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[54] PROCESS FOR BENEFICIATING MOLYBDENATE CONCENTRATE TO PRODUCE MOLYBDENUM TRIOXIDE

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[57] **ABSTRACT**

A process for the beneficiation of molybdenite concentrate comprising preheating the concentrate under inert conditions and contacting the concentrate with oxygen when the concentrate is at a temperature that will sustain an exothermic reaction with the oxygen to produce molybdenum trioxide, the conditions being such that the maximum temperature reached by the concentrate while it is in contact with the oxygen is within the range of from 500°C to 900°C.

12 Claims, No Drawings

PROCESS FOR BENEFICIATING MOLYBDENATE CONCENTRATE TO PRODUCE MOLYBDENUM TRIOXIDE

This invention relates to the beneficiation of molybdenite.

Molybdenite concentrate is prepared from molybdenite-containing ores by repeated flotation which is intended to lessen the proportion of copper in the ore. The resulting concentrate can contain as much as 50 – 58 percent of molybdenum, the principal impurities being copper, iron, silicon, alkali metals and alkaline earth metals. The concentrate is wet and oily in appearance because of the oil used in the flotation process.

Usually the concentrate is then roasted in air to convert it to a crude form of molybdenum trioxide according to the equation

$$2MoS_2 + 7O_2 \longrightarrow 2MoO_3 + 4SO_2$$

This is normally performed in a rotating tube furnace, or in a flame or muffle furnace in which the charge is raked manually, or in a multiple hearth furnace in which the charge is raked mechanically. A suitable multiple hearth furnace, such as Herreshoff's furnace, usually consists of 10 hearths situated vertically above one another, the charge being fed in at the top of the roaster and discharged at the bottom. In such a furnace, the charge is caused to fall from hearth to hearth by means of a rotating rake. The roaster is fired internally by means of gas burners and air is passed up through the roaster. As much as 20 to 30 percent of the charge can be carried away as dust and, therefore, the gas emerging from the roaster is generally passed through an electrostatic precipitator or cyclone and scrubbed with water to remove dust. Sulphur dioxide and sulphur trioxide in the effluent gases can be treated with lime to convert it to a mixture of calcium sulphite and calcium sulphate. Alternatively, or in addition to this treatment, the percentage of sulphur dioxide in the effluent gases can be reduced by dilution with air.

The molybdenum trioxide thus obtained can be used for direct smelting to a ferro-molybdenum alloy, in which case it is desirable that the sulphur content and the copper content should be as low as possible after roasting and should each not exceed 0.1 percent by weight of the roast. Alternatively, the molybdenum trioxide can be treated by various wet chemical processes to give substantially pure compounds of molybdenum and/or molybdenum metal (the metal being formed, for example, by hydrogen reduction of substantially pure molybdenum trioxide) in which case it is desirable that the molybdenum content of the roast should have high solubility in alkaline solutions which implies a low molybdenum sulphide content and the sulphur content should not exceed 0.5 percent by weight of the roast.

The preparation of molybdenum trioxide in this manner does, however, present a number of difficulties. First, unless the copper content of the charge before roasting is below about 3 percent by weight serious difficulties can arise during roasting because of the formation of a liquid phase component. A decrease in the copper content of the charge by flotation before roasting is, however, accompanied by a loss of molybdenum, the loss of molybdenum increasing, for a given starting material, as the final copper content is decreased. With some starting materials, if an attempt is made to decrease the copper content before roasting to 0.1 percent by weight (which is low enough to enable the oxide product to be used for direct smelting to a ferromolybdenum alloy) the loss of molybdenum may be as high as 25 to 30 percent by weight based on the original molybdenum content.

Secondly, even if the copper content of the charge before roasting is small, the charge must generally be roasted very slowly using large quantities of air to dissipate the heat of reaction so as to avoid balling or crusting of the charge because of the formation of a liquid-phase component which results from strong heating of the sulphur content of the charge. The retention time of the charge in the roaster is therefore long and the throughput/size ratio of the roaster is low. Thirdly, the concentration of sulphur dioxide given off in the effluent gases is usually about 5 percent by volume which is lower than that which would maks its recovery economically practicable. This concentration is too high, however, to permit the gases to be discharged directly into the atmosphere unless they are discharged at a high altitude or diluted with air before being discharged. The sulphur dioxide is therefore generally removed from the effluent gases and disposed of. Further, although oxidation of molybdenum sulphide proceeds well at 550°C, some of the sulphates of iron, copper and alkali metals present as impurities will only decompose at much higher temperatures. Although it is unnecessary that these sulphates should be decomposed when the product is intended for wet chemical treatment provided that the total sulphur content is below 0.5 percent by weight, it is usually found to be necessary that they should be decomposed when it is required to reduce the sulphur content below 0.1 percent to make the product suitable for direct smelting to ferro-molybdenum alloys. At the same time, however, the roasting temperature must be carefully controlled if severe sublimation of the molybdenum trioxide is to be avoided.

The invention provides a process for the benefication of molybdenite concentrate, which comprises preheating the concentrate under inert conditions and then causing the concentrate to react with oxygen to effect the formation of molybdenum trioxide in a sustained exothermic manner by contacting the preheated concentrate with the oxygen when the concentrate is at a temperature of at least 385°C., the conditions being such that the maximum temperature reached by the concentrate while it is in contact with the oxygen is within the range of from 500°C to 900°C.

In this manner, it is possible to reduce considerably the necessary retention time of the charge in the roaster. Thus, the difficulties arising from the formation of a liquid-phase component encountered in conventional processes with the resultant crusting of the charge can be considerably reduced. The throughput/-size ratio of the roaster can be increased and the concentrate can be roasted in smaller batches allowing easier temperature control.

The invention also makes it possible to roast molybdenite concentrate containing a considerably higher proportion of copper than the maximum proportion of copper tolerated in conventional roasting techniques. Thus, although the purpose for which the molybdenum trioxide is intended may require the copper content to be the same or lower than the level tolerated in conventional roasting techniques, the invention makes it possible for the copper to be removed after the roasting process, thereby avoiding the loss of molybdenum that occurs in the flotation process.

Further, it is possible to increase the concentration of sulphur dioxide in the effluent gas sufficiently to make its recovery economically practical. Also the proportion of the charge carried away as dust in the effluent gases is considerably reduced.

The preheated concentrate is advantageously contacted with substantially pure oxygen in which case the concentration of sulphur dioxide in the effluent gas is in general very much higher than in the effluent gas of the known process. It is then economically possible to recover it either as liquefied sulphur dioxide or for the catalytic conversion to sulphur trioxide for use in the manufacture of sulphuric acid.

Further, with some starting materials, quantities of other substances such as rhenium oxides can be recovered from the effluent gases and, as compared with the known processes, these quantities can be increased, especially when the preheated concentrate is contacted with substantially pure oxygen.

On contacting the preheated concentrate with oxygen, no reaction appears to occur for about 10 seconds. There then follows a period of about 45 seconds during which the temperature of the charge rises sharply. The reaction which takes place during this period is exothermic and the conversion to molybdenum trioxide is self-sustaining. The temperature then gradually decreases.

Although molybdenum trioxide sublimes at 795°C., it will usually be found that, if the transient temperature of the charge is now allowed to exceed 900°C., the charge is not at a temperature above 795°C. long enough for severe sublimation to occur.

The temperature of the concentrate may be controlled by varying a number of factors which are, first, the rate of reaction, secondly, the rate of loss of heat, and thirdly, the temperature to which the concentrate is preheated.

First, the rate of reaction depends upon the composition of the concentrate (in particular, the formation of a liquid phase inhibits the reaction and, for given roasting conditions, the tendency for a liquid phase to form depends on the composition of the concentrate) and the concentration of the oxygen with which the charge is contacted. If it is found that the use of substantially pure oxygen causes the concentrate to reach too high a temperature during the oxidation reaction the oxygen may be diluted with nitrogen or air.

Preferably, however, the rate of loss of heat from the reaction mixture is controlled by varying the charge layer thickness. As the heat is lost mainly by radiation, it will usually be found necessary to have a very thin layer of charge of about one-half inch in thickness, but a thicker layer of the order of 1½ to 2 inches may be used if the charge is raked during the reaction so that unexposed concentrate is brought to the surface. Even when using a very thin layer of charge it is usually advantageous to rake the charge in this manner.

Thirdly, it will usually be found that the charge should not be at a temperature of more than 700°C. when contacted with the oxygen, but it is necessary that the concentrate should be preheated above 385°C. in order that the reaction shall be self-sustaining. It will also be found that preheating the charge to above 385°C. suffices to cause the charge to be dried and oil to be distilled off. Advantageously, the concentrate is preheated to a temperature of at least 600°C. preferably, about 660°C.

The requirement that the material should be preheated under inert conditions implies primarily that it should be preheated in the absence of oxygen. The purpose of preheating the material is simply to ensure that it is at a desired elevated temperature when it is contacted with oxygen, and not to effect any chemical change in the material. Thus, in addition to excluding oxygen, the material will be preheated in the absence of any substance with which it would react to any substantial extent during the preheating.

The concentrate may be preheated in an inert atmosphere, for example, in an atmosphere of nitrogen, or it may be preheated while it is confined in a region, for example, the interior of a tube, that is substantially completely filled by the charge so that at most a small quantity of air can initially be present. When concentrate is preheated in an atmosphere of an inert gas, it may be preheated by heating the gas and fluidising a bed of the concentrate by passing the hot inert gas upwardly through it.

The process is advantageously carried out continuously, the concentrate being carried in turn through a preheating zone and an oxidation zone. Preferably, the concentrate is carried, at least through the oxidation zone, in the form of a shallow static bed supported on a conveyor, which may be a rotary hearth. Advantageously, stationary members are arranged above the conveyor to disturb the bed of concentrate as it passes through the oxidation zone so that unexposed concentrate is brought to the surface of the bed.

The effluent gases can then be cooled, filtered and passed through an ethanolamine solution to decrease the sulphur dioxide content of the gases. The sulphur dioxide can then be released from the ethanolamine solution by heating the solution with a steam coil, the released sulphur dioxide being liquefied by a compressor.

A series of experiments was carried out to show how the sulphur content of the product and the percentage of the molybdenum content of the product that is insoluble under alkaline conditions vary with the time of exposure of the preheated concentrate to oxygen. An analysis of the starting material gave the following results:

Mo	51.70%
S	32.2 %
Fe	6.6 %
Cu	1.2 %
H_2O	0.42%
Oil	0.13%

The temperature of the concentrate on exposure to the oxygen was recorded by a thermo-couple buried in the concentrate. During the exposure to oxygen no extra heat was supplied, the increase in the temperature being entirely due to the exothermic oxidation reaction. After exposure the concentrate was allowed to cool to room temperature in an atmosphere of nitrogen.

The results of this series of experiments, in which the concentrate was in a layer of one-half inch in thickness and was preheated in an atmosphere of nitrogen to a temperature of 660°C. before exposure to oxygen, are set out in Table 1 below:

Table 1

Experiment No.	Maximum Transient temperature on exposure to O_2, in °C.	Exposure time, in min.	Percentage sulphur content of product	Percentage of product insoluble in alkali
1	—	nil	27.48	90.0
2	875	1.0	26.97	84.9
3	860	2.0	21.33	79.3
4	880	3.0	16.54	75.7
5	890	4.0	13.03	65.3
6	890	5.0	10.66	65.1
7	870	6.0	3.13	52.6
8	870	7.0	3.56	44.5
9	870	8.0	0.406	29.3
10	820	9.0	0.296	25.1
11	830	10.0	0.075	16.7
12	850	12.0	0.057	12.4
13	870	14.0	0.010	10.1
14	825	28.0	0.027	11.0
15	—	60.0	0.01	10.0

The percentage of the product insoluble under alkaline conditions might be expected to be due solely to the sulphur content of the product, but it is clear from Table 1 that this is not so. The apparent disparity probably results from the formation of brown oxide of molybdenum by reaction between MoS_2 and MoO_3.

A further series of experiments was carried out to show how the exposure time in oxygen required for completion of roasting varies with the concentrate layer thickness for inert preheating temperatures of 600°C. and 650°C. The completion of roasting was determined experimentally for each layer thickness by allowing a number of charges to cool in an atmosphere of nitrogen after exposure to oxygen for different periods of time. If the roasting is not complete when the charge is removed from the oxygen and placed in an atmosphere of nitrogen a sharp change is observed in the gradient of the temperature-time curve of the charge. If the roasting is complete, on the other hand, no such sharp change is observed.

The results of this series of experiments are as shown in Table 2.

Table 2

Experiment No.	Preheating temperature, in °C.	Charge layer thickness, in in.	Time required for completion of roasting, in min.
1	600	0.05	1.0
2	600	0.10	2.5
3	600	0.15	3.0
4	600	0.20	3.5
5	600	0.25	>4.0
6	650	0.05	1.0
7	650	0.10	1.5
8	650	0.15	2.5
9	650	0.20	3.25
10	650	0.25	3.50
11	650	0.30	>4.00

The following Example illustrates the invention: Dry, oil-free molybdenite concentrate in a layer of 1.0 cm in thickness on a moving conveyor was preheated by electric heaters in a stream of nitrogen flowing in the same direction as the conveyor. An analysis of the concentrate before it was preheated gave the following results:

Mo	51.70%
MoS_2	86.18% (Calculated)
Cu	1.2 %
Fe	3.6 %
S	32.2 %
Residual oil and water	0.55%

The concentrate was preheated to a temperature within the range of from 630°C. to 670°C. It was then exposed to oxygen for 3.5 minutes, the conveyor being passed through a stream of oxygen flowing in the opposite direction to that of the conveyor. The transient temperature of the charge did not exceed 800°C. and the product contained 2.74 percent by weight of sulphur. An analysis of the effluent gases given off after exposure to oxygen gave the following approximate results, the percentages being by volume:

SO_2	51.2%
SO_3	3.8%
O_2	1.0%
N_2	44.0%

A further series of experiments was carried out using, as a starting material, concentrate having the above analysis. The roasting was carried out continuously, the concentrate being carried through a preheating zone in the absence of oxygen on an externally heated screw conveyor. The hot concentrate was then passed to a single hearth, where it was brought into contact with oxygen, the charge being maintained at a temperature of 600°C. Concentrate that had been on the hearth long enough for the hearth to make nearly one complete rotation was removed by means of a plough. Keeping the other parameters constant, the sulphur content of the concentrate after roasting was measured for different rates of flow of oxygen, three measurements of the total sulphur content of the concentrate being made at different times for each different rate of flow of oxygen. The average of the three values of the sulphur content of the concentrate was then used to calculate the average reduction in the total sulphur content for each different rate of flow of oxygen. The results of the experiments are shown in Table 3.

Table 3

Oxygen feed expressed as a multiple of the rate required for stoichiometric reaction with concentrate	Composition of effluent gas in percent by volume			Total sulphur content of product in percent by weight	Average reduction in total sulphur content of concentrate in percent by weight based on sulphur content before roasting
	SO_2	SO_3	O_2		
2.84	18.5	1.2	61.0	0.63	
				0.65	98.5
				0.52	
2.00	27.0	2.3	56.0	0.98	
				0.93	97.6
				0.95	
1.00	38.0	4.1	41.2	2.66	
				2.80	92.6
				3.10	

Depending on the composition of the concentrate after roasting and the purpose for which the concentrate is intended, it may be desired to decrease further the sulphur and/or copper contents of the concentrate.

To reduce further the sulphur content, the concentrate may be crushed in, for example, a hammer mill and re-roasted in an atmosphere of air. Because of the significant decrease in the sulphur content of the ore caused by the initial roasting process, the disadvantages of the conventional roasting processes are not encountered in this secondary roasting process. It is therefore unnecessary to preheat the concentrate in an inert atmosphere before subjecting it to the secondary roasting process. The sulphur remaining in the concentrate after the secondary roasting is largely or substantially wholly in the form of sulphate compounds which can be removed easily by leaching.

In an experiment, concentrate having a total sulphur content of 2.62 percent by weight after primary roasting was stage ground to −65 mesh (B.S.S.) and then fed into a kiln where it was subjected to a secondary roasting at 600°C. in an atmosphere of air. The total sulphur content of the product was measured for different residence times of the charge in the kiln. The results are given in Table 4.

Table 4

Residence time in hours	Total sulphur content of product after secondary roasting in percent by weight	Reduction in total sulphur content of concentrate from primary and secondary roasting in percent by weight based on the sulphur content of the material before primary roasting
0.5	0.29	99.3
1.0	0.27	99.5
1.5	0.30	99.2
2.0	0.28	99.3
2.5	0.27	99.3
3.0	0.31	99.2
3.5	0.33	99.1
4.0	0.27	99.3

Where the concentrate is to be used for direct smelting to a ferro-molybdenum alloy for use, for example, in the steel industry, the copper content of the concentrate should be below 0.1 percent by weight. To decrease the copper content of molybdenum concentrates after roasting the concentrate has generally been treated with lime but a substantial proportion of the molybdenum thus obtained is in the form of calcium molybdate which cannot be used directly for smelting to a ferro-molybdenum alloy. Further, with such a process, any residual sulphur remaining in the concentrate is not removed.

Advantageously, the copper content of the concentrate roasted in accordance with the invention is decreased by treating the roasted concentrate with hydrochloric acid and ferric chloride, thereafter adding sodium carbonate or ammonium hydroxide to the solution to give the solution a pH within the range of from 1.8 to 4.5, and, preferably, to give the solution a pH within the range of from 2.9 to 3.1, so as to precipitate ferric molybdate, and separating precipitated ferric molybdate from the solution. The roasted concentrate may either be leached with the hydrochloric acid in the presence of the ferric chloride or the concentrate may be first leached with hydrochloric acid and then treated with a solution of ferric chloride.

After separating precipitated ferric molybdate from the solution further sodium carbonate is preferably added to the solution to give the solution a pH within the range of from 5.7 to 6.5 so as to precipitate copper carbonate. Instead of adding further sodium carbonate, sodium sulphide or hydrogen sulphide can be used to precipitate the copper as copper sulphide.

An example of the leaching process is as follows: Roasted concentrate containing 55.5 percent molybdenum, 1.35 percent copper and 0.23 percent sulphur, the percentages being by weight, based on the weight of the roasted concentrate, was leached with water and hydrochloric acid solution for 30 minutes at 50°C. Forty pounds of 36 percent hydrochloric acid were consumed per ton of concentrate. Fifty percent of the resultant slurry was solid matter. The solids after leaching contained 56.7 percent by weight of molybdenum, 0.05 percent by weight of copper, and less than 0.01 percent by weight of sulphur, the percentages being based on the total weight of the solids after leaching. The leach liquor contained 7.3 percent by weight of dissolved molybdenum based on the total molybdenum content of the concentrate before leaching and 97 percent by weight of dissolved copper based on the total copper content of the concentrate before leaching. To recover these the liquor was treated with ferric chloride solution and sodium carbonate was added to adjust the pH of the solution to 3 so as to precipitate the dissolved molybdenum as ferric molybdate leaving the copper in solution. The solids were then filtered off. On adding more sodium carbonate to the filtrate to bring the pH to 6, copper carbonate was precipitated. The total recovery of the molybdenum was 99 percent by weight based on the total molybdenum content before leaching and that of the copper 81 percent by weight based on the total copper content before leaching, the proportion of copper in the copper carbonate precipitated being 41.4 percent by weight, based on the weight of the copper carbonate.

A further example of the leaching process is as follows:

Roasted concentrate of the same composition as in the above example and containing 3.4 percent iron, the percentage being by weight and based on the total weight of the concentrate, was leached with dilute hydrochloric acid solution in the presence of ferric chloride for 30 minutes at 50°C. The pH of the slurry was adjusted to 3 by adding sodium carbonate to precipitate ferric molybdate. The mixture was then filtered and the solids washed off with water. The concentrate contained 55.0 percent molybdenum, 0.05 percent copper, 4.9 percent iron and 0.11 percent sulphur, the percentages being by weight based on the total weight of the concentrate after leaching, and the recovery of the molybdenum was 99.9 percent by weight based on the total molybdenum content before leaching. The filtrate and wash were treated with sodium carbonate to bring the pH to 6 so as to precipitate copper carbonate. 81 percent By weight of the copper was recovered the percentage being based on the total copper content before leaching, and the proportion of the copper in the copper carbonate precipitated was 41 percent by weight, based on the weight of the copper carbonate. The consumption of the reagents in pounds used per pound of molybdenum were as follows:

Reagents	Pounds of reagent used per pound of molybdenum obtained after leaching
Ferric chloride	0.077
Hydrochloric acid (calculated as 36% hydrochloric acid)	0.054
Sodium carbonate (to adjust pH to 3)	0.073
Sodium carbonate (to adjust pH to 6)	0.043

When it is desired to remove substantially all the copper from the concentrate, as when it is desired to obtain molybdenum metal, it is necessary to use the more sophisticated and expensive solvent-extraction or ion-exchange techniques. Nevertheless, it may be found advantageous to reduce the copper content of the concentrate as far as possible by treatment with hydrochloric acid and ferric chloride as described above, especially because, when the concentrate is roasted in accordance with the invention, the concentrate can contain a much higher proportion of copper (about 7 to 10 percent by weight) than that (about 2 to 3 percent by weight) which can be tolerated in conventional roasting processes.

I claim:

1. A process for the beneficiation of molybdenite concentrate, which comprises (1) preheating the concentrate under inert conditions to a temperature of at least 385°C at which said concentrate will react exothermically with oxygen, and (2) then causing the concentrate to react with oxygen to effect the formation of molybdenum trioxide in a sustained exothermic manner by contacting the preheated concentrate with the oxygen while said concentrate is at a temperature of at least 385°C, under conditions such that the maximum temperature reached by the concentrate while it is in contact with the oxygen is within the range of from 500°C to 900°C.

2. The process of claim **1**, wherein the preheated concentrate is contacted with substantially pure oxygen.

3. The process of claim **1**, wherein the oxygen with which the preheated concentrate is contacted is diluted with nitrogen or air.

4. The process of claim **1**, wherein the temperature to which the concentrate is preheated under inert conditions does not exceed 700°C.

5. The process of claim **1**, wherein the temperature to which the concentrate is preheated under inert conditions is at least 600°C.

6. The process of claim **1**, wherein the temperature to which the concentrate is preheated under inert conditions is about 660°C.

7. The process of claim **1**, wherein the concentrate is preheated in an inert atmosphere.

8. The process of claim **7**, wherein the concentrate is preheated in an atmosphere of nitrogen.

9. The process of claim **1**, wherein the concentrate is preheated while it is confined in a region that is substantially completely filled by the concentrate.

10. The process of claim **1**, wherein the copper content of the roasted concentrate is decreased by treating the roasted concentrate with hydrochloric acid and ferric chloride, thereafter adding sodium carbonate or ammonium hydroxide to the solution to give the solution a pH within the range of from 1.8 to 4.5 so as to precipitate ferric molybdate, and separating precipitated ferric molybdate from the solution.

11. The process of claim **10**, wherein the sodium carbonate or ammonium hydroxide is added to the solution to give the solution a pH within the range of from 2.9 to 3.1 so as to precipitate ferric molybdate.

12. The process of claim **10**, wherein further sodium carbonate is added to the solution from which ferric molybdate has been separated to give the solution a pH within the range of from 5.7 to 6.5 so as to precipitate copper carbonate.

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