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CONCENTRATION OF COPPER OXIDE ORES WITH NITRITES

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1

This invention relates to the concentration of copper bearing ores and it relates more particularly to an improvement in the flotation process for concentrating ores of copper oxide or mixtures of copper oxide and copper sulphide, which contain such minerals as malachite, azurite, cuprite, tenorite, melaconite and chrysocolla and the like.

The recovery and concentration of copper sulphide minerals by flotation processes is a highly developed art and the reagents that are used to advantage in such process are well known. With copper oxide ores or ores rich in copper oxide, a different situation exists. Practically all of the methods heretofore proposed for oxide recovery and concentration have involved the preliminary steps of sulphidizing the mineral to provide a sulphide coating on the oxide to render it more susceptible to flotation in accordance with the processes of completion for the flotation of sulphide minerals. Sulphidizing of copper oxide ores presents many difficulties and conversion to sulphide is not complete in many instances. As a result, present processes for the recovery of oxides by flotation is insufficient and wanting in many respects.

It is an object of this invention to provide an improved flotation process for the concentration of copper oxide ores. Another object is to provide a flotation process for the concentration of ores rich in copper oxide or rich in mixtures of oxide and sulphide employing an activator to render normal flotation materials more effective thereby to provide a more efficient process.

To the accomplishment of the foregoing objects, the invention comprises the addition to constituents of the type used for normal flotation of an agent which modifies the surface characteristics of the copper oxide mineral to activate and render more effective the sulphidization and collector compounds. Thus by the use of the activator in standard procedures, the recovery of oxide mineral is simplified and rendered more efficient and is therefore desirable from the standpoint of cost and yield.

Broadly stated, my invention comprises a flotation process for concentrating ores rich in copper oxide wherein a minor amount of a metal nitrite is incorporated to activate the flotation ingredients and increase the efficiency of the process to reduce the cost of recovery per unit weight of material.

The reagents employed in flotation serve a number of specific purposes. Collectors or promoters have the function of collecting the mineral particles into aggregates and to encourage attachment of the formed aggregates to bubbles generated upon aeration. Collectors which have been used successfully in the practice of this invention include phosphorous pentasulphide,

2

potassium ethyl xanthate and other xanthates, thiocarbanilid and dithiophosphates. These collecting agents are old in the flotation of sulphide minerals.

Frothing agents have the function of supplying stability to the bubbles for raising the attached aggregates to the surface of the fluid whereby the aggregate is separated from the gangue. Suitable frothers include pine oils, cresylic acids and their derivatives, glycine compounds and the like.

Conditioning agents, which have the function of freeing the solution of heavy metal salts and establishing a hydrogen ion concentration most effective for flotation of the type described, include such materials as hydrated lime but may also include other basic metal compounds.

In accordance with my invention, the metal nitrite activator changes the surface characteristics or surface structure of the copper oxide mineral by forming chemically what appears to be a slightly soluble monomolecular film. In the presence of sulphidizing agents, reaction quickly takes place with the more receptive soluble film to form a comparatively insoluble sulphide that confers non-wettability to the oxide material so that it is of a character more suitable for flotation in the usual manner. As the activator having the characteristics of the type described, use may be made of one or more of the soluble metal nitrites, such as sodium nitrite, potassium nitrite, ammonium nitrite, or other alkali metal nitrites. Instead, the nitrites of alkaline earth metals may be used, such as barium nitrite, calcium nitrite, magnesium nitrite and the like. Mixtures of such nitrites might also be used. The amount of nitrite is not critical so long as it is present in sufficient quantity to bring about the desired reactivity. The amount depends chiefly upon the type of ore being concentrated.

In the practice of this invention, the ore containing copper oxide is crushed, ground, and classified in the manner usually employed prior to flotation in the concentration of minerals.

During the grinding, pine oil (a frother) and hydrated lime (a condition agent or alkalinity producer) and sodium nitrite (an activator for copper oxide) are added. Just before the ground and classified pulp is admitted to the flotation cells, a sulphidizer or collecting agent such as phosphorous pentasulfide and the xanthates is added. The pulp is aerated and agitated in the usual manner in the flotation cells and the desired mineral floats to the surface and is removed with the froth from the surface. When an ore constituted with a mixture of copper oxide and copper sulphide is treated for concentration by flotation, the frother, the conditioning agent and the nitrite

activator are incorporated in the same way but the froth that is removed after the first flotation will be rich in copper sulphide and low in copper oxide. To recover a greater proportion of the copper oxide, the tailings from the concentration cells are returned to a reconditioning or pretreatment tank where sodium sulphide is added. After conditioning to provide a sulphide coating on the mineral oxide surfaces in the presence of the nitrite activator (the conditioning period may be shortened by reaction at elevated temperatures), the pulp is returned to the flotation cells where it is again aerated and agitated to float the mineral now rich in oxide for removal with the froth.

The recovery of the oxide in a mixed ore is aided by the occasional addition of sodium sulphide to the flotation cells. For more complete recovery, the tailings from the second flotation may be aerated anew with nitrite activator and sodium sulphide to produce a low grade concentrate which may be upgraded.

If ore is made up exclusively of copper oxide the procedure is similar to that for the second stage of the mixed ore except that, after the collectors and sodium sulphide are added, the pulp is pretreated for a period before flotation. The concentrate of the flotation is a high grade copper oxide while the tailings are a low grade mineral and may be upgraded if desired.

It has been found that recovery of 80 to 93 percent of the mineral may be achieved by the described procedure employing an alkali metal nitrite or an alkaline earth metal nitrite as an activating agent in addition to the collectors, frothers and conditioning or alkalinity agents of the type which has been customarily used in such processes. The use of the nitrite activator provides for greater efficiency and higher recovery of ore constituted with copper oxides.

The following are specific tests that illustrate the practice of this invention. The amounts of reagents are given by way of illustration and not by way of limitation. The amount of nitrite may be increased or decreased over the concentrations designated depending upon the type of ore, the amount of oxide present and the surface area available for activation. It has been found that concentrations of nitrite in excess of a minimum might be used without harmful effect and therefore the amount which can be employed in the practice of this invention extends over a relatively wide range. It is desired, for best operation, to adjust the pH of the pulp to the alkaline side and preferably in the range of 11 to 12.

Example A

The treatment of ore that is predominantly malachite and has some azurite and a calculated head assay of 0.69 percent copper:

Reagents used	Lbs. per ton ore
Pine Oil	0.05
Sodium Nitrite	0.125
Sodium Sulphide	0.125 to 0.25
Aerofloat (flotation agent)	0.05
Xanthate	0.05

Results.—The concentrate contained 33,02 percent copper and the tailings contained 0.062 percent copper. The recovery of copper in the above test was 91.19 percent.

Example B

The treatment of ore of the type malachite and cuprite having a calculated head assay of 5.97 percent total copper:

Reagents used	Lbs. per ton ore
Pine Oil	0.05
Sodium Nitrite	2.0
Xanthate	0.25
Aerofloat	0.10
Sodium Sulphide	5.0

Results.—The concentrate contained 34.94 percent copper and the tailings contained 1.37 percent copper. The recovery of copper was 80.17 percent.

In the above example the alkalinity of the pulp was maintained at a pH of 11 to 12.

Example C

The treatment of a mixed copper oxide and copper sulphide ore having a calculated head assay of 2.77 percent total copper:

Reagents used	Lbs. per ton ore
Pine Oil	0.05
Sodium Nitrite	0.5
Xanthate	0.10
Aerofloat	0.075
Sodium Sulphide	0.5 to 1.5

The akalinity of the pulp was adjusted to a pH of 11 to 12.

Results.—The concentrate contained 12.95 percent copper as the oxide and 8.20 percent copper as the sulphide which gave a total of 21.15 percent copper in the concentrate. The tailings contained 0.24 percent copper as the oxide and 0.09 percent copper as the sulphide which amounted to 0.33 percent copper in the tailings. The total of the copper oxide recovered was 87.9 percent and the total of the copper sulphide 92.3 percent which gave an 89.4 percent total recovery.

It will be understood that numerous changes may be made in the amounts of materials employed and their order of incorporation as well as in the conditions for flotation without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. In the method of concentrating ores containing copper oxide by flotation processes, the step of conditioning the ore with a metal nitrite selected from the group consisting of ammonium nitrite, alkali metal nitrites and alkali earth metal nitrites in preparation for the froth flotation thereof with suitable frothers, sulphidizers and collectors for sulphide ores.

2. In the method of concentrating ores containing copper oxide by froth flotation with suitable frothers, conditioners for adjusting the hydrogen ion concentration and sulphidizers, the step of treating the ore with an activator selected from the group consisting of ammonium nitrite, alkali metal nitrites and alkaline earth metal nitrites for accelerating the formation of an insoluble sulphide film on the surfaces thereof upon reaction of the sulphidizing agent.

3. In the method of concentrating ores containing copper oxide by froth flotation with suitable frothers, conditioners for adjusting the hydrogen ion concentration and sulphidizers, the

step of conditioning the ore with a water soluble metal nitrite in advance of contact by the sulphidizing agent.

4. In the method of concentrating ores containing copper oxide by froth flotation with suitable frothers, conditioners for adjusting the hydrogen ion concentration and sulphidizers, the step of conditioning the ore with a water soluble metal nitrite in concentrations ranging from 0.15–2.0 pounds per ton of ore whereby a soluble film is formed on the surface of the copper oxide and reacts with the sulphidizer to form an insoluble film capable of subsequent treatment more efficiently in the normal froth flotation process.

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