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3,435,952

PROCESS AND REAGENT FOR RECOVERY OF MOLYBDENITE FROM COPPER SULFIDE-MOLYBDENITE FLOTATION CONCENTRATES

Burton Corbett, Miami, Ariz., assignor to Miami Copper Company, Division of Tennessee Corporation, New York, N.Y., a corporation of Delaware
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16 Claims

ABSTRACT OF THE DISCLOSURE

A flotation reagent useful as a depressant of copper and iron sulfides, but not molybdenum sulfide, is prepared by mixing an arsenical compound selected from yellow or red arsenic sulfides and arsenic oxide with Nokes reagent (phosphorous pentasulphide in aqueous NaOH). Preferred reagents are produced by mixing the arsenical compound, preferably arsenic trioxide, with Nokes reagent containing a higher-than-ordinary proportion of NaOH.

This invention relates to processes of differential froth flotation, involving the depression of various metallic sulfide minerals while floating various other sulfide minerals, and to chemical reagents for the purpose. It is primarily concerned with the depression of copper and iron sulfide minerals while floating molybdenite.

In Nokes U.S. Patent No. 2,811,255 granted Oct. 29, 1957, there is given a generalized background of the art of recovering, from copper sulfide flotation concentrates, the relatively small proportion of molybdenum sulfide mineral, i.e., molybdenite, that is contained therein in instances where the copper sulfide ores being treated contain small percentages of molybdenum values, and there is disclosed a process utilizing the so-called "Nokes" reagent of U.S. Patent No. 2,492,936 for overcoming certain difficulties encountered in the previous use of such reagent as a depressant for the copper and iron sulfide minerals associated with the molybdenite. Thus, although use of the "Nokes" reagent has eliminated the need for an expensive heating step, such as roasting, boiling, or autoclaving, to be applied to the copper sulfide flotation concentrates before differential flotation for the recovery of molybdenite, it has required a preconditioning treatment involving washing, filtration, and re-pulping for most successful application.

The flotation reagent of the present invention is related to the "Nokes" reagent, in that it is derived from the most commonly used form thereof, i.e., from sodium thiophosphate (Example 2, Nokes et al. Patent No. 2,492,936), but it is unique, in that it is a reaction product of sodium thiophosphate and an arsenical selected from the group consisting of arsenic trioxide and arsenic sulfide, the arsenic trioxide being preferred because of its availability and ease of handling.

This reaction product is highly stable, in contrast to the Nokes sodium thiophosphate reagent, which breaks down quite readily to yield hydrogen sulfide. Used as a depressant for copper and iron sulfides during the flotation of molybdenite, it does not require the application of expensive processing or conditioning steps, such as roasting, autoclaving, or filtering, to the flotation pulp in advance of the flotation operation, nor does it require the use of other expensive reagents for accomplishing the desired depression of copper and iron sulfides. Moreover, it operates effectively in a highly alkaline, non-corrosive circuit; in fact, usually the higher alkalinity, the better the reagent performs. Accordingly, operating and capital costs are

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low, and both ores and ore concentrates lower in grade than usual can be treated profitably.

A feature of the invention is the use of a greater ratio of sodium hydroxide to phosphorous pentasulphide in the preparation of the sodium thiophosphate than is suggested by the Nokes et al. patent, which results in greater stability for the sodium thiophosphate and a superior reaction product in accordance with this invention. However, it is not necessary that this greater ratio be used; reasonably satisfactory results but with reduced stability and reduced effectiveness, can be obtained by using the ratio indicated in the Nokes patent.

Addition of the arsenic trioxide or sulfide to a sodium thiophosphate solution produces a reaction that changes the yellow color of the solution to crystal clear. The resulting solution is the reagent of the invention.

As disclosed in the aforementioned Nokes et al. U.S. Patent No. 2,492,936, the sodium thiophosphate solution is produced by reacting an aqueous solution of sodium hydroxide (NaOH) and phosphorous pentasulphide (P_2S_5) in the ratio of 13 parts by weight NaOH to 10 parts by weight P_2S_5 . However, as previously mentioned, instead of following the Nokes ratio, the process of this invention preferably utilizes an increased quantity of the NaOH, resulting in a more stable sodium thiophosphate solution that will not readily decompose. Although this ratio can be increased, so that a great excess of NaOH is present, the ratio presently preferred from the standpoint of economy as well as stability is 14.3 parts NaOH to 10 parts P_2S_5 . However, stability is increased correspondingly with an increase of the quantity of NaOH above the 13 parts set forth in the patent.

Tests have indicated that when arsenic trioxide is added to the sodium thiophosphate solution prepared in accordance with the preferred practice of this invention, it is effective in the amount of about 2.4 parts by weight. That is, when 14.3 parts sodium hydroxide and 10 parts phosphorous pentasulphide are used, 2.4 parts of arsenic trioxide will produce a highly satisfactory reaction product. Smaller amounts of the arsenic reactant will produce a reagent giving poorer results, while a considerably larger amount will yield only minor improvement, if any.

In preparing the reagent of this invention in the laboratory, it is convenient to dissolve 14.3 grams of sodium hydroxide in somewhat less than 200 cc. of water in any suitable container such as a glass beaker. The heat of solution is allowed to dissipate, either by permitting the solution to stand at room temperature until cool, or preferably by cooling the container with cold running water. To the cooled sodium hydroxide solution are slowly added 10 grams of phosphorous pentasulphide, with constant stirring of the solution while continuously cooling the container with cold running water. Best results have been obtained when the temperature of solution is maintained below 50° C. during addition of the phosphorous pentasulphide. The reaction is completed in about 10 minutes, and volume is brought up to 200 cc. by the addition of water. Thereupon, 2.4 grams of arsenic trioxide is added slowly to the so-derived sodium thiophosphate solution, with constant stirring.

The reagent can be made in quantities larger than 200 cc. by using the same relative proportions of water, sodium hydroxide, phosphorous pentasulphide and arsenic trioxide. However, due to the greater amount of heat evolved in the larger quantities, more care is required in heat dissipation. Also, care must be taken in the preparation of the sodium thiophosphate solution to completely dissolve the sodium hydroxide, or decomposition of the sodium thiophosphate will take place rapidly, with considerable evolution of hydrogen sulfide gas.

When arsenic sulfide is used instead of the trioxide, it can be either the red or yellow variety. As previously men-

tioned, however, the trioxide is preferred because of its availability and ease of handling.

The reagent has been found to perform better under conditions of high alkalinity, although it performs satisfactorily under all alkaline conditions. Best results are obtained when the pH of the flotation pulp is no less than 11.4 and preferably about 12.0.

Because lime circuits are usual for copper flotation, and because lime is alkaline, regular mill water from such circuits can be advantageously utilized in the present process to give a flotation pulp of the desired alkalinity. This is an important factor in most mills where water must be conserved. It is also important from the standpoint of eliminating need for filtration and repulping of the general copper sulfide flotation concentrates or other metallic sulfide concentrates used prior to flotation for the recovery of molybdenite.

A conventional collector reagent for the molybdenite, such as kerosene, is used along with the depressant reagent of this invention in a flotation procedure that is standard except for the presence of the novel depressant reagent.

Numerous tests on final copper concentrate samples, taken at various times during normal operations at the Copper Cities mill of the Miami Copper Division of Tennessee Corporation, Miami, Ariz., and varying in molybdenite content, have been made in accordance with the following procedure:

A 600 gram dry weight sample of concentrate was pulped in a Fagergren laboratory flotation machine with enough mill circuit water to give a final pulp density of 20% solids, A 2.0 g. quantity of calcium hydroxide was added and the pulp conditioned, with air valve closed, for approximately 30 seconds; three drops of kerosene distillate and 5 ml. of the novel depressant reagent, made with arsenic trioxide as previously described, were then added and the pulp conditioned, with the air valve closed, for approximately 30 seconds. The air valve was then opened and the resulting froth skimmed for 5 minutes. The froth concentrates were caught, dried, weighed and assayed. The tails were filtered, dried, weighed and assayed, and from these data the percent weight of concentrate and the distribution of the molybdenite were calculated.

The results of typical tests are shown in the following table:

Test No.	Product	Percent wt.	Assay, percent MoS ₂	Distribution, percent
I.....	Hds.....	100.00	0.317	100.0
	Conc.....	1.72	17.000	91.5
	Tls.....	98.28	0.028	8.5
II.....	Hds.....	100.00	0.229	100.0
	Conc.....	2.10	9.600	88.5
	Tls.....	97.90	0.028	11.5
III.....	Hds.....	100.00	0.577	100.0
	Conc.....	2.92	18.800	95.3
	Tls.....	97.08	0.031	4.7
IV.....	Hds.....	100.00	0.600	100.0
	Conc.....	2.35	24.100	94.3
	Tls.....	97.65	0.035	5.7
V.....	Hds.....	100.00	0.340	100.0
	Conc.....	1.08	30.100	96.0
	Tls.....	98.92	0.015	4.0
VI.....	Hds.....	100.00	0.320	100.0
	Conc.....	3.83	7.900	94.5
	Tls.....	96.17	0.018	5.5

It will be noted from the above that conditioning time is short and that no special procedures are required.

Although sodium thiophosphate is much preferred because of availability, low cost, and the excellent results attained from the reagent of this invention produced therefrom, other alkali metal thiophosphates may also be employed, but generally with less satisfaction, for example, calcium thiophosphate is much less stable than is sodium thiophosphate.

I claim:

1. A flotation reagent useful as a depressant for various metallic sulfides such as copper sulfides and iron sulfides but not molybdenum sulfides, comprising the reaction mixture of an aqueous alkali metal thiophosphate solu-

tion and an arsenical compound selected from the group consisting of arsenic trioxide, red arsenic sulfide and yellow arsenic sulfide.

2. A flotation reagent useful as a depressant for various metallic sulfides such as copper sulfides and iron sulfides but not molybdenum sulfides, consisting essentially of the reaction mixture of an aqueous sodium thiophosphate solution and an arsenical compound selected from the group consisting of arsenic trioxide, red arsenic sulfide and yellow arsenic sulfide.

3. The flotation reagent recited in claim 1, wherein the sodium thiophosphate is the reaction mixture of sodium hydroxide and phosphorous pentasulfide in the ratio by weight of at least about 13 parts of the sodium hydroxide to about 10 parts of the phosphorous pentasulfide.

4. The flotation reagent recited in claim 3, wherein the ratio is about 14.3 sodium hydroxide to about 10 phosphorous pentasulfide, and wherein the final product is the reaction mixture of the sodium thiophosphate solution and about 2.4 parts of arsenic trioxide.

5. A method for producing a depressant flotation reagent for various metallic sulfides such as copper sulfides and iron sulfides but not molybdenum sulfides, comprising forming an aqueous solution of an alkali metal hydroxide; mixing phosphorous pentasulfide and said solution to form a thiophosphate solution; and mixing said thiophosphate solution with an arsenical compound selected from the group consisting of arsenic trioxide, red arsenic sulfide and yellow arsenic sulfide.

6. The method for producing a depressant flotation reagent as recited in claim 5, wherein the alkali metal hydroxide is sodium hydroxide and the ratio by weight of the sodium hydroxide to the phosphorous pentasulfide is greater than 13 to 10.

7. The method for producing a flotation depressant reagent as recited in claim 6, wherein the ratio by weight of sodium hydroxide to phosphorous pentasulfide is about 14.3 to 10, and the arsenical compound is arsenic trioxide in the amount of about 2.4 parts by weight.

8. A froth flotation process, comprising subjecting an aqueous pulp containing a molybdenum sulfide mineral and one or more other sulfide minerals, such as a copper sulfide mineral and an iron sulfide mineral, to froth flotation in the presence of a collector reagent for the molybdenum sulfide mineral and a depressant reagent for the said one or more other sulfide minerals, said depressant reagent being the reagent of claim 1.

9. The froth flotation process of claim 8, wherein the depressant reagent is the reagent of claim 2.

10. The froth flotation process of claim 8, wherein the depressant reagent is the reagent of claim 3.

11. The froth flotation process of claim 8, wherein the depressant reagent is the reagent of claim 4.

12. The flotation reagent of claim 1 wherein the arsenical compound is arsenic trioxide.

13. The flotation reagent of claim 2 wherein the arsenical compound is arsenic trioxide.

14. The method of claim 5 wherein the arsenical compound is arsenic trioxide.

15. The process of claim 8 wherein the depressant reagent is the reagent of claim 12.

16. The process of claim 8 wherein the depressant reagent is the reagent of claim 13.

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HARRY B. THORNTON, *Primary Examiner*.

ROBERT HALPER, *Assistant Examiner*.

U.S. CI. X.R.