United States Patent [19]
Mercade

[11] 3,893,915
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[54] FLUORSPAR ORE FLOTATION

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[22] Filed: **June 14, 1973**

[21] Appl. No.: **369,892**

[52] **U.S. Cl.** **209/166**
[51] **Int. Cl.** **B03d 1/02**
[58] **Field of Search** 209/166, 167

[56] **References Cited**

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[57] **ABSTRACT**

Flotation of fluorite from calcareous gangue with a fatty acid collector in an aqueous alkaline ore pulp is improved by adding an alkali metal bisulfite salt or an alkali metal thiosulfate salt before adding the collector.

5 Claims, No Drawings

FLUORSPAR ORE FLOTATION

BACKGROUND OF THE INVENTION

Fluorite (CaF_2) frequently occurs in fluorspar ores containing appreciable quantities of calcareous gangue, especially calcite. Fluorite can be floated from the calcite and silica and silicate gangue minerals with a fatty acid collector. Preferably silicate dispersant is employed. However, fluorite and calcite have similar surface properties and the grades and/or recoveries of the fluorite concentrates generally leave something to be desired when the ores are rich in calcite.

Various reagents have been suggested for use to improve the selective flotation of fluorite from calcite. Among these reagents are metal salts, which may be added to sodium silicate to form gels, oxidants such as dichromate salts and gangue depressants such as quebracho.

An object of the invention is to improve the efficiency with which fluorite can be floated from calcereous gangue with a fatty acid collector in an aqueous alkaline ore pulp.

The essence of the present invention resides in adding a small amount of an alkali metal bisulfite salt, an alkali metal thiosulfate salt or mixtures thereof, to an aqueous alkaline pulp of fluorspar ore before adding a fatty acid collector and subjecting the ore pulp to froth flotation to produce a fluorite-rich froth product and a tailings which is a concentrate of calcareous and siliceous gangue.

The alkali metal bisulfite and thiosulfate salts used in the practice of my invention are capable of reacting with calcium ions to form highly soluble calcium salts. It is believed that the outstanding effectiveness of such salts in improving the selective flotation of fluorite from calcite is attributable to the selective solubilization of calcium from the fluorite mineral particles. This in turn results in improved collection by the fatty acid reagent. Initially, the beneficial effect of these salts on the selective flotation of fluorite from calcite was attributable to the fact that the salts were functioning as reducing agents. However, it was found that a wide variety of other reducing agents, including a hydrosulfite salt, were not beneficial. Consequently, the initial theory was discarded.

DESCRIPTION OF THE INVENTION

In putting the invention into practice, the fluorspar ore is ground to a size sufficiently small to liberate the fluorite, e.g., 100 mesh (Tyler) or finer. The pulp is then alkalized by adding soda ash or caustic soda. Preferably, the pulp is dispersed with a mineral dispersant such as sodium silicate or a sodium silicate-polyvalent metal salt hydrosol of the type used in the flotation process described in U.S. Pat. No. 3,337,048. An alkali metal bisulfite or thiosulfate salt is generally used in amount in the range of about ¼ to 2 lbs./ton. The salt is added before adding the fatty collector which may be, for example, oleic acid or tall oil. Preferably, starvation amounts of collector reagent are used. Flotation is carried out at a pH in the range of 8.0 to 10.5, preferably about 9.5.

Preliminary sulfide flotation is recommended when sulfide minerals are present in the gangue. Conventional sulfide collectors may be employed.

The following examples are given for illustrative purposes.

A chemical assay of the starting ore used in the examples indicated that it contained 23.2 percent CaF_2. Gangue was predominantly $CaCO_3$ with some silica and sulfide minerals also present.

EXAMPLE I

A sample of the minus 10 mesh ore was wet ground to minus 325 mesh (Tyler) in a rod mill. The ore was pulped in water at about 25 percent solids. The pulp was alkalized by adding soda ash, 10 lbs./ton and then it was dispersed by incorporating a hydrosol obtained by mixing a 1 percent solution of $ZnSO_4.7H_2O$ with a solution of "O" sodium silicate diluted to 5 percent and containing the equivalent of 15 lbs./ton "O" and 1.9 lbs./ton $ZnSO_4.7H_2O$.

A sulfide flotation was carried out after adjusting pH to 9.5 with soda ash and adding Z–6 (potassium amyl xanthate) in amount of 0.25 lb./ton. "Dowfroth 250" was used as the frother in amount of 0.20 lb./ton. After conditioning the pulp for 5 minutes, a sulfide froth was removed for 5 minutes.

In one test carried out in accordance with this invention, portions of the tailings from the sulfide flotation were treated with sodium bisulfite (0.5 lb./ton) added as a 1 percent aqueous solution, followed by conditioning for 5 minutes, addition of oleic acid (0.36 lb./ton), followed by conditioning for 12 minutes. The conditioned pulp was subjected to froth flotation using a Denver Sub-A cell operating at 900 r.p.m. The rougher froth concentrate was cleaned 3 times by flotation. The procedure was repeated using 1 lb./ton sodium bisulfite. The froth products using 0.5 and 1.0 lb./ton bisulfite as activators were assayed and recoveries were obtained by weighing products.

A control test was carried out with another portion of the tailings from the preliminary sulfide flotation.

Results are summarized in table form.

The term "flotation index" which is used in the table is a calculated value that is indicative of flotation efficiency.

The following equation is used to compute flotation index.

$$\text{Flotation index} = 100 = \sqrt{\frac{\text{grade X Recovery (actual)}}{\text{grade X Recovery (perfect separation)}}}$$

The grade of a perfect separation would be 100 percent and recovery would be 100 percent.

ACTIVATION OF FLUORITE WITH SODIUM BISULFITE-OLEIC ACID COLLECTOR, pH 9.5

$NaHSO_3$, lb./ton	Flotation Concentrate			Flotation Index
	Wt. %	CaF_2, %	Recovery,* %	
0.5	22.7	81.8	80.1	80.9
1.0	18.0	92.5	71.7	81.4
0 (control)	18.9	82.7	67.4	74.6

*based on head assay of 23.2 percent $CaCF_2$

Data in the table show that the flotation index was improved by adding 0.5 and 1 lb./ton sodium bisulfite to the pulp before conditioning the pulp with oleic acid and floating fluorite. The higher index was attributed to both higher grade and higher recovery when using 1 lb./ton $NaHSO_3$. When using 0.5 lb./ton $NaHSO_3$ the higher index value was due to the higher recovery.

EXAMPLE II

The experimental and control tests of Example I were repeated with the exception that fluorite was floated at pH 8.5. In other tests, fluorite was floated at pH 10.5. In tests carried out in accordance with the invention, sodium bisulfite was added in amount of 0.5 lb./ton and it was incorporated into the pulp before adding oleic acid (0.36 lb./ton). It was found that the sodium bisulfite improved grade and increased flotation index at pH values of 8.5 and 10.5. However, recoveries and flotation indices were better when using sodium bisulfite at pH 9.5 (Example I) than they were when flotation was carried out with the same amount of sodium bisulfite at pH 8.5 or 10.5.

EXAMPLE III

The procedure of Example I was repeated with another source of the ore pulp using 1 lb./ton sodium thiosulfate. The thiosulfate salt was added as a 1 percent solution. The results were similar to those obtained

with 1 lb./ton sodium bisulfite.

I claim:

1. In the froth flotation of fluorite from a calcareous gangue with a fatty acid collector for the fluorite in an aqueous alkaline ore pulp, the improvement which consists in activating said pulp for the selective flotation of fluorite by adding a material selected from the group consisting of alkali metal bisulfite, alkali metal thiosulfate and mixtures thereof.

2. The process of claim **1** wherein said alkali metal thiosulfate is sodium thiosulfate used in amount within the range of ¼ to 2 lbs./ton.

3. The process of claim **2** wherein the fluorite is floated at a pH of about 9.5.

4. The process of claim **2** wherein said alkaline ore pulp is dispersed with sodium silicate.

5. In the froth flotation of fluorite from a calcareous gangue with a fatty acid collector for the fluorite in an aqueous alkaline ore pulp, the improvement which comprises activating said pulp for the selective flotation of fluorite by adding sodium bisulfite in amount within the range of ¼ to 2 lbs./ton.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,893,915
DATED : July 8, 1975
INVENTOR(S) : Venancio V. Mercade

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2 - line 46, the equation should read:

$$\text{Flotation index} = 100 \times \sqrt{\frac{\text{grade X recovery (actual)}}{\text{grade X recovery (perfect separation)}}}$$

Signed and Sealed this

sixteenth **Day of** *September 1975*

[SEAL]

Attest:

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Commissioner of Patents and Trademarks