United States Patent

[11] 3,539,002

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[21] Appl. No. **697,255**
[22] Filed **Dec. 11, 1967**
[45] Patented **Nov. 10, 1970**

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[54] PROCESS FOR SEPARATING MOLYBDENITE FROM COPPER SULFIDE CONCENTRATES

7 Claims, 1 Drawing Fig.

[52] U.S. Cl. 209/3, 209/11, 209/167
[51] Int. Cl. B03b 1/00
[50] Field of Search 209/3, 11, 166, 167

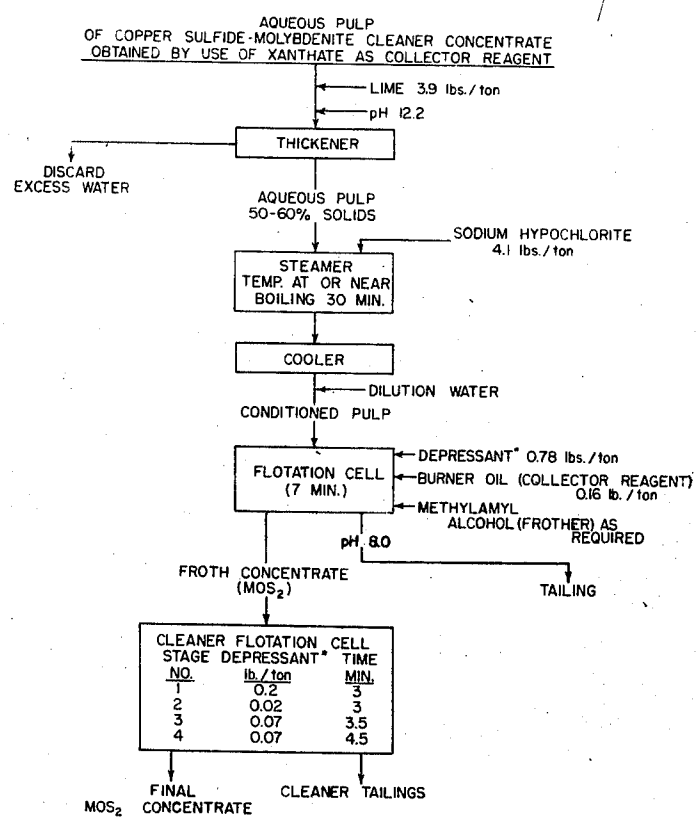
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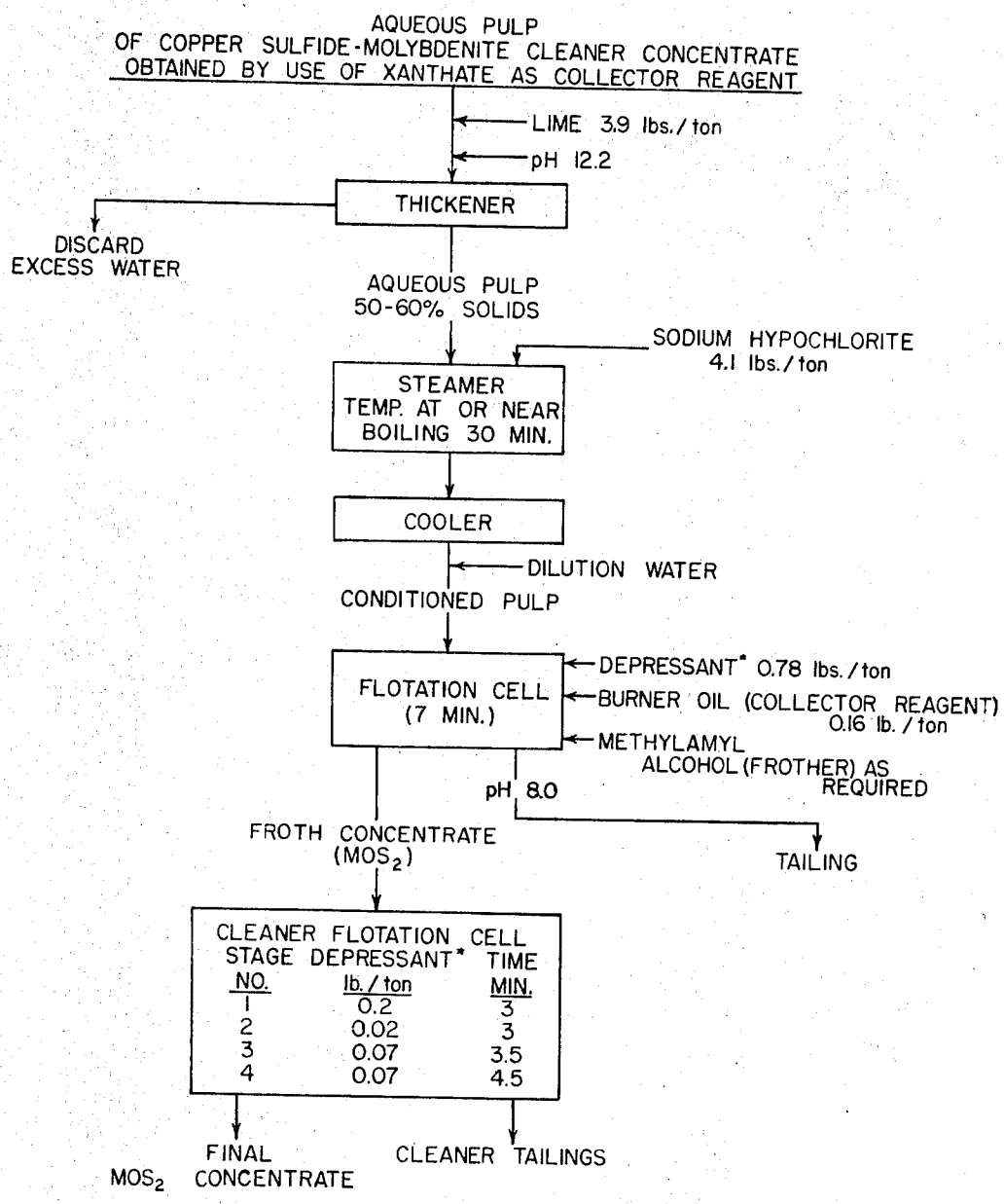
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ABSTRACT: An improved conditioning and flotation process for the separation of molybdenite from copper sulfide concentrates. A copper sulfide concentrate containing molybdenite is heated, preferably to boiling or near boiling, in the presence of an oxidizing agent such as sodium hypochlorite. Following dilution and cooling, the resulting pulp is subjected to flotation in the presence of a collector reagent for molybdenite to produce a molybdenite froth concentrate substantially free from copper sulfide minerals.



*CRUDE SODIUM THIOPHOSPHATE AS DESCRIBED IN U.S. PATENT NO. 2,492,936 REAGENT CONSUMPTION IS GIVEN IN POUNDS OF CONTAINED P_2S_5 PER TON OF PROCESS FEED SOLIDS.



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PROCESS FOR SEPARATING MOLYBDENITE FROM COPPER SULFIDE CONCENTRATES

BACKGROUND OF INVENTION

1. Field of the Invention

The invention relates to the art of froth flotation. It is particularly concerned with conditioning flotation concentrates of copper sulfide minerals containing relatively small amounts of molybdenite prior to subjecting the concentrates to differential flotation for the recovery of molybdenite mineral.

2. Description of the Prior Art

Froth flotation involves the fine grinding of mixtures of different minerals or of minerals and gangue materials and subjecting them, in the form of an aqueous suspension or pulp, to agitation and aeration in the presence of chemical reagents which produce froth. Conditions are controlled to cause particles of one or more of the component materials to cling to the bubbles of the froth and rise therewith away from the body of pulp. When finely ground copper ores are subjected to flotation, there is typically recovered a concentrate including copper sulfide, iron sulfide and molybdenite. Additional processing is required to recover the individual constituents from these concentrates.

Various flotation processes have been previously developed and widely used industrially for separating molybdenite minerals from copper sulfide-molybdenite concentrates. These processes are concerned with either floating the molybdenite while depressing the copper sulfide minerals or vice versa. The collector reagents which accumulate in the concentrate from the original ore pulp interfere with subsequent selective flotation procedures. Accordingly, the concentrates must be conditioned to remove or modify these reagents prior to reflotation. Heating of the concentrates, as a conditioning step prior to reflotation, has long been practiced, but Arbiter et al., U.S. Pat. No. 2,559,104, propose the conditioning of such a concentrate with an oxidizing agent, *e.g.* a hypochlorite, prior to reflotation for recovery of the molybdenite, to avoid the customary heating procedure.

The copper producing industry has long sought less costly and more efficient processes for separating molybdenite from copper sulfide flotation concentrates. Despite the cost of heating large volumes of flotation pulp, processes based upon steaming (heating) as a means of removing copper flotation circuit reagents and modifying mineral surfaces for reflotation have been favored and have continued to be employed in at least certain stages of an overall flotation procedure involving both roughing and cleaning stages.

SUMMARY OF THE INVENTION

In accordance with the present invention the prior art steaming process is significantly improved, from the standpoint of recovery and overall cost efficiency, by introducing an oxidizing agent into the pulp during the heating stage. Thus, instead of substituting the use of an oxidizing agent in a conditioning step for the customary conditioning by heating, we have found that results superior to those obtained by either heating or oxidizing are achieved by combining the two. Overall efficiency is enhanced and economic returns are increased by the practice of this invention.

Any oxidizing agent that functions as an oxidant for the organic collector under the conditions of the treatment may be employed. Thus, any of the oxidants suitable for use under ambient conditions, such as those taught by the aforesaid U.S. Pat. 2,559,104, may be used in accordance with the instant invention. Some oxidizing agents, *e.g.*, the dichromates, are more effective under acid conditions while others are more effective under basic conditions. Present commercial practices employ alkaline flotation conditions, so those oxidizing agents which are effective oxidants under alkaline conditions are of most immediate interest. Suitable oxidants of this type are readily determinable by those skilled in the art, but include, by way of example, the peroxides, the hypochlorites, the chlorates, and the permanganates of the alkali and alkaline earth metals to the extent they are soluble in the alkaline pulp or suspension.

The quantity of oxidant employed is highly variable and depends in part upon the oxidizing power of the particular oxidant selected for use. An effective amount of the oxidant is all that is required. By "effective amount" is meant an amount sufficient to result in significantly more effective treatment of the concentrate that would result from the application of heat alone. Skilled operators can readily determine the amounts of oxidizing agent required by observing the characteristics of the treated concentrate when it is fed to a differential flotation circuit. Inadequately treated concentrate carries undesirable amounts of frother into the flotation machine. The presence of this frother is immediately apparent to the operator. Amounts of oxidizing agent less than the amounts employed at ambient temperature in accordance with the prior art are effective in the practice of this invention. The upper limit to the quantity of oxidizing agent present is generally established by economic rather than process considerations. When sodium hypochlorite is the oxidizing agent employed, the amount used typically ranges from about 1 to about 10 pounds per ton of the solids fed to the process. Other oxidizing agents are used in amounts sufficient to provide oxidizing power equivalent to between about 1 and about 10 pounds of sodium hypochlorite on the aforestated basis.

According to this invention, the concentrate is supplied to a treatment vessel in the form of an aqueous suspension or pulp. An effective amount of oxidizing agent is supplied to the pulp. The pulp is then subjected to heating for sufficient duration to effect the treatment. The temperature of the pulp is raised to substantially above ambient, *i.e.*, above the equilibrium temperature of the concentrate due to its being processed under ambient conditions. Although heating to lesser degrees is beneficial, the pulp is ideally heated to at least approximately its normal boiling point. At these temperatures, treatment times as low as 5 minutes are often sufficient. In commercial practice, somewhat longer treatment times, *e.g.*, about 15 to about 30 minutes, rarely more than 1 hour, are preferred. The temperature of the treatment may be raised to above the normal boiling point of the pulp, if desired, by employing elevated pressure conditions.

According to the most preferred embodiments of the invention, the treatment is conducted under conditions of high lime alkalinity. That is, the pH of the pulp is raised to above about 11, ideally between about 11 to about 12.2 by the addition of lime prior to or during the treatment. It is also desirable to adjust the water content of the pulp to provide about 50 to about 60 percent by weight solids in the pulp during the claimed treatment.

THE DRAWING

The flowsheet in the accompanying drawing illustrates a preferred embodiment of the process applied to a concentrate containing both molybdenite and copper sulfide minerals. The procedures indicated represent the best mode presently contemplated of carrying out the invention.

DESCRIPTION OF THE ILLUSTRATED EMBODIMENT

As illustrated, feed concentrate, in the form of an aqueous pulp, is preferably first conditioned with lime to raise the pH above 11, *e.g.* to 12.2. It is then partially dewatered by thickening in customary manner to produce an aqueous pulp containing 50 to 60 percent solids. The oxidizing agent, which is preferably sodium hypochlorite because of its availability, low cost, and excellent performance, is added on the basis of 4.1 pounds per ton of solids fed to the process. The resulting pulp is then subjected to the usual steaming treatment, wherein live steam is injected thereinto to raise it to or near its boiling point. The pulp is held at elevated temperature for an appropriate duration, typically about 30 minutes, after which it is cooled and diluted with water. Sufficient water is added to

effect a pulp density suitable for the subsequent reflotation step by which molybdenite is floated away from the copper and iron sulfides with which it is mixed.

Flotation of the molybdenite is carried out in customary manner, with the usual collector and frother reagents specific to molybdenite. Nokes reagent can be used, as indicated, as a supplementary depressant for the copper sulfide minerals. In the illustrated instance, the rougher flotation stage was followed by four cleaner stages to produce the final MoS_2 concentrate. The number of stages employed in any given instance will, of course, depend upon the particular ore concerned. Small additions of the Nokes reagent are advantageously made in the several cleaning stages to assist the cleaning operation.

It has been found that not only are the amounts of chemical reagents and processing stages reduced over prior practices, but the economic recovery of molybdenite is enhanced in terms of grade of the concentrate recovered, percent MoS_2 recovered, or both.

Example I

As an example of the effectiveness of the present process, the following comparative tests are given:

TEST NO. 1

This test was carried out in standard laboratory equipment utilizing 1,530 grams of a copper sulfide-molybdenite flotation concentrate analyzing as follows:

MoS_2, 0.43%
Cu, 26.60%

and conditioned and processed as indicated in the flowsheet. The rougher concentrate contained 98.98 percent of the MoS_2 present in the initial feed. Three stages of cleaning yielded a concentrate assaying 94.5 percent MoS_2 with a recovery of 85.55 percent of the MoS_2 present in the initial feed; four stages yielded a concentrate assaying 97.6 percent MoS_2 with a recovery of 72.52 percent of the MoS_2 present in the initial feed.

A table of metallurgical results follows:

		Molybdenite		Copper	
	Weight, percent	Percent	Percent dist.	Percent	Percent dist.
Tailing (sink)	88.49	0.005	1.02	26.5	88.17
No. 1 Cl. tailing	9.30	0.18	3.88	28.6	10.00
No. 2 Cl. tailing	1.62	1.03	3.88	27.0	1.64
No. 3 Cl. tailing	0.20	12.2	5.67	21.8	0.16
No. 4 Cl. tailing	0.07	80.1	13.03	6.50	0.02
MoS_2 Cl. conc	0.32	97.6	72.52	0.70	0.01
Calc. feed	100.00	0.43	100.00	26.6	100.00

TEST NO. 2

This test was made on another batch (1,518 grams) of the copper sulfide-molybdenite concentrate of test no. 1, but followed the so-called "Morenci" process of the aforementioned prior art U.S. Pat. No. 2,559,104. Thus, an oxidizing agent was employed instead of heating to modify pulp and mineral conditions.

Based on the solids in the pulp, the initial feed was treated, with 4.4 pounds/ton of lime to raise the pH to 12.2 and was thickened as in the first test. It was then conditioned with 6.2 pounds/ton of sulfuric acid, 32.7 pounds/ton of sodium hypochlorite, 26.7 pounds/ton of sodium ferrocyanide, and 9.36 pounds/ton of burner oil and subjected to rougher flotation for 7 minutes at pH 7.6. The MoS_2 concentrate from this stage was then cleaned twice, 2.3 pounds/ton sodium hypochlorite and 4.4 pounds/ton sodium ferrocyanide being used for the first cleaning stage (7 minutes), and 0.4 pounds/ton of sodium cyanide for the second cleaning stage (3 minutes).

The metallurgical results were as follows:

		Molybdenite		Copper	
	Weight, percent	Percent	Percent dist.	Percent	Percent dist.
Tailing (sink)	53.15	0.022	2.19	22.6	45.44
No. 1 Cl. tailing	40.36	0.10	7.55	31.3	47.79
No. 2 Cl. tailing	2.07	0.28	1.08	30.9	2.42
MoS_2Cl. conc	4.42	10.8	89.18	26.0	4.35
Calc. feed	100.00	0.54	100.00	26.4	100.00

The rougher stages of the flotation procedure produces a low grade froth containing 97.81 percent of the molybdenite. The two cleaning stages produced a concentrate assaying 10.8 percent MoS_2 with an 89.18 percent recovery. These results compare with the 91.22 percent Recovery from froth concentrate assaying 66.3 percent MoS_2 in the first two cleaning stages of test no. 1, where the process of the invention was employed. In the latter, only 4.1 pounds/ton of sodium hypochlorite was used, while in the former 35 pounds/ton of the hypochlorite and 31.1 pounds/ton of sodium ferrocyanide were used.

Thus, it can be seen that the process of the invention yielded marketable grade concentrates with three stages of cleaning, while the prior art process produced concentrates of only 10.8 percent grade. In all, reagent consumption was considerably reduced by the process of the invention.

EXAMPLE II

This example compares results from several laboratory flotation tests. Tests A and B correspond to present commercial practices. Tests C, D, E, and F are illustrative of the present invention. In each of the tests, an aqueous pulp of copper sulfide-molybdenite cleaner concentrate, collected by a xanthate collector in the presence of pine oil, was mixed with lime on the basis of about 6.5 pounds/ton of solids to adjust the pH of the suspension to about 12.2. The pulp was thickened to about 50—55 percent solids by the removal of excess water. The thickened concentrate was treated for 30 minutes by boiling, contact by an oxidant, or both, as indicated in the table. In test C, D, E and F, the oxidant was added just before the pulp reached boiling temperature. The conditioned pulp was cooled and diluted to suitable pulp density for feed to the molybdenite flotation machines. The following table reports metallurgical values.

	Test					
	A	B	C	D	E	F
	Steam					
	No	Yes	Yes	Yes	Yes	Yes
	Oxidant					
	NaOCl	No	NaOCl	$KMnO_4$	$KClO_3$	H_2O_2
Tailing (sink):						
Weight, percent	45.87	93.46	95.07	96.65	96.23	95.76
MoS_2, percent	.07	.07	.07	.09	.06	.05
Cu, percent	8.21	18.1	17.1	19.3	17.5	18.1
Distr. MoS_2, percent	5.76	11.61	10.75	13.96	11.07	8.94
Distr. Cu, percent	19.90	91.96	93.96	97.39	96.31	96.69
MoS_2 rougher concentrate:						
Weight, percent	54.13	6.54	4.93	3.35	3.77	4.24
MoS_2, percent	.97	7.61	11.2	16.0	12.3	11.5
Cu, percent	28.0	22.6	21.2	14.9	17.1	18.4
Distr. MoS_2, percent	94.24	88.39	89.25	86.04	88.93	91.06
Distr. Cu, percent	80.10	8.04	6.04	2.61	3.69	4.31
Calculated feed:						
MoS_2, percent	.56	.56	.63	.62	.52	.54
Cu, percent	18.9	18.4	17.3	19.2	17.5	18.1
Reagents, lb./ton feed solids:						
Lime	6.5	6.5	6.5	6.5	6.5	6.5
Oxidant	4.2	-------	4.2	6.0	2.3	2.0
Burner oil	.2	.2	.2	.2	.2	.2

Methyl amyl alcohol added as required to maintain froth

Whereas this invention is here described and illustrated with respect to certain forms thereof, it is to be understood that variations are possible without departing from the inventive subject matter particularly pointed out in the following claims.

We claim:

1. In the conditioning of copper sulfide-molybdenite flotation concentrates containing accumulated collector reagent, thereby to facilitate separation of the molybdenite from the copper sulfides by a subsequent flotation step, the improvement which comprises introducing into an aqueous suspension of said flotation concentrates at atmospheric pressure an oxidizing agent, other than air; and subsequently heating at atmospheric pressure and under alkaline conditions said aqueous suspension with said oxidizing agent therein at a temperature and for a period of time sufficient to oxidize said collector reagent.

2. The improvement of claim 1 wherein the aqueous suspension is heated to a temperature at least approximately its boiling point.

3. The improvement of claim 1 wherein the oxidizing agent is present in an amount to provide oxidizing power equivalent to between about 1 and about 10 pounds of sodium hypochlorite per ton of process feed solids.

4. The process of claim 1 wherein the solids content of the aqueous pulp is adjusted to about 50 to about 60 percent solids before the pulp is subjected to heating.

5. The improvement of claim 1 wherein the heating is conducted under conditions of high lime alkalinity.

6. The improvement of claim 5 wherein the pH of the aqueous suspension is adjusted to between about 11 and about 12.2 during heating and the oxidizing agent employed is an oxidant for the flotation reagent under alkaline conditions.

7. The improvement of claim 6 wherein the oxidant is selected from the group consisting of the inorganic peroxides, hypochlorites, chlorates and permanganates which are soluble in the alkaline aqueous suspension.