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[54] **METHOD OF COPPER SULFIDE ORE FLOTATION**

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[58] **Field of Search** 209/166, 167; 252/61

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[57] **ABSTRACT**

A novel flotation promoter used in the concentration of copper bearing ores for the efficient selective flotation of copper values, including chalcopyrite, with suppression of iron pyrites; the promoter comprising a sodium sulfate of an aliphatic hydrocarbon having a carbon chain in excess of 12 carbons and chemically combined with at least one mole of the C_2—C_3 alkylene oxides.

4 Claims, No Drawings

METHOD OF COPPER SULFIDE ORE FLOTATION

BACKGROUND OF THE INVENTION

The present invention relates to ore flotation processes. More specifically, the present invention relates to a novel collector material in froth flotation circuits to facilitate increased recovery of copper ore values with suppression of non-cuprous iron compounds.

Froth flotation has been widely used over a period of years to beneficiate sulfide and oxide ores of a large number of metals. The process is capable of treating high volumes of relatively low-grade ore materials to produce concentrated fractions of ore-values having a much higher assay than the starting ore being processed. Typically, such froth flotation processes utilize an ore pulp prepared by adding finally comminuted ore to an aqueous liquid which liquid is conditioned by various chemicals and agitated in a flotation machine which introduces dispersed air in the form of fine bubbles throughout the pulp. These chemicals enhance the tendency of the desired ore values selectively to adhere to the fine air bubbles and float to the surface to form a froth highly concentrated with the desired ore values. The froth is removed as a concentrate with the gangue remaining in the pulp as a tailing product.

Typically, the chemicals added to the froth flotation systems to aid in the selective concentration of the desired ore values are generally classified as frothers, collectors and modifiers. Quite typically, frothers are compounds, crdinarily organic, consisting of one or more hydrocarbon groups which function as a mechanism for transporting the ore values selectively from the pulp to the froth thereabove, as a concentrate having a relatively high assay in the desired ore values. Collectors, on the other hand, specifically and selectively alter the surfaces of the minerals in the ore in the aqueous solution so as to cause selective adherence to the froth bubbles passing upwardly therethrough thereby promoting flotation of the desired ore values in preference to gangue or undesired ore values, thereby causing collection of desired ore values in the froth. Modifiers, on the other hand, operate to change the surface of the minerals desired so as to modify their amenability to froth floation in given collector — frother combination. Such agents are sometimes termed activators, depressants, inhibitors, pH regulators and the like. A proper combination of the above noted reagents permits one skilled in the art to perform selective or differential flotation of predetermined desired fractions of minerals and/or gangue in a given ore by maintaining a selected chemical condition on the surface of the ore so as to allow selective removal of the same from the body of the ore and aqueous solution by the adherence to fine air bubbles.

With the changing economics of the mining industry, a constantly increasing effort has been made to recover greater percentages of valuable minerals from ores of even lower assay. This has caused, for example, the tailings of many mining facilities previously considered uneconomic, to be reexamined and reprocessed for the further extraction of valuable ores. Likewise, in an initial mining operation, improved processes have continually been sought to maximize the amount of valuable ore recovered in the initial ore processing steps.

Just as important as the successful increase in concentration of one ore element in a given solution, is the depression, if possible, of other undesired ore materials. For example, the present invention deals particularly with ores bearing copper, and is largely concerned with ores having a substantial constituency of copper sulfide and iron sulfide. Iron sulfide (iron pyrites) is typically, in copper sulfide bearing ores being concentrated by the froth flotation process, an undesirable element in the final ore concentrate. In the first place, it is generally deleterious to the equipment employed in the reduction of the copper sulfide ores to copper and adds significantly to the air pollution problems at the smelter. Accordingly, it is desired that in the handling of ores containing both copper sulfide and iron sulfide, that the copper sulfide be selectively floated in the froth, if possible, More specifically, a principal object is to cause copper, zinc, lead and molybdenum sulfides to be floated into the froth and to, at the same time, improve the rejection of iron pyrites where possible to reduce smelter penalties, to reduce smelter air pollution, and to reduce freight costs incident to ore concentrate shipment.

SUMMARY OF THE INVENTION

In accordance with the principles of the present invention, a highly selective process is provided that preferentially floats copper iron sulfide ore material, commonly called calcopyrite bearing desirable copper and yet rejects iron pyrite which is the iron sulfide mineral bearing no copper. Since much of the copper containing ores mined in the United States and elsewhere contain chalcopyrite as a significant constituent, and, further, since chalcopyrite is quite often intimately mixed with iron pyrite, the reagent of the present invention operates as a collector in a particularly desirable manner in providing improved extraction of chalcopyrite from iron pyrite and other gangue materials. Furthermore, the reagent of the present invention operates as an effective collector, or promoter, for metallic sulfide minerals other than iron sulfide with the ability to float such minerals as well as heretofore commonly used xanthate and dithiophosphate collectors. Whereas such prior collectors have objectionable odor and/or cause in some situations uncontrolled frothing or defrothing, the reagents of the present invention are bland in odor and provide a more controllable and a more desirable type of froth and allows a reduction in the amount of frother additive required for optimum flotation. The reagents of the present invention actually are more effective than the prior collectors in the ability to selectively float very finely ground minerals. It should be noted that the reagents of the present invention, while utilizable without prior reagents such as xanthate or dithiophosphate, are not incompatible therewith, particularly in the treatment of ore of relatively coarse particle sizes. It has been found in such circumstances that the reagent of the present invention tends to float more of the very small particle materials while the prior xanthates and dithiophosphates may be somewhat more effective in floating the larger, middling particles.

Since the reagent is a particularly good depressant of pyrites, it is preferred to employ the present reagent in the initial stages of the typical ore flotation rougher circuit in order to float most of the mineral in the somewhat larger particle sizes while rejecting the iron pyrites. Then a low dosage of conventional collectors such as xanthates or dithiophosphate is added in the final scavenger cells to pick up the middling sized min-

erals without any substantial picking up of iron pyrites. In the case of copper recovery which is the principal subject of the present invention, the use of the reagent of this invention increases recovery of minor metals therewith, such as molybdenite and sphalerite, both highly desirable. These minerals are extracted by flotation in subsequent flotation circuits and this can be accomplished with the use of the present invention. The use of the reagent in place of, or in partial substitution for, these conventional collectors, such as xanthates and dithiophosphates in the rougher flotation of copper-bearing ores containing molybdenite and sphalerite, show a very substantial increase in recovery of these minor materials, oftentimes in the range of 15 to 20 percent. At the same time, the amount of frother required is reduced substantially, and the recovery of pyrite is reduced by approximately two-thirds.

The various known collectors that may be used according to the present invention include the dithiophosphates sold by American Cyanamid Co. under the trademark "AEROFLOAT" and under designations 238 and 242 (hereinafter referred to as AF238 and AF242), and the xanthate collectors sold by Dow Chemical Co. under the designation Z-4, Z-6 and Z-10.

The ore flotation process ingredients of this invention may be termed collectors although they are also in the manner of a modifier. Due to the complex, and not fully understood, operation of the reagent material of the present invention, it is preferred to term it a "flotation promoter." In the preferred embodiments, the materials comprise sulfate salts of fatty alcohols having carbon atoms in excess of C_{12}. The hydrophobicity characteristics of the sulfates under consideration decreases with the reduction in carbon atoms to a point at about 12 carbons where the reagent operates to cause an excess of froth. It has been found that an optimum product of acceptable hydrophobicity comprises $R—(OCH_2CH_2)_N—OSO_3Na$ where R is a $C_{16}—C_{18}$ fatty alcohol ethoxylated to at least one mol but preferably where N is approximately 4mols. The related material $R—OSO_3Na$ without ethylene oxide is satisfactory but somewhat more difficult to keep in solution. At least one mol of propylene oxide (OCH_2CHCH_3) may replace ethylene oxide in this optimum formulation. Furthermore, the addition of propylene oxide improves the hydrophobicity which in turn enhances the bubble attachment.

In use, the water solution of the fatty alcohol sulfate is added at the first rougher flotation cell or following the grinding of the ore material. Following this rougher stage, an additional portion of the reagent is added in the scavenger stage, along with conventional xanthate or dithiophosphate materials to provide a maximum recovery of copper with a minimum of iron pyrites. In this operation, it is found that several important and desirable results have been achieved; manely: (1) the amount needed of conventional frother material, such as pine oil, MIBC or methyl isobutylcarbinol or DOWFROTH 250, a propoxylated methanol, or the like, is substantially reduced without degradation of froth; (2) the iron pyrites is more effectively suppressed than heretofore; (3) the recovery of copper is very high and is at least as high as prior systems known to me without increased iron recovery.

Using ore from the Mission Unit of the American Smelting and Refining Company as a basis for study, the ore was prepared on a standard basis to provide a mill ground mixture containing 1,000 grams ore, 600 cc H_2O, 0.75 grams CaO to provide: pH = 10.5, 0.005 lb./ton collector mix of 60 percent AF238 and 40 percent Z-6 xanthate, pine oil at 0.18 lb./ton and was ground 14 minutes to 5 percent + 65 mesh and 53 percent − 200 mesh. The ore is a sulfide copper ore containing heads of approximately: copper 0.45, iron 3.4, molybdenum 0.006, and zinc 0.06 per ore sample. Prior flotation of this ore has employed, in the floation cell, the addition of pine oil as required to optimize froth, ordinarily resulting in a total pine oil concentration of about 0.24 lb./ton. Collector mix was initially added in the amount of 0.01 lb./ton and the mixture floated three minutes, whereupon additional 0.01 lb./ton collector mix is added and an additional three minutes float undertaken. As a final rougher scavenger flotation stage 0.5 lb./ton $CuSO_4$, 0.4 cc of 1/2 percent fuel oil solution and 0.01 lb./ton collector mix were added and floated for three minutes. Recoveries on this basis rather consistently over a series of tests, provided a recovery of about 91 percent of the copper heads and about 48 percent of the iron.

By comparison, the reagent of the present invention was employed in the following Examples:

EXAMPLE I

An ore mixture, using ore from the same mine run, of 1,000 grams ore, 14 minute grind, 600 cc H_2O, 0.75 grams CaO to give a pH of 10.5, pine oil frother of 0.12 lb./ton, Applicant's Reagent No. 1: $C_{16}—C_{18}$ fatty alcohol—$(OCH_2CH_2)_4—OSO_3Na$ at 0.01 lb./ton, AF238 at 0.001 lb./ton and $CuSO_4$ at 0.5 lb./ton with 0.4 cc of 1/2 percent fuel oil solution emulsion during the scavenger float. As in the case of the standard or reference system, a nine minute total float was employed but with the following sequential conditions: pH was adjusted, 0.005 lb./ton Reagent No. 1 and 0.0005 lb./ton AF238 were added and the mixture floated three minutes; then 0.0025 lb./ton Reagent No. 1 and 0.00025 lb./ton AF238 were added and the mixture floated three minutes. A scavenger float of three further minutes was conducted with addition of 0.0025 lb./ton Reagent No. 1, 0.00025 lb./ton AF238; 4 cc fuel oil emulsion and 0.5 lb./ton $CuSO_4$. Using this procedure an average of about 87 percent copper and 14.5 percent iron were recovered.

The above example provided a very material reduction in frother required, was substituted for, rather than added to prior collector materials, and very substantially reduced the iron pyrites floated. We found in the tests that while the total copper recovered in Example I was very slightly less than recovered in prior systems, the iron recovery had dropped more than two-thirds. The penalties incident to high iron is an end in itself in superior ore flotation. However, we have found that slight additional amounts of AF238 and Reagent No. 1 added to the rougher concentrate will bring the total copper recovery up to any prior art system, but in so doing, still retains the iron recovery at substantially less, on the order of 50 percent less, than such prior art systems.

EXAMPLE II

Reagent No. 2 comprised a related material as flotation promoter, namely, $R—OSO_3Na$ where R = 16–18 carbons and employing no added ethylene oxide or

propylene oxide. In other respects Reagent No. 2 and its addition to the system were the same as Reagent No. 1. The results showed a requirement for more frother material (pine oil), showed a substantial suppressance of iron and slightly less recovery of total copper, still providing superior flotation characteristics.

Experimentation showed at the same time that lauryl alcohol sulfate, or reagents with R equals on the order of C_{12} becomes excessively frothy for successful separation of copper values from sulfide ores of the type described. It has been found, accordingly, that fatty alcohol sulfates provide a unique combination of hydrophobicity and hydrophilicity for the selective collection of copper-bearing sulfides and selective suppression of iron pyrites in sulfide ores. Successful control of froth by use of these reagents is also achieved when carbon chain molecules greater than C_{12} are employed. It has been found, further, that wereas frothing is excessive, brittle and uncontrolled at $R = C_{12}$ when pine frother is employed, reduction in pine oil quantity with the use of longer carbon chain fatty alcohols provide superior frothing and collecting characteristics. Hydrophobicity which improves attachment to the flotation air bubbles is enhanced by the longer carbon chain alcohol, while hydrophilicity increases by reduction in length of carbon chain and/or by addition of ethylene oxide or propylene oxide in the range of from 1-5 mols per mol of alcohol sulfate. Accordingly, the flotation promoter of the invention comprises an aliphatic hydrocarbon sodium salt having a C_{16}—C_{18} carbon chain and having at least one mol of a C_2—C_3 alkylene oxide chemically combined therewith.

The substantial reduction in collection of iron pyrites from sulfide ores has permitted substantial reduction in air pollution in the vicinity of the smelter and has reduced the cost of shipping ore from the mining and flotation site to the smelter itself. The reduction in air pollution is, accordingly, accomplished at a reduced rather than increased production cost. Even if an ultimate maximum recovery of copper is required and the expenses entailed with a greater recovery of iron pyrite are to be accepted, the subsequent addition of known collectors provide a substantial increase in copper as well, so that copper recovery in such a combined system is substantially increased over prior systems, iron pyrite notwithstanding.

I claim as my invention:

1. A method of mineral flotation comprising the steps of grinding a copper-bearing sulphide ore material to release the metal values from a gangue containing iron pyrites, adding water and calcium oxide to adjust the pH to about 7 to 11.5, passing air bubbles through the solution and adding an amount of a flotation promoter comprising $R—(OCH_2CH_2)N—OSO_3Na$ and a frother thereto, where R is a C_{16}—C_{18} fatty alcohol and N lies in the range of 1 to 5 and floating said copper ore from said gangue.

2. The method of claim **1** wherein the amount of flotation promoter is about 0.02 lb./ton.

3. The method of claim **1** wherein collectors are used in combination with said flotation promoter.

4. A flotation promoter for selective water flotation of thin, finely ground, copper-bearing sulfide ores and suppression of iron pyrites therein, consisting essentially of an aliphatic hydrocarbon sodium sulfate having a C_{16}—C_{18} carbon chain chemically combined with at least one mol of ethylene oxide and chemcially combined with at least one mol of propylene oxide.

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