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SEPARATION OF SULFIDE ORES

Aldo De Benedictis, Berkeley, and Gerald J. Hills, San Mateo, Calif., assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware

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This invention relates to the flotation separation of sulfide ores and deals with an improved method for separating one or more metal sulfides from other metal sufides or from non-sulfide ore components whereby higher recoveries of the desired mineral of better grade can be achieved cheaply and efficiently.

Froth flotation is widely used for the separation of valuable minerals from ores in which they are present in admixture with other materials of different surface characteristics such that differential wetting of the particles of the finely ground ore takes place in the flotation process. Various treatments have been proposed as aids in effecting better separations in this way. These treatments have included certain applications of oxidizing agents in different ways. In commercial practice these have generally been found not to be economically attractive either because the cost of the oxidizer was too great or because the advantage obtained was too small to warrant the expense involved in modifying the process. Also certain of the proposed oxidizers introduce ions which can have an adverse effect on other mill operations.

An important object of the present invention is the provision of a method of treating ground sulfide ores to improve the separation of valuable minerals therefrom by froth flotation. A more particular object is to provide a method of using hydrogen peroxide in the froth flotation of sulfide ores so as to make depressants of the cyanide type more effective and thus secure more efficient separation of the desired mineral. A further object is the provision of a method of froth flotation of sulfide minerals using hydrogen peroxide at elevated temperatures with alkali metal ferrocyanide under controlled conditions of pH to separate a sulfide mineral from flotation concentrates by depressing other minerals present. A special object of the invention is the provision of an improved method for the separation of molybdenite from flotation concentrates by depressing the other minerals present and removing therefrom a molybdenite concentrate as float. A more specific object is the provision of a method for the recovery of better grade molybdenite in higher yields from copper flotation concentrates to which copper depressants have been added. A still more specific object is the improvement of the effectiveness of cyanide depressants for copper in the separation of molybdenite float therewith. Other objects and advantages of the new process will be apparent from the following description of some of the more advantageous modifications of the invention.

In accordance with the invention sulfide minerals are recovered from flotation concentrates containing the same in admixture with other minerals by adjusting the pH of the mixture to a value not greater than about 7, and adding to the concentrate hydrogen peroxide and a sulfide depressant of the cyanide type before taking off a float of the desired mineral.

Because of the special advantages of the process in the recovery of molybdenite, the invention will be first described in detail in connection with its application to this separation. It will be understood, however, that this is for purposes of simplifying the description only and that this application of the new process is intended to be exemplary only since the process is capable of application to the separation of other sulfide minerals from flotation concentrates of many kinds.

In most cases molybdenite is found as a minor constituent in ores which contain larger amounts of other metal sulfides, especially copper. It has generally been the practice in the recovery of molybdenite as a by-product with copper, to float it with the copper minerals so as to obtain a concentrate in which the MoS_2 content is usually of the order of about 0.3 to about 3% together with a much larger amount of copper—typically about 25% to 30%—although more or less copper is often present. The molybdenite may be separated from the copper using soluble starch as a depressant as described in U.S. Patent 2,070,076, whereby a copper float is separated from a molybdenite-enriched non-float. More usually, however, the copper minerals are depressed and the molybdenite floated off therefrom using a liquid hydrocarbon, for example, as a smearing collector for the molybdenite. Where collection of the concentrate initially involves the use of xanthate, the separation of the molybdenite float can be facilitated by a light oxidizing bake or roast to destroy the collector. This is not adequate where dithiophosphates are used for the collection of the copper since these are more stable than the xanthates. Copper depressants such as alkali sulfides, cyanides, cuprocyanides, ferrocyanides, etc. are added in such cases. Profitable operations have been carried out on a large scale in this way in many mills for a number of years. However, it is not feasible to obtain good recoveries of copper-free molybdenite in this way. Since the specifications for molybdenite concentrate penalize the producer for copper content, much recleaning of the molybdenite float is necessary and considerable molybdenite is left in the copper.

It has been found that molybdenite can be recovered efficiently and economically from copper concentrates by adjusting the pH of the concentrate, for example, to about 6 preferably after heating the concentrate to about 35° to 60° C., then adding a small amount of hydrogen peroxide and a ferrocyanide to the mixture to depress the copper sulfide, subjecting the mixture to a differential froth flotation and taking off the molybdenite as float.

Peroxides have been suggested in U.S. Patent 2,559,104 as equivalents to hypochlorites for use under alkaline conditions in oxidizing the collector in the flotation recovery of molybdenite. Only operations without a copper depressant are shown in the patent. When hydrogen peroxide was tested in the separation of molybdenite using a copper depressant according to established modern mill practice, no improvement could be obtained. However, it was found, unexpectedly, that the effectiveness of cyanide-type copper depressants in flotation separation of molybdenite can be substantially improved so that higher recovery and better grade of molybdenum sulfide can be obtained by using these depressants in conjunction with hydrogen peroxide added after, or simultaneously with, adjustment of the pH of the concentrate to bring it into the acid to neutral range.

Any of the cyanide-type depressants for sulfides can be used in the new process. Especially good results have been obtained with alkali metal or ammonium cyanide compounds, particularly the ferrocyanides. However, any of the other known cyanide-type depressants for sulfides can be successfully used. Examples of such other depressants are sodium cyanide, potassium cyanide, the cuprocyanides and the like. The amount of cyanide-type depressant which it will be most advantageous to use will depend to a certain extent upon the composition of the ore being treated and the nature and amount of the collector employed in the preparation of the concentrate but as a general rule amounts which provide about 0.5 to about 5 pounds of available cyanide ion per ton of concentrate will be suitable. Larger amounts can be used but will usually provide no compensating advantage for the increased cost. Amounts of the order of about 1 to

about 3 pounds per ton are ordinarily most desirable from the point of view of both economy and effectiveness.

The amount of hydrogen peroxide employed can also be varied although as a general rule amounts in the range of about 0.5 to about 5 pounds of H_2O_2 per ton of dry weight concentrate are suitable. The best results have been obtained when using sufficient hydrogen peroxide to at least partially oxidize the cyanide depressant. Thus when using sodium or potassium ferrocyanide, oxidation of at least part, and preferably a substantial part, to the ferricyanide should take place in the process of the invention. The oxidizing action of the hydrogen peroxide can be supplemented by adding other oxidizing agents such as the chlorites, but it has been found to be essential for attainment of the improved results of the invention to use hydrogen peroxide as at least one third of the total effective oxidizing agent employed in the process. Instead of hydrogen peroxide, compounds which generate hydrogen peroxide under the prevailing conditions, for instance sodium peroxide or the like, can be employed, but as a rule aqueous solutions of hydrogen peroxide of about 10% to 90% concentrate give the best results.

As previously indicated it is essential that the concentrate under treatment be treated to make it about neutral or acid. A pH of about 6 can be used, but more preferably the pH is adjusted to about 6.5 to about 7. For this adjustment any suitable acid can be added to the concentrate. Sulfuric and hydrochloric acids have the advantage of low cost and are generally preferred on this account but other acids can be used equally well. The pH may be lower than 6.5 but low pH increases corrosion and may cause undesirable side reactions with the minerals in the concentrate.

The new process can be carried out in standard flotation equipment. It has been found most advantageous

to add the hydrogen peroxide, with or without supplemental oxidizing agent, to the flotation concentrate prior to introduction of the cyanide-type depressant. The pH of the concentrate can be adjusted to the required range simultaneously but is preferably adjusted by addition of the required amount of acid before the hydrogen peroxide is added. Adjustment of the pH after the hydrogen peroxide addition is usually less desirable. For best results the process should be carried out at elevated temperature. Usually heating of the concentrate to about 30° to 60° C. is sufficient, steaming being a convenient method of bringing the mixture to the required temperature. Higher temperatures can, however, be used if desired.

The following examples illustrate in more detail, suitable methods of putting the process of the invention into practice.

EXAMPLE I

Tests on the separation of molybdenite from copper ore were made in a 2000 gram Denver laboratory flotation cell. The frother used in the copper circuit was a 3:1 mixture of hardwood creosote and methyl isobutyl carbinol, the promotor being ethyl xanthate (Dow Z–11). The copper concentrate contained 26.6% copper, mainly chalcocite with about 10% chalcopyrite, and 0.92% molybdenum sulfide. The pH of the pulp was adjusted to between 6.5 and 7.0 by adding a 1:1 sulfuric acid-water mixture. Hydrogen peroxide was then added as a 35% aqueous solution in the molybdenite rougher and cleaners as shown in the following tables, the additions being made and the pulp being stirred for one minute prior to addition of sodium ferrocyanide as copper depressant. Fuel oil and methyl isobutyl carbinol were also added as indicated in the tables. The results for three different ores are shown in Tables 1, 2 and 3.

Table 1

DIFFERENTIAL FLOTATION OF COPPER AND MOLYBDENUM

Conditions and Reagents										Chalcosite Ore, Cu Concentrate from Plant—Metallurgical Products					
Point of Addition	Conditions			Reagents, Pounds Per Ton						Product	Tons in 100 Tons Feed Using H_2O_2	Assays Using H_2O_2		Percent of Total Using H_2O_2	
	Time, Mins.	Percent Solids	Initial pH	35% H_2O_2	Ferrocyanide	Fuel Oil	MIBC	Final pH	Collecting time (min.)			Cu	MoS_2	Cu	MoS_2
Molybdenum Rougher.	4.0	20	6.6	2.6	1.3	0.09	0.11	7.6	6.0	Feed Cu Conc.	100.00	[1] 29.56	[1] 0.92	100.0	100.0
Cleaner No. 1	3.0	2.8	6.7	0.6	0.6	0.06	0.06	8.3	4.0	Mo Conc.	0.56	0.71	95.40	-------	58.4
Cleaner No. 2	2.0	-------	6.8	0.1	0.1	0.06	-------	7.7	3.0	#3 & #4 C.T.	0.26	18.60	57.80	0.2	16.4
Cleaner No. 3	2.0	-------	6.6	0.1	0.1	0.03	-------	7.3	2.0	C. Tails #2	1.07	50.00	7.86	1.8	3.3
Cleaner No. 4	2.0	-------	6.5	0.1	0.1	0.03	0.02	7.2	1.5	C. Tails #1	14.71	47.90	1.25	23.8	20.1
Total	-------	-------	-------	3.5	2.2	0.27	0.19			Mo. R. Tails	83.40	26.30	0.02	74.2	1.8

[1] Calculated.

Table 2

DIFFERENTIAL FLOTATION OF COPPER AND MOLYBDENUM

Conditions and Reagents										Chalcosite Ore, Cu Concentrate from Plant—HP-35, Hydrogen Peroxide 35 Percent—Metallurgical Products					
Point of Addition	Conditions			Reagents, Pounds Per Ton						Product	Tons in 100 Tons Feed	Assays		Percent of Total	
	Time, Mins.	Percent Solids	Initial pH	35% H_2O_2	Ferrocyanide	Fuel Oil	MIBC	Final pH	Collecting time (min.)			Cu	MoS_2	Cu	MoS_2
Molybdenum Rougher.	5.0	25	6.6	4.5	1.0	0.09	0.03	7.7	6.5	Heads	100.0	[1] 43.49	[1] 1.15	100.0	100.0
Cleaner #1	4.0	2.4	6.4	0.1	0.5	0.05	-------	7.4	3.0	Molybdenum Conc.	0.94	1.7	90.4	0.1	73.8
Cleaner #2	2.0	-------	6.6	0.1	0.5	0.05	-------	8.3	3.0	C. Tails #3	0.06	23.2	40.22	-------	2.1
Cleaner #3	2.0	-------	6.6	0.1	0.5	0.02	-------	8.4	3.0	C. Tails #2	0.62	36.8	16.22	0.5	8.7
Cleaner #4	2.0	-------	6.5	0.1	0.1	-------	-------	7.9	3.0	C. Tails #1	9.70	48.0	1.75	10.7	14.7
Total	-------	-------	-------	4.9	2.6	0.21	0.03	-------	-------	Molybdenum Rougher Tails.	88.68	43.5	0.01	88.7	0.7

[1] In another test on the same ore carried out in the same way but using only 1 pound of hydrogen peroxide in the molybdenum rougher per ton of ore, the rougher tails amounted to only 71.7 tons per 100 tons of feed and the MoS_2 content of these tails was 0.28%.

Table 3

DIFFERENTIAL FLOTATION OF COPPER AND MOLYBDENUM

Conditions and Reagents										This is a different chalcosite ore copper concentrate from laboratory—Metallurgical Products					
Point of Addition	Conditions			Reagents, Pounds Per Ton						Product	Tons in 100 Tons Feed	Assays		Percent of Total	
	Time, Mins.	Percent Solids	Initial pH	35% H_2O_2	Ferrocyanide	Fuel Oil	MIBC	Final pH	Collecting time (min.)			Cu	MoS_2	Cu	MoS_2
Molybdenum Rougher.	4.0	7.4	6.6	3.2	2.0	1.3	2.1	8.1	5.0	Feed Cu Conc	100.0	[1] 44.15	[1] 5.51	100.0	100.0
Cleaner #1	2.0		6.7	0.2	1.0	0.7		8.2	2.0	Molybdenum Conc.	4.56	1.25	91.57	0.1	75.7
Cleaner #2	2.0		6.6	0.2	0.2	0.3	0.15		2.0	#1 & #2 C. Tails	3.67	24.20	33.96	2.0	22.6
Total				3.6	3.2	2.3	2.25			Molybdenum Rougher Tails.	91.77	47.08	0.10	97.9	1.7

[1] Calculated.

EXAMPLE II

A mill test of recovery of molybdenite from ore which is principally chalcopyrite containing an average of about 0.8 to 0.9% copper was carried out. With this ore it had been possible to recover with the available equipment only about 30% of the molybdenite from the copper concentrate when processing by steaming and use of sodium cyanide depressant to effect the preliminary separation, after which the molybdenite-containing stream was concentrated, roasted and subjected to a second flotation.

In the process of the invention, the concentrate containing about 20% copper and 0.4 to 0.5% molybdenite was heated with steam to 35–40° C. and acidified with sulfuric acid. About 3 pounds of 50% hydrogen peroxide per ton of concentrate was then added with good agitation, after which 2 to 3 pounds of sodium ferrocyanide were added to depress the copper. After steady state operation was attained, the rougher tails averaged $0.1 \pm 0.04\%$ of MoS_2 compared with 0.3% in the usual method of operation without addition of the hydrogen peroxide. The heads from the first cleaner assayed 30% MoS_2 instead of the usual value of about 6%. The overall molybdenite recovery rose to about 80%. Equally good results can be obtained by use of potassium ferrocyanide or ammonium ferrocyanide in the same way.

EXAMPLE III

The necessity for using hydrogen peroxide in the new process rather than other oxidants is shown by the following results of tests carried out with the same concentrate of molybdenite-containing copper ore under comparable conditions.

The tests were made in a laboratory Fagergren flotation cell designed for operation with about 600 grams of solids at 25% dilution. The copper concentrate was obtained from regular mill operation and was steamed before treatment by boiling for 30 minutes. The steamed concentrate was poured into the cell and the pH was adjusted to 7 by adding sulfuric acid. The oxidizer was then added and the mixture was stirred for 1 to 10 minutes without addition of air. Five drops of stove oil were introduced during the final stirring to act as a molybdenite collector. Sodium ferrocyanide was then added as copper depressant in a ratio of one pound per ton of concentrate after readjusting the pH to 7. An additional 30 seconds stirring to distribute the ferrocyanide was given before the air was introduced into the cell and the froth was collected over a period of 5 minutes. The float which was removed in this flotation and the tails which remained in the cell were both filtered, dried, weighed and separately analyzed. The results obtained in this rougher separation were as follows:

Oxidant	Amount of Oxidant (lbs. per ton of concentrate)	Rougher Concentrate		Rougher Tails, Wt. percent MoS_2	Remarks
		Wt. percent of Feed Concentrate	Wt. percent of MoS_2		
50% H_2O_2	0.5	12.8	7.91	0.020	
$KMnO_4$	1	36.7	3.46	0.023	
$Na_2Cr_2O_7 \cdot 2H_2O$	1	43.5	2.27	0.013	
$NaClO_3$	2	56.3	1.45	0.011	Different concentrate. Not steamed.
NaOCl	6	82.4	Not analyzed		Do.
$CaO_2 \cdot 8H_2O$*	[1] 12.7	70.5	Not analyzed		Do.

*pH lowered to 7 every two minutes during 10 minutes stirring.
[1] Equivalent to 2 lbs. H_2O_2 per ton.

The hydrogen peroxide was substantially better in these tests, both on a performance and economic basis, than any of the other oxidants. It resulted in a concentrate of higher quality. The same difference is obtained when operating in a continuous circuit in which the tailings from successive cleaning stages are recycled to the previous stage, the tailings from the rougher being sent to the smelter. The use of hydrogen peroxide minimizes recycle load by depressing the copper mineral more completely in the rougher.

As previously pointed out, the process is applicable to the separation of a wide variety of sulfide minerals from other minerals, including other sulfide minerals, which are capable of depression by cyanides under froth flotation conditions. Representative of such separations, which can be carried out according to the method of Example I, are, for instance, the separation of bornite as float from the non-sulfide gangue with which it occurs, the separation of the chalcopyrite as float from pyrite as tailings, the separation of chalcocite float from marcosite tailings, the separation of sphalerite float from pyrrhotite as tailings, the flotation of bornite galena from arsenopyrate tailings, and the flotation of gold from arsenopyrite and/or pyrite as tailings.

It will be seen that the invention offers many advantages over prior methods of separating sulfide ores and is capable of wide variation not only with respect to the type of ores with which it may be applied but also in regard to the procedures which can be employed in putting it into practice. The invention is therefore not limited to the examples which have been given by way of illustration only, nor is it restricted by any theory proposed in explanation of the improved results which have been attained by the new process.

This application is a continuation-in-part of applicants'

copending application Serial No. 46,069, filed July 29, 1960, now abandoned.

We claim as our invention:

1. In a process for the separation of a first sulfide mineral concentrate obtained by froth flotation in the presence of an organic collector and which contains said first sulfide mineral together with a second sulfide mineral which is depressed by cyanide depressants, the improved method for recovering said first sulfide mineral in more concentrated form which comprises:

adjusting the pH of said concentrate to a value not greater than 7,

adding to the nonbasic concentrate a small amount of hydrogen peroxide, then after an interval of 1 to 10 minutes, adding said cyanide depressant,

subjecting the mixture to differential froth flotation, and

taking off said first sulfide mineral as float from tailings containing said second sulfide mineral.

2. A process in accordance with claim 1 wherein the mixture of minerals is heated to about 35° to about 60° C., an alkali metal ferrocyanide is used as the depressant and sufficient hydrogen peroxide is employed to oxidize the ferrocyanide to ferricyanide.

3. A process in accordance with claim 2 wherein a sulfide of the group consisting of sulfides of copper, lead, molybdenum and zinc is separated as float from an iron sulfide.

4. In a process for the separation of molybdenite from other metal sulfides in a concentrate obtained by froth flotation in the presence of a collector, the improvement which comprises:

adjusting the pH of the concentrate to not greater than about 7,

adding hydrogen peroxide to the nonbasic concentrate, then,

after an interval of 1 to 10 minutes, adding a cyanide depressant for said other metal sulfides,

subjecting the mixture to differential froth flotation, and

taking off molybdenite float of high concentration from tailings containing said other metal sulfide.

5. A process in accordance with claim 4 wherein a ferrocyanide is added as the depressant and sufficient oxidant is used to convert the ferrocyanide substantially to ferricyanide.

6. A process in accordance with claim 4 wherein the hydrogen peroxide is added to the concentrate at elevated temperature.

7. A process in accordance with claim 16 wherein a ferrocyanide depressant is added and the hydrogen peroxide is used in an amount sufficient to provide at least partial oxidation of the ferrocyanide to ferricyanide.

8. In a process for the separation of molybdenite from a concentrate of copper and molybdenum sulfides obtained by froth flotation in the presence of an xanthate collector, the improvement which comprises:

heating the concentrate to about 35° to about 60° C.,

adjusting the pH of the concentrate to a value between about 6 and 7,

adding about 0.5 to about 5 pounds of hydrogen peroxide per ton of concentrate to the nonbasic mixture,

after a period of 1 to 10 minutes,

adding sodium ferrocyanide as depressant for the copper sulfide,

subjecting the mixture to differential froth flotation, and

taking off molybdenite float from the depressed copper sulfide as tailings.

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