alkaline earth metal and recovering the so-precipitated alkaline earth metal molybdate from the resulting caustic alkali-containing mother liquor.

4. Process of purifying a solution containing an alkali metal molybdate and one or more impurities of the group consisting of alkali metal phosphates, arsenates and carbonates, which comprises contacting said solution with a finely divided compound of the group consisting of the...
alkaline earth metal molybdates and soluble alkaline earth metal compound capable of reacting with alkali metal molybdates to the formation of alkaline earth metal molybdates, the latter in quantity insufficient to convert the bulk of the alkali metal molybdate content of the solution to alkaline earth metal molybdate, separating the precipitated impurities from the solution and reacting the purified solution with an hydroxide of an alkaline earth metal in quantity sufficient to precipitate the bulk of the molybdate content thereof as alkaline earth metal molybdate.

5. Process which comprises leaching a material containing molybdenum oxide with a solution containing alkali metal hydroxide, separating the resulting solution containing alkali metal molybdate from undissolved residue, purifying the alkali metal molybdate solution by agitating it with an alkaline earth metal molybdate, separating the so-purified solution from solid matter, reacting the purified solution with an alkaline earth metal hydroxide thereby precipitating the molybdenum content of the solution as alkaline earth metal molybdate and regenerating the alkaline metal content of the solution as alkaline metal hydroxide, separating the alkaline earth metal molybdate from the solution containing regenerated alkali metal hydroxide and using said solution for leaching a fresh quantity of material containing molybdenum oxide.

6. In the process of recovering a molybdate from sulphide ores containing molybdenum, the steps which consist in roasting a concentrate thereof in the presence of sufficient added metal compound of the group consisting of the sulphides and oxids of iron and copper to convert the molybdenum content to a molybdate of said metal, and leaching the roasted concentrate with a caustic alkali solution.

7. Process for the precipitation of a molybdate from a solution containing an alkali metal molybdate and free caustic alkali which comprises agitating the solution at a temperature of at least about 85°C. with a mixture of calcium molybdate and calcium hydroxide, the latter in quantity insufficient to precipitate all of the molybdenum content of the solution as calcium molybdate, separating the resulting precipitate, agitating the separated solution at a temperature of at least about 85°C. with an excess of calcium hydroxide thereby producing a mixture of calcium molybdate and calcium hydroxide, and using said mixture of calcium molybdate and calcium hydroxide in the treatment of a further quantity of solution containing alkali metal molybdate.

8. In the process for the recovery of a molybdate from a solution containing an alkali metal molybdate an alkali metal sulfate and free caustic alkali the step which comprises agitating the solution with calcium sulphate in quantity sufficient to convert all of the caustic alkali and all of the alkali metal of the molybdate into the alkali metal sulphate.

9. Process which comprises roasting a molybdenum sulphide ore concentrate at a temperature not materially exceeding 600°C. and with free access of air, to the conversion of at least a part of the molybdenum sulphide content thereof to molybdenum trioxide, leaching the roasted concentrate with a solution containing caustic soda, the concentration of which at the termination of the leaching operation is equivalent to at least 0.5 gram of caustic soda per liter, separating the resulting solution containing alkali metal molybdate from undissolved residue, purifying the molybdate solution by agitating it with caustic alkali, separating the so-purified solution from solid material, reacting the purified solution, at a temperature of at least about 85°C. with a mixture of calcium molybdate and calcium hydroxide, the latter in quantity insufficient to precipitate all of the molybdenum content of the solution as calcium molybdate, separating the resulting precipitate, agitating the separated solution at a temperature of at least about 85°C. with an excess of calcium hydroxide thereby producing a mixture of calcium molybdate and calcium hydroxide, and using said mixture of calcium molybdate and calcium hydroxide in the treatment of a further quantity of solution containing alkali metal molybdate.

10. In the process of recovering a molybdate from ores containing molybdenum the steps which consist in leaching a material derived from the ore containing molybdenum trioxide and molybdenum dioxide with a solution containing caustic alkali in the presence of sodium hypochlorite.