United States Patent [19]

Fischer

[11] **3,780,860**

[45] **Dec. 25, 1973**

[54] **FLOTATION OF COPPER SULFIDE ORES**

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[22] Filed: **May 17, 1971**

[21] Appl. No.: **144,232**

[52] **U.S. Cl.** **209/167,** 252/551

[51] **Int. Cl.** **B03d 1/06**

[58] **Field of Search** 209/166, 167; 260/98, 458; 252/551

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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 of less than 12 carbons.

8 Claims, No Drawings

FLOTATION OF COPPER SULFIDE ORES

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 finely 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, ordinarily 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 flotation 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 chalcopyrite 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 paricularly 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 minerals 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 floatation 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 percent 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 slats of fatty alcohols having less than 12 carbon atoms. Normally, I have found that the sulfates of such alcohols in this range are excessively hydrophilic and hence too frothy in use. However, I have discovered that the hydrophobicity can be increased with the addition of propylene oxide. I have found that an optimum product of acceptable hydrophobicity comprises R - $(OCH_2CHCH_3)_N$-OSO_3Na where R is a C_8 - C_{10} fatty alcohol and N is approximately 10 mols.

The use of fatty alcohols approaching C_{14} require less propylene oxide and, for example, it is desirable to add approximately 5 mols propylene oxide to C_{12} alcohols. Similarly, with decreasing carbon chain alcohols increasing mols of propylene oxide are needed to prevent excessive hydrophilicity. Although addition of propylene oxide at levels higher than 10 mols may prove difficult, I have found that the addition of ethylene oxide at levels of about 5 percent by weight based on the propoxylated alcohol will promote addition of propylene oxide. Accordingly, I prefer to include approximately one mol of ethylene oxide to the product during propoxylation.

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; namely: (1) the amount needed of conventional frother material, such as pine oil, MIBC or methyl isobutycarbinol, or DOWFROTH 250*a* proposylated 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, 0.05 lb./ton collector mix of 60 percent AF238 and 40 percent Z–6 xanthate, pine oil at 0.18 lb./ton and was ground fourteen 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 3.5, molybdenum 0.006, and zinc 0.06 per ore sample. Prior flotation of this ore has employed, in the flotation 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 3 minutes float undertaken. As a final rougher scavenger flotation stage 0.5 lb./ton $CuSO_4$, 0.4 cc of one-half percent fuel oil solution and 0.01 lb./ton collector mix were added and floated for 3 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 Example:

EXAMPLE

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: C_8 - C_{10} fatty alcohol - $(OCH_2CHCH_3)_{10}$ -OSO_3Na at 0.007 lb./ton, AF238 at 0.001 lb./ton and $CuSO_4$ at 0.5 lb./ton with 0.4 cc of one-half 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, 0.003 lb./ton Applicant's Reagent and 0.0005 lb./ton AF238 were added and the mixture floated 3 minutes; then 0.002 lb./ton applicant's reagent 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 0.002 lb/ton applicant's reagent, 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. It was found in the tests that while the total copper recovered in the Example 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 applicant's reagent 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.

Experimentation showed at the same time that lauryl alcohol sulfate, or reagents where R equals on the order of C_{12} or less, but without propylene oxide becomes excessively frothy for successful separation of copper values from sulfide ores of the type described. It has been found, however, that the fatty alcohol sulfates here described 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 achieved in the case of carbon chain molecules of less than C_{12} by adding propylene oxide in amounts on the order of 5 mols or more, with a standard optimum being a C_8 - C_{10} alcohol with approximately 10 mols of propylene oxide and a small amount of ethylene oxide where desired to facilitate addition of propylene oxide.

In a further test of the effectiveness of applicant's reagent, the well known Sierrita ore was subjected to a series of corresponding tests made with applicant's reagent and the previous standard reagent applied to Sierrita ore.

In test procedures the standard for operation comprised Sierrita ore ground 12 minutes to a fineness permitting passage of 44 percent through a 200 mesh screen and using 1.0 lb/ton CaO, .01 lb/ton Dow Z-6, and 0.0229 lb/ton AF3302, 0.10 lb/ton stove oil, all in the grind step, with an additional 0.08 lb/ton MIBC (AF-71), a compatible frother, in a 6-minute float.

In comparison procedures, the product of the present invention was applied to the same ore at the same grind fineness. There, a typical collector, Dow Z-200, was applied at the rate of 0.0076 lb/ton during grind along with a typical compatible frother such as Union Carbide R-39 (butoxy ethoxy propanol), applied at a rate of 0.023 lb/ton. The reagent of the present invention was applied at the rate of 0.004 lb/ton during the 6-minute float along with additional R-39 at the rate of 0.023 lb/ton and significantly superior results were achieved. These results are shown below:

	Standard Reagent		Applicant's Reagent	
	Weight (%)	Copper Recovery (%)	Weight (%)	Copper Recovery (%)
	3.10	93.45	3.20	94.16
	3.27	91.85	3.84	95.25
	2.98	92.86	3.74	94.80
	3.09	92.46	3.71	95.34
	2.95	92.04	3.48	94.91
	2.92	90.72	3.94	95.84
	3.38	92.15	3.97	93.68
	2.88	91.32	3.49	93.71
	3.70	94.00	3.37	94.29
	3.09	92.93	3.52	94.87
Averages	3.14	92.38	3.63	94.69

The results of the series of corresponding tests thus show that the copper recovery is greater by a small but commercially very significant amount when using applicant's reagent instead of the standard reagent.

While the above data includes a change in frother (Union Carbide R-39) and collector (Z-200), the use of the standard frother (MIBC) and collector (Z-6, AF 3302), has been found not to substantially change these results. For example, a similar Esperanza ore from the Esperanza mine of Duval Corporation, an ore body adjacent the Sierrita ore body, was so treated. The only substitution in that case was the applicant's reagent in place of AF 3302. There, the substitution of applicant's reagent also improved copper recovery significantly by 0.45 percent and molybdenum recovery by 1.18 percent.

The substantial reduction in collection of iron pyrites from sulfide ores containing that material has permitted substantial reduction in air pollution in the vicinity of the smelter and recovery 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 in the face of some reduction in pyrites rejection and the expenses entailed with a greater recovery of iron pyrite are to be accepted, the addition of known collectors to my promoter at a subsequent flotation stage provides a substantial increase in copper as well, so that copper receovery in such a combined system is substantially increased over prior systems while still obtaining some reduction in iron pyrite recovery.

I have found that the promoter reagent of the present invention has advantages in the field over systems employing alcohols with molecules in the above C_{12} range. Particularly, products in the range of C_8 - C_{10} propoxylated with 5 to 30 mols of propylene oxide are much more liquid and readily mixed with the flotation system. The availability of such molecules, when propoxylated, as herein described, has provided a superior flotation promoter not known in the art and also provided an economically advantageous flotation promoter.

I claim as my invention:

1. A flotation promoter for the selective water flotation of thin finely ground copper-bearing sulfide ores and the suppression of iron pyrites therein, finely ground state consisting essentially of an aliphatic hydrocarbon sodium sulfate having a C_8 - C_{10} carbon chain and having propylene oxide chemically combined therewith in an amount in the range of 5 to 30 mols.

2. The flotation promoter of claim **1** and wherein the propylene oxide is combined in an amount approximating 10 mols.

3. The flotation promoter of claim **1** wherein ethylene oxide in an amount approximating 5 percent by weight based on said aliphatic hydrocarbon sodium sulfate is chemically combined thereiwth.

4. The flotation promoter of claim **1** wherein said aliphatic hydrocarbon sodium sulfate consists of R $-(OCH_2CHCH_3)_N-OSO_3Na$ where R is a C_8 - C_{10} fatty alcohol and N is in excess of 5 and not more than 10.

5. A flotation promoter for selective water flotation of thin finely ground copper-bearing sulfide ores and the suppression of iron pyrites therein consisting essentially of a reagent having the general formula R - $(OCH_2CHCH_3)_{10}-OSO_3Na$ wherein R is a C_8 - C_{10} fatty alcohol.

6. The process of mineral flotation comprising the steps of grinding a copper-bearing sulfide 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 flotation promoter comprising R - $(OCH_2CHCH_3)_N-OSO_3Na$ and a frother thereto, where R is a C_8 - C_{10} fatty alcohol and N approximates 10 and floating said copper ore from said gangue.

7. The process of claim **6** wherein the amount of flotation promoter about 0.004 lb/ton.

8. The process of claim **6** wherein at least one collector is used in combination with said flotation promoter.

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