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FROTH FLOTATION OF OIL-BEARING METAL SULFIDE WASTES

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R. L. Miller

Idaho National Engineering
Laboratory
P. O. Box 1625
Idaho Falls, ID 83415-2210

R. L Atwood and Yi Ye

Advanced Processing Technologies
Inc.
P. O. Box 1855
Salt Lake City, UT 84110-1855

Abstract

An industrial wastewater, including plating wastes, is treated with sodium sulfide and ferrous sulfate to form a sulfide-oxide precipitate containing chromium and other toxic metals. Hydrocarbons, in the water, coat the sulfide-oxide particles, impeding metal recovery. Froth flotation, without reagent addition, was found to recover 93.9% of the solids from the sludge with simultaneous rejection of 89% of the water. Methyl isobutyl carbinol (MIBC) improved recovery and potassium amyl xanthate improved both recovery and grade. The process design has wastewater feed (without MIBC) to the rougher circuit. The rougher concentrate is conditioned with MIBC and fed to a cleaner circuit to achieve a high grade concentrate. About 95% of the water is recirculated to the waste treatment plant.

Introduction

Froth flotation has been used to treat oily wastes for some time and is often the preferred technology for separating oil from oil tanker ballast, from oil well production waters, and from oil processing facilities.[1,2] In the mineral processing industry, froth flotation is used to concentrate copper, phosphates, and iron from their ores, and reduce the sulfur content of coal.[3] Xanthates are the most frequently used collectors for sulfide ore, so potassium amyl xanthate was tested in the present study. Molybdenite, MoS_2, however, is usually floated using fuel oil or kerosene as the collector. This mineral-collector combination is thought to have a surface similar to the oil-bearing metal sulfides being studied here. Thus, it was thought that the solids in the sludge might be naturally floatable; this was found to be the case.

The industrial wastewater, which includes plating wastes, is treated in an industrial waste treatment plant (IWTP). The nominal inflow to the IWTP, about 700,000 gallons per day, has a chromium concentration of about 1 mg/L and other toxic metals in lower concentrations. The toxic metal concentrations exceed EPA discharge limits for the plant. The inlet water is treated to remove floating hydrocarbons, leaving a small amount in suspension or solution. This water is then treated in the chromium reduction unit with sodium sulfide and ferrous sulfate to reduce the chromium to the Cr(III) state and form a mixed metal oxide/sulfide precipitate. Cationic and anionic polymers are used to improve sedimentation in a solids contact clarifier (SCC). The overflow from the SCC, about 700,000 gallons per day, contains a small amount of pin floc from the precipitator. This overflow is sent to an activated sludge digester for further treatment.

About 5,000 gallons of SCC underflow is produced per day, which is the subject of the present study. The underflow contains most of the heavy metals and has a pH of 7.2 to 7.5. Suspended/dissolved oils coat the precipitated particles. Sedimentation tests showed that some particles float while others settle, indicating significant differences in specific gravity among the particles. The differences in particle density are attributed to the oil and grease that are sorbed onto the particles, to entrained gases, and to the hydrophobicity of these particles.

Experimental

The flotation tests reported here were conducted at the laboratories of Advanced Processing Technologies, Inc., Salt Lake City, UT. The flotation experiments were designed to test the ability of air sparged hydroclones (ASH), as well as conventional flotation cells, to separate solids from the sludge.

The sludge had a solids content of about 0.35 wt%. The sample was gathered, at the SCC sludge recirculation line, by filling a five gallon carboy and then allowing the solids to settle. A portion of the supernatant was decanted and the carboy again filled with sludge. From the description of the sampling procedure, the underflow was estimated to be about 0.2 to 0.3 weight percent solids. The sludge had been previously reported to have a solids concentration in the range of 1 to 3 weight percent. Point source treatment of the plating wastes has significantly reduced the amount of heavy metal entering the IWTP and, therefore, the solids produced at the underflow of the SCC.

A Denver Model D-12 laboratory flotation machine with a 1.0 L cell was used for the present tests. The cell walls and standpipe were washed down with water during flotation. A frother was tested by adding methyl isobutyl carbinol (MIBC) dropwise, using a syringe that yielded 5 mg/L of MIBC in the pulp per drop of frother added.

Nine flotation tests were made. In the first eight tests the as-received sludge was tested. In each run, two rougher concentrates and a tailings fraction were produced. The test conditions for the first eight tests are shown in Table 1.

For Test 9 the protocol was changed significantly. Eight liters of sludge were filtered, yielding 23.7 g of solids (dry weight). One liter of the filtrate was then used to disperse the solids to make one liter of pulp having 2.37% solids. This simulates the previously reported nominal solids content of the sludge i.e., 1 to 3% solids. The filtrate was more or less clear, but had a light straw color as it was collected. Upon standing for a few minutes it started to become cloudy with a yellow-white precipitate; the cloudiness increased with time. This precipitate was thought to be elemental sulfur, formed as a result of air oxidation of the excess sulfide in the filtrate. Test 9 was important in estimating the amount of solids that could be expected from a bank of froth flotation cells operating as a rougher circuit and in estimating the number of flotation cells necessary to achieve the required separation. Table 2 shows the conditions for Test 9.

In each test the rougher concentrates were weighed, then the concentrates and tailings from each test were pressure filtered. The residue was dried and weighed to obtain a mass balance for the solids.

Results

The variations in conditions for Tests 1 through 8 are summarized in Table 1, and the results are summarized in Table 3. Visual observations, not given in Table 3, showed that MIBC caused the bubble size to be more uniform, about 1 to 2 cm in diameter, as compared to bubbles of vastly varying size, up to 4 cm diameter, without MIBC. This frother also improved water rejection into the tailings.

The addition of polymers provided only marginal improvement in solids recovery. The function of the polymers is to modify the particle surface, i.e., make it cationic, or anionic, or neutral. Since both cationic and anionic polymers are used to improve agglomeration and sedimentation of the particles, the addition of more polymer is thought to provide little change in the surface and thus small change in flotation properties. These polymers are also thought to bind significant amounts of water to the particles.

Potassium amyl xanthate, a bulk sulfide collector, improved solids recovery and grade; however, the improvement was less than expected. The sulfide particles are thought to be covered with oil and organic polymer materials. The small improvement in solids recovery upon application of the collector is attributed to oil/polymer occlusion of the particles and exclusion of the xanthate from the sulfide surface.

Potassium monopersulfate was used in Test 4 to determine the effect of an in-cell oxidizer on solids recovery. The results were negative.

In Test 9 the concentrated pulp was treated with MIBC to a concentration of 25 mg/L in the first stage, no additional frother was added and no collector was used. After conditioning for one minute, air was admitted to the cell and the first rougher concentrate was collected. Most of the solids separated from the sludge in 3.5 min. At that time more than 30% of the

Table 1. Input conditions for tests 1-8 for froth flotation of an oil-bearing mineral sulfide sludge.

	First Rougher Concentrate				Second Rougher Concentrate		
	Collector						
Test No.	Name	Added concentration mg/L	Frother concentration mg MIBC/L	Flotation Time min	Collector added concentration mg/L	Frother concentration mg MIBC/L	Flotation Time Min
1	None	0	0	1	0	5	--
2	None	0	25	1	0	25	3
3	Potassium Amyl Xanthate	25	25	1	5	25	3
4	Potassium Mono-Persulfate	2000	25	1	0	25	3
5	Betz Polymer 1175	10	25	1	0	25	3
6	Betz Polymer 1190	10	25	1	0	25	3
7	Betz Polymer 1180	10	25	1	0	25	3
8	Betz Polymer 1180	25	25	1	0	25	3

Table 2. Input conditions for test 9 for froth flotation of an oil-bearing mineral sulfide sludge, no collector was used.

	Frother Addition	Flotation Time	
Stage No.	mg MIBC/L	Min/Stage	Cumulative
1	25	1.0	1.0
2	0	1.0	2.0
3	0	1.5	3.5
4	0	2.0	5.5
5	0	3.0	8.5

water would have been left in the cell with the remaining solids. A plot of cumulative weight of dry solids recovered as a function of the number of stages is shown in Figure 1. This curve suggests that four stages of rougher collection gives about the maximum economic recovery. When the cumulative weight of dry solids recovered is plotted as a function of cumulative flotation time (Figure 2), the curve is smooth but shows that the rate of recovery decreases very rapidly after about 4 min. Figure 3 is a plot of cumulative weight of dry solids recovered as a function of the weight of water recovered. The ratio of solids recovered to liquid recovered is nearly linear for the first three stages; the amount of solids recovered per volume of water decreases dramatically after stage four. These data suggest that a four stage rougher flotation circuit should result in about optimum solids recovery. Data for Test 9 are shown in Table 4.

Conclusions and Recommendations

The major conclusion from the tests reported here is that froth flotation is a viable unit operation for processing the solids contact clarifier underflow from the industrial waste treatment plant. The tests show that in the absence of added flotation reagents 90% of the sludge solids are floated along with 10% of the water, i.e., 90% of the water was rejected. Addition of a frother, methyl isobutyl carbinol, gives better water rejection.

Potassium amyl xanthate, a commonly used collector for sulfide minerals, did not significantly improve the flotation process. Addition of potassium monopersulfate, an oxidizing agent, to the slurry resulted in lower solids recovery and is not recommended. Use of polymers as collectors for the oil, as suggested by a major froth flotation system fabricator and by a major supplier of polymers, did not significantly improve solids recovery. The addition of flotation reagents to the SCC underflow would result in additional burden to the activated sludge digester and should be avoided if feasible. Potassium monopersulfate did not improve solids recovery and its use is not recommended.

The primary recommendation is that the sludge be treated by froth flotation with appropriate conditioning of the slurry. The flotation concentrate should then be treated by unit processes or operations to generate end products that can be recycled to the electroplating plant, sold to commercial users, or placed in a matrix that is nonhazardous, e.g., a ceramic waste form.

A four-stage froth flotation rougher circuit with an appropriate conditioning step is recommended for the first pilot-plant runs. One

Table 3. Results of tests 1-8 for the froth flotation of solids from an oil-bearing metal sulfide sludge.

	Test Number							
	1	2	3	4	5	6	7	8
1st Rougher Concentrate								
Time, min	--	3.0	3.0	3.0	1.0	1.0	1.0	1.0
Pulp, g	52.0	151.3	55.2	77.5	66.5	66.1	55.7	59.9
Solids, g (dry)	2.2	2.2	2.6	2.2	2.3	2.5	2.2	2.4
Solids, %	4.23	1.45	4.7	2.8	3.5	3.8	3.9	4.0
Solids Distribution	66.7	63.0	68.0	54.0	66.0	64.0	51.0	69.0
Water Rejection, %	95.0	85.0	94.0	92.0	93.0	93.0	94.0	94.0
2nd Rougher Concentrate								
Time, min	--	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Pulp, g	60.6	89.0	44.2	45.0	48.3	52.3	58.8	32.3
Solids, g (dry)	0.9	1.2	1.0	0.7	1.1	0.8	1.4	0.6
Solids, %	1.48	1.34	2.3	1.6	2.3	1.5	2.4	1.9
Solids Distribution	27.3	34.0	26.0	17.0	31.0	20.0	33.0	17.0
Water Rejection, %	94.0	90.0	95.0	95.0	95.0	94.0	94.0	97.0
Combined Concentrate								
Pulp, g	112.6	240.3	99.4	122.5	114.8	118.3	114.5	92.2
Solids, g (dry)	3.1	3.4	3.6	2.9	3.4	3.3	3.6	3.0

Table 3. (Continued)

	Test Number							
	1	2	3	4	5	6	7	8
Solids, %	2.75	1.41	3.6	2.4	3.0	2.8	3.2	3.3
Solids Distribution, %	93.9	97.0	95.0	71.0	94.0	85.0	84.0	86.0
Water Rejection, %	89.0	76.0	90.0	88.0	86.0	88.0	86.0	91.0
Tailings								
Solids, g (dry)	0.2	0.1	0.2	1.2	0.1	0.6	0.7	0.5
Solids, %	0.02	0.01	0.02	0.14	0.01	0.07	0.08	0.55
Solids Distribution, %	6.1	3.0	5.0	29.0	3.0	15.0	16.0	14.0
Computed Head								
Solids, g (dry)	3.3	3.5	3.8	4.1	3.5	3.9	4.3	3.5
Solids, %	0.33	0.35	0.38	0.41	0.35	0.39	0.43	0.35
Solids Distribution, %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 4. Results of Test 9 for froth flotation of an oil-bearing mineral sulfide sludge.

		Flotation time (min)	Concentrate pulp (grams)	Dry concentrate (grams)	Concentrate Solids (%)	Solids distribution (%)	Water refection (%)
1	Rougher Concentrate	1.0	134.4	5.3	3.9	22.0	87
2	Rougher Concentrate	1.0	173.8	7.5	4.3	32	80
3	Rougher Concentrate	1.5	120.9	5.6	4.6	24	83
4	Rougher Concentrate	2.0	93.9	3.5	3.7	15	84
5	Rougher Concentrate	3.0	29.3	0.7	2.4	3	94
	Combined Concentrate			22.6		95	49
	Tailings			1.1	5		
	Computed Head				2.37	100	

Note: This test was made using 5 drops of MIBC for stage 1. The feed was pulp filtered from 8 L of as-received feed and re-pulped to 1.0 L for flotation. Stopping the flotation at 3.5 min would yield 57% water rejection with 78% solids recovery.

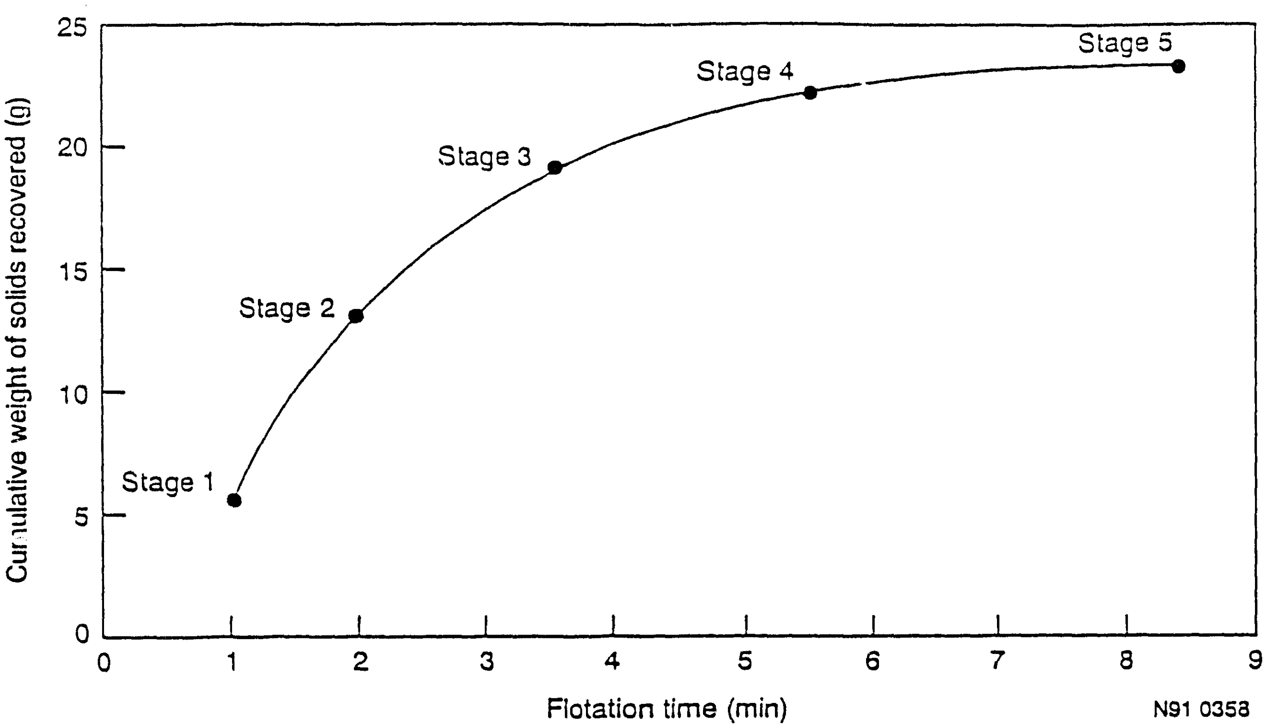

Figure 2 - Solids recovered in stages of Test 9 as a function of cumulative time of flotation.

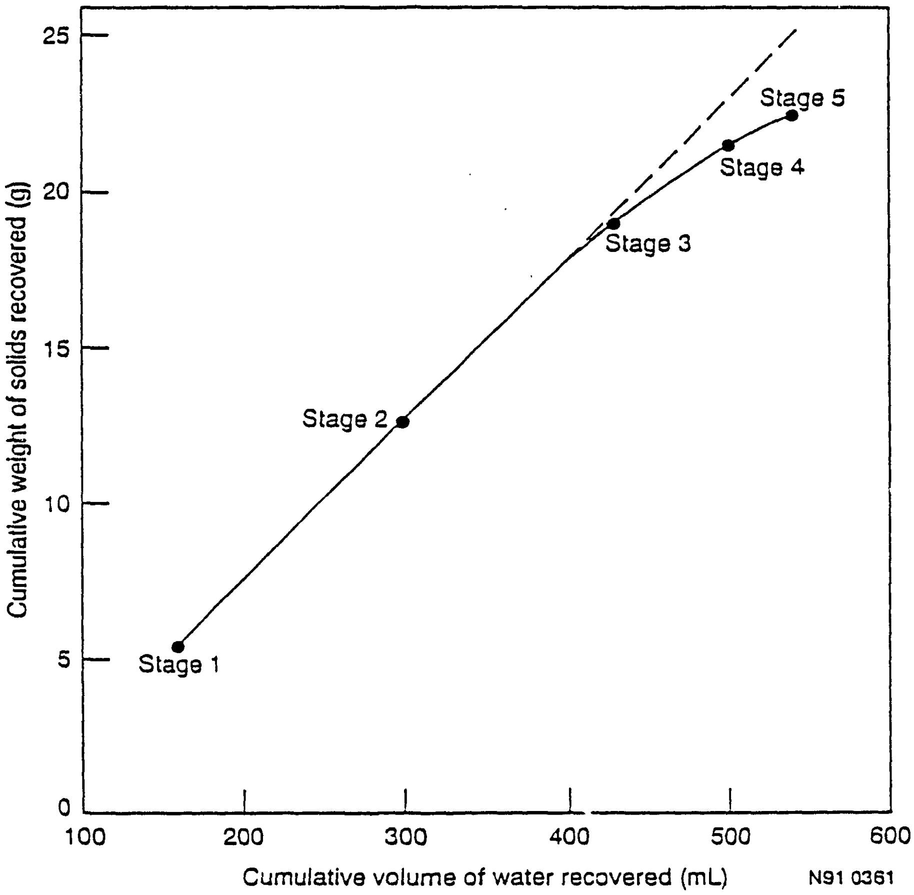

Figure 3 - Solids recovered in Test 9 as a function of the volume of water recovered during flotation.

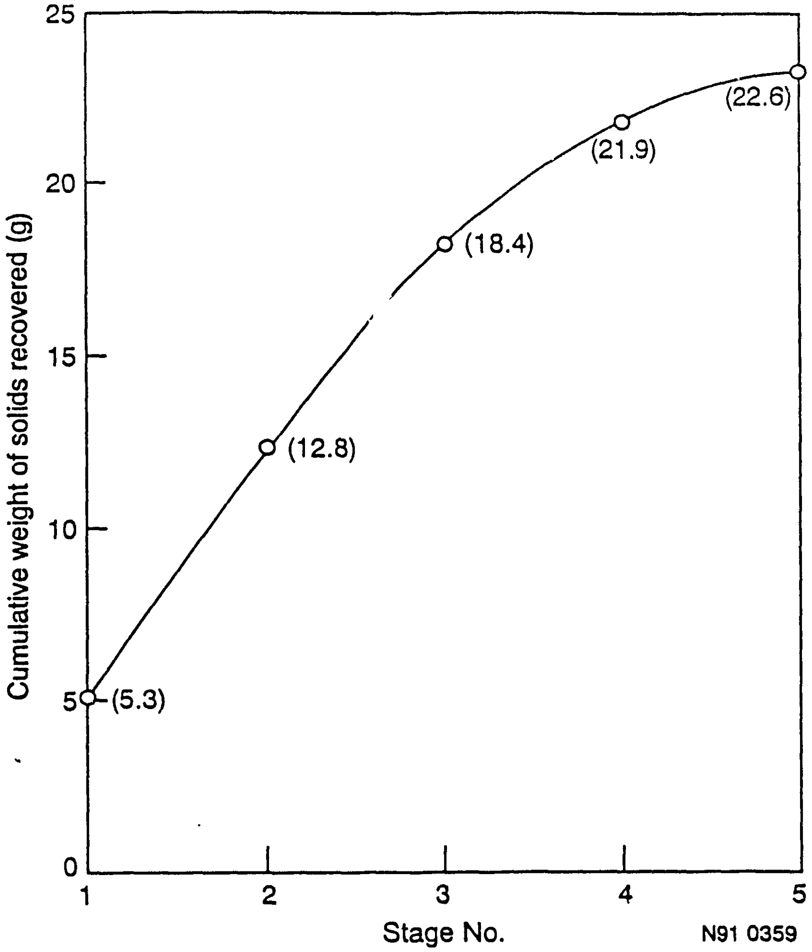

Figure 1 - Solids recovered in Test 9 as a function of number of flotation stages.

alternative to be tested would be to condition the rougher concentrates with a collector and/or a frother, and then send them to a cleaner circuit; the cleaner concentrate would be sent to the next stage of waste treatment and the middlings recycled to the front end of the rougher circuit. Another alternative would be to follow the rougher with a scavenger circuit; the middlings from the scavenger would be returned to the rougher conditioner. In all approaches the tailings from the flotation section would be recycled to the front end of the chromium reduction unit.

Acknowledgments

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