Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Benn, F. W.(1995) 'Using Alternative Chemicals in the Flotation of Heavy Metals from Lead Mill Tailings', Separation Science and Technology, 30: 7, 1555 — 1571

To link to this Article: DOI: 10.1080/01496399508010362

URL: http://dx.doi.org/10.1080/01496399508010362

SEPARATION SCIENCE AND TECHNOLOGY, 30(7-9), pp. 1555-1571, 1995

USING ALTERNATIVE CHEMICALS IN THE FLOTATION OF HEAVY METALS FROM LEAD MILL TAILINGS

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ABSTRACT

The U.S. Bureau of Mines (USBM) investigated alternative chemicals for the flotation of heavy metal values from southeast Missouri lead mill tailings. The objectives of the study were to lower the Pb remaining in the reprocessed tailings to <500 ppm, concentrate the metal values, and lower the overall toxicity of the flotation reagent scheme. Due to the high toxicity of classic flotation chemicals, collectorless flotation, as well as nontoxic or less-toxic chemicals, was studied for use in the flotation process. The investigation centered on the National tailings pile in Flat River, MO. Advantages to using alternative chemicals for the flotation process are presented. Novel reagent schemes are discussed for the treatment of the tailings. Various nontoxic or less-toxic oils were tested, and a substitute for sodium sulfide was investigated. Using a food additive oil, soda ash, and a frother as the reagent scheme, froth flotation recovered 89% of the Pb values. Further scavenging lowered the Pb remaining in the reprocessed tailings to <500 ppm. A less-toxic substitute for sodium cyanide was also studied for use in the cleaner flotation stages. Preliminary results indicate that the food additive oil, canola oil, to be as effective as classic sulfide flotation reagents.

INTRODUCTION

Under its Environmental Technology Research Program, the USBM investigated the use of alternative chemicals for the flotation of heavy metal values from southeast Missouri lead mill tailings. These tailings are the waste rock and unrecovered minerals of value from the processing of lead sulfide ores.

The USBM had previously investigated flotation techniques for heavy metal removal from lead mill tailings (*1*). The objectives of the previous study were to lower the Pb remaining in the reprocessed tailings to <500 ppm and to attempt to recover a marketable product to offset a portion of the potential remediation costs. The first objective of lowering the Pb remaining in the reprocessed tailings to <500 ppm is in accordance with U.S. Environmental Protection Agency guidance for levels of Pb remaining in residential soils. In keeping with these objectives, the reprocessed tailings would virtually be the final product, and if a marketable product could be recovered, it would only enhance the economic aspect of the process. The reprocessed tailings might then be used as mining backfill for ground stabilization, or, since the reprocessed tailings would be mainly dolomite, they might be used as agricultural lime.

For this study, the previous objectives were retained, and another, to lower the toxicity of the chemicals used in the flotation process, was added.

Classic sulfide flotation chemicals (thiol collectors) are highly toxic to both man and animals (see Table 1).

This investigation was undertaken with the objective of lowering the overall toxicity of the flotation reagent scheme while maintaining high metal-value recovery in the flotation stages. Potential advantages to using nontoxic or less-toxic chemicals may be (1) less worker exposure to toxic chemicals, (2) less monitoring of toxic chemicals in the work environment, (3) fewer disposal problems, and (4) reduced collector costs to from one-half to two-thirds of classic sulfide collectors.

TABLE 1. LD50 (RATS) VALUES FOR ORAL INGESTION

Collector Group	LD50*
Xanthates (various)	500-2,000 (*2-3*)
Mercaptans (various)	300-500 (*4*)
Dithiophosphates (various)	1,540-3,540 (*5-6*)
Mercaptobenzothiazole	3,120 (*7*)

*LD50: lethal dosage to kill 50% of test subjects, in milligrams per kilogram of body weight.

BACKGROUND

The southeast Missouri lead mill tailings can be divided into two groups: (1) the pre-1968 tailings, which were generated from the Old Lead Belt situated in Washington, St. Francois, and Madison counties; and (2) the post-1968 tailings, which are currently being generated from the New Lead Belt in southern Washington, Iron, and Reynolds counties (see Figure 1).

Southeast Missouri contains an estimated 180 to 275 million mt of lead mill tailings. About one-third of these tailings are stored above ground in populated areas. This area extends to approximately 100 km^2 around the town of Flat River, MO. This study concentrated on the tailings from the Old Lead Belt, and, more specifically, on the tailings from the National pile in Flat River, MO (see Figure 2).

FIGURE 1. Map of Missouri Showing "Old" and "New" Lead Belts.

National Tailings

The National Lead Company mined and processed Pb ores in the Flat River, MO, area at the end of the last century and the start of this century (*8*). The processing methods used at that time included jigs and shaking tables. These methods were somewhat inefficient; thus, their tailings were a coarse product containing small amounts of heavy metal values. The tailings were stockpiled at the processing site. In the following years, the town grew around the tailings pile.

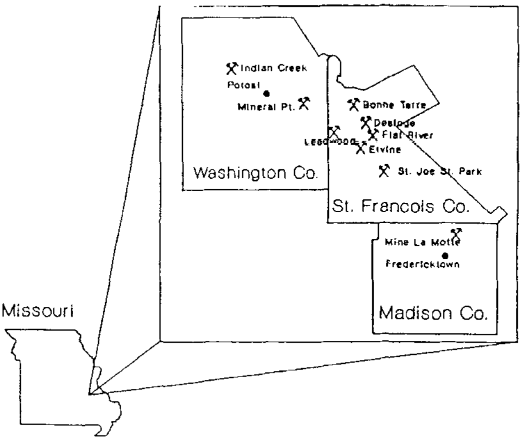


FIGURE 2. Location of Tailings Sites in Missouri's "Old" Lead Belt.

The jig tailings pile at the National site encompasses 0.18 km^2 and is approximately 580 m long, 320 m wide, and 55 m high. The pile, which is elliptical in shape with the long axis running east to west, has a dome on the eastern half. About 0.06 km^2 of slime pits are located on the northeast corner and the eastern side. The entire site encompasses approximately 1.3 km^2, including the area developed by industry (*9*). Tonnage estimates for the National pile range from 5.9 to 9.1 million mt. Samples of the tailings were taken using a wheel-mounted, gasoline-powered auguring device that allowed sample retrieval to a depth of 6.4 m.

Chemical analyses of the tailings show large variations in the metal value content from sample to sample. From the samples taken, the jig tailings portion of the National pile contains, on the average, in percent, 0.87 Pb, 0.035 Cu, 4.6 Fe, 0.11 Zn, 0.029 Co, and 0.029 Ni.

Mineralogical examination revealed the sulfide minerals galena, chalcopyrite, sphalerite, marcasite, cobaltiferous pyrite, and nickeliferous pyrite, with the gangue being massive dolomite and a small amount of limestone. Almost all of the sulfides have an oxidation layer or show partial alteration. In the case of galena, it has been estimated that between 15 and 20% has altered to anglesite ($PbSO_4$) or cerussite ($PbCO_3$). The liberation size for the sulfides from the gangue was determined to be 150 μm. Table 2 shows a typical screen analysis of the National tailings. Size analyses of the pile show large variations for the average particle size, ranging from 950 to 6,250 μm. The large particle size would coincide with tailings from a gravity separation plant. In some of the coarser samples, >75% of the metal values are present in the +1,700 μm fraction.

EXPERIMENTAL PROCEDURE

Laboratory-scale equipment was used in all the testing procedures. Testing involved milling to liberation (minus 150 μm) with a rod mill. The length of the rod mill was 22.23 cm, and the outside diameter was 21.6 cm. The mill was charged with six 1.27-cm-diam rods, seven 1.59-cm-diam rods, and eight 2.54-cm-diam rods. The milling procedure consisted of a two-stage grind of the as-received tailings with the undersize (minus 150 μm) removed after the first stage. This would ensure fresh mineral surfaces for subsequent flotation testing. The feed for each test was 500 g and was milled at 50-wt% solids. The oversize (plus 150 μm) remaining after the first stage was approximately 40 to 50% of the original weight and was reground at 50-wt% solids. The two-stage milling procedure reduced the amount of fines generated. The normal grinding times were 10 min for the first stage and 5 min for the second stage. In some cases, the flotation reagents or some of the reagents were added directly to the rod mill to give a more intimate contacting period. The ground pulp was then transferred to the flotation cell. The standard flotation procedure consisted of

TABLE 2. TYPICAL SCREEN ANALYSIS OF NATIONAL TAILINGS

Size (µm)	Wt %	% Pass	Chemical Analysis %		
			Cu	Pb	Zn
Plus 4,750	27.31	72.69	T	0.34	0.04
Plus 2,360	42.86	29.83	T	1.10	.06
Plus 1,700	8.58	21.25	.02	1.20	.09
Plus 1,180	4.54	16.71	T	.80	.05
Plus 600	4.47	12.24	.07	.44	.06
Plus 425	1.49	10.75	.04	.32	.07
Plus 300	1.53	9.23	.04	.30	.10
Plus 212	1.24	7.99	.06	.34	.09
Plus 150	1.19	6.80	.05	.24	.09
Plus 106	1.24	5.56	.07	.36	.11
Plus 74	.77	4.79	.07	.36	.11
Minus 74	4.79	0	.30	1.50	.25
Totals	100	NAp	.026	.82	.07
			Distribution %		
Plus 4,750	NAp	NAp	4.18	11.34	16.01
Plus 2,360	NAp	NAp	6.56	57.59	37.68
Plus 1,700	NAp	NAp	6.56	12.58	11.31
Plus 1,180	NAp	NAp	.69	4.44	3.33
Plus 600	NAp	NAp	11.95	2.40	3.93
Plus 425	NAp	NAp	2.28	.58	1.53
Plus 300	NAp	NAp	2.33	.56	2.24
Plus 212	NAp	NAp	2.84	.51	1.63
Plus 150	NAp	NAp	2.28	.35	1.57
Plus 106	NAp	NAp	3.32	.54	2.00
Plus 74	NAp	NAp	2.05	.34	1.24
Minus 74	NAp	NAp	54.95	8.77	17.54
Totals	NAp	NAp	100	100	100

NAp Not applicable.
T Trace (0.004 % for calculation).

pulping the feed from 5 to 20% solids, agitation at 1,300 rpm, addition of appropriate additives, pH adjustment (if needed), addition of collector, addition of frother, and introduction of air at 6.2 L/min. The normal conditioning time was 3 min/addition, with a 15-min conditioning time for the nontoxic or less-toxic collector. The normal flotation time was 5 min or until no solids were observed in the froth.

RESULTS AND DISCUSSION

Flotation without a traditional sulfide collector (collectorless) was initially tested using previously developed optimum pH and modifier additions: sodium sulfide, a pulp pH of 9.5, and a frother (in this case a mixture of hydrocarbon oil and C_4 to C_7 alcohols). The reagent dosages consisted of sodium sulfide at 0.5 kg/mt, a pulp pH of 9.5, and the frother at 0.05 kg/mt. This reagent scheme recovered 88% of the Pb values at a grade of 18% Pb, thus lowering the tailings fraction to 800 ppm Pb (0.08% Pb).

Various nontoxic or less-toxic chemicals were tested in the flotation process. The natural starting point was the collectors. Fatty acids have been used successfully for many years in industrial minerals flotation, and since many food additive oils contain fatty acids, several suitable candidates were identified.

The first alternative chemical tested was Canola oil (referred to in the literature as rapeseed oil). The Canola oil contained, in g/100g of fatty acids, Erucic acid, 50; Oleic acid, 32; Linoleic acid, 15; Linoleic acid, 1; and palmitic acid, 1 (*10*).

Toxicity data for Canola oil are difficult to obtain, but some of the components available are shown in Table 3 (*4*).

Comparing the toxicity data from Table 1 to those in Table 3, the Canola oil is much less toxic than the normal sulfide flotation collectors. The Canola oil is, for all practical purposes, nontoxic

TABLE 3. LD50 (RATS) VALUE FOR ORAL INGESTION

Compound	LD50*
Erucic acid	ND
Oleic acid	74,000
Linoleic and oleic acid . .	33,000

ND Not Determined.
*LD50: Lethal dosage to kill 50% of test subjects, in milligrams/kilogram of body weight.

(listed as a food additive by the Food and Drug Administration) and inexpensive. Preliminary costs show bulk Canola oil to be \$0.64/kg versus \$1.65 to \$2.09/kg for xanthates and >\$2.21/kg for dithiophosphates and other classic galena collectors.

Typical dosages for classic galena collectors are in the range of 0.05 to 0.15 kg/mt. Comparing the reagent cost of Canola oil to the xanthates and dithiophosphates, the Canola oil would be \$0.15/mt (at 0.24 kg dosage), the xanthates would be \$0.08 to \$0.31/mt, and the dithiophosphates would be \$0.11 to \$0.33. These costs would be dependent on the type and dosage of the individual classic galena collector. From the economic standpoint, the Canola oil compares very favorably with these two galena collectors, besides being a less toxic food additive.

ROUGHER FLOTATION

The Canola oil was tested on a single elimination basis with other classic flotation additives. Since previous research (*1*) had shown the necessity of sodium sulfide for the galena flotation, the initial testing included it. Other additives, such as copper sulfate and creosote oil, were used and subsequently eliminated (see Figure 3).

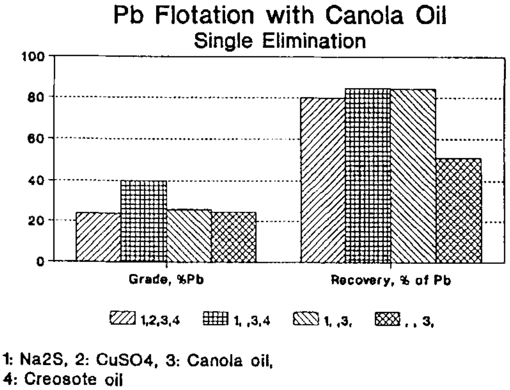


FIGURE 3. Lead Flotation Results Using Canola Oil, Single Elimination.

The testing revealed that sodium sulfide was needed for the flotation of galena when using the Canola oil; typically, sodium sulfide is used to activate tarnished galena surfaces. Without the sodium sulfide, the Pb recovery dropped from about 84 to 51%. Efforts were made to reduce the toxicity of the reagent scheme even further and omit sodium sulfide while still maintaining high Pb recovery. Since the LD50 for the sodium sulfide is 53 mg/kg body weight (*4*), subsequent testing for an alternative for the sodium sulfide showed that the combination of sodium carbonate and sodium hydroxide could be successfully substituted. This indicated that the function of the sodium sulfide may have been strictly for the pH adjustment, as opposed to being used to activate the tarnished galena. When the sodium carbonate and sodium hydroxide were added in place of the sodium sulfide, and using the Canola oil, the Pb recovery increased to 89% (with a resulting increase in the Cu and Zn recovery), and the concentrate grade was 5.4% Pb. The remaining tailings fraction contained >91% of the original weight with a Pb grade of 620 ppm (0.062%). The reagent scheme, with dosages, is shown in Table 4.

A second flotation concentrate (scavenging stage) was removed after conditioning with the food additive soya lecithin (used as an emulsifier in candies). This lowered the Pb remaining in the reprocessed tailings to 200 ppm. However, there was an additional 35% of the original weight removed. This left only 56.4% of the original weight in the reprocessed tailings containing 200 ppm Pb. The scavenging stage increased the overall Pb recovery to 97.8%.

TABLE 4. REAGENT SCHEME EMPLOYING CANOLA OIL

Reagent	kg/mt	Pulp pH	Conditioning Time, Min
Na_2CO_3	1.5	9.2	5
NaOH	0.24	10.2	2
Canola oil	0.24	10.2	15
Polypropylene glycol frother	0.08	10.2	3

The soya lecithin (conditioned for 5 min) was at a dosage of 0.29 kg/mt and a pulp pH of 10.2. No frother was used in the scavenging stage. The other metal values remaining in the tailings were, in parts per million, 100 Cu and 400 Zn. The metal value recoveries and weight percent are shown in Table 5.

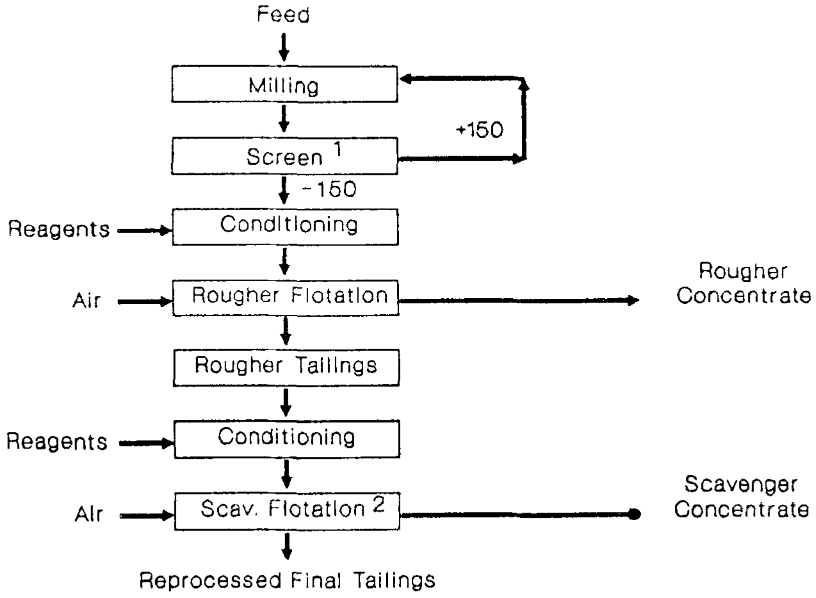
While the soya lecithin stage did lower the remaining Pb to <500 ppm, the weight percent removed was excessive (35%) and >31% of the Fe values were in the second (scavenger) concentrate. This may be improved with optimization of dosages and pH. A typical flow schematic for the rougher and scavenger flotation process is shown in Figure 4.

Another alternative chemical tested was cod liver oil. The constituents of cod liver oil are, measured in g/100g total fatty acids, Myristic Acid, 5.8; Palmitic Acid, 8.4; Stearic Acid, 0.6; Palmitoleic Acid, 20.0; Oleic and Linoleic Acids, 29.1; C_{20} Polyethenoic Acids, 25.4; and C_{22} Polyethenoic Acids, 9.6 (*10*). The tests using cod liver oil did not recover as high a percentage of Pb values as the Canola oil in the rougher stage. One area of use for the cod liver oil which did produce significant results was in the scavenging stages. When using sodium sulfide (0.5 kg/mt) and Canola oil (0.24 kg/mt) in the rougher stage, the tailings were scavenged with cod liver oil at a dosage of 0.18 kg/mt. The remaining tailings contained 500 ppm Pb and included >94% of the original weight. The results of this test are shown in Table 6.

TABLE 5. PERCENT METAL VALUE RECOVERIES

Product	Wt %	Cu	Fe	Pb	Zn
Conc 1 . . .	8.58	61.5	7.8	89.0	52.4
Conc 2 . . .	35.01	14.8	31.6	8.8	11.3
Tails	56.41	23.7	60.6	2.2	36.3
Total . .	100	100	100	100	100
Tailings Grade (%) . .	NAp	0.01	4.8	0.02	0.04

NAp Not applicable.



1: 150 micrometers
2: Scavenger Flotation

FIGURE 4. Typical Flow Schematic for the Rougher and Scavenger Flotation Process.

TABLE 6. RESULTS OF CANOLA OIL ROUGHER AND COD LIVER OIL SCAVENGER

	Rougher	Scavenger	Combined Concentrate
Pb recovery, % . .	91.0	3.4	94.4
Pb grade, %	22.3	1.1	13.2
Wt % removed . . .	3.4	2.5	5.9
Tailings (% Pb) . .	0.08	0.05	NAp

NAp Not Applicable.

The combination of Canola oil in the rougher and cod liver oil in the scavenger did reduce the Pb remaining in the reprocessed tailings to the target value of 500 ppm or less, but the reagent scheme still used sodium sulfide. The target value may be achieved using the combination of the Canola oil and sodium carbonate for the rougher and scavenging with the cod liver oil.

Cleaner Flotation

The goal for cleaner flotation was to produce a galena concentrate containing >70% Pb, while eliminating the use of sodium cyanide. Previous research (*1*) had indicated the need for sodium cyanide in two of the three cleaning stages, in order to upgrade the rougher concentrates, from processing of the Pb tailings. Testing was performed to determine if an alternative to sodium cyanide (NaCN) could be established. One less hazardous substitute for the cyanide may be a combination of sodium bromide (NaBr) and hydrogen peroxide (H_2O_2).

From a toxicity standpoint, the LD50 (rat) for sodium bromide is 3,500 mg/kg body weight versus only 6.44 mg/kg body weight of sodium cyanide (*4*). If a comparable grade can be obtained, then the substitution of sodium bromide and hydrogen peroxide for sodium cyanide would be a viable and environmentally responsible alternative.

TABLE 7. LEAD RECOVERY COMPARISON BETWEEN SODIUM CYANIDE AND THE COMBINATION OF HYDROGEN PEROXIDE AND SODIUM BROMIDE

Cleaner Stage	Pb Recovery %	
	With NaCN	H_2O_2 With NaBr
1	90	92
2	83	81
3	79	78

TABLE 8. LEAD GRADE COMPARISON BETWEEN SODIUM CYANIDE AND THE COMBINATION OF HYDROGEN PEROXIDE AND SODIUM BROMIDE

Cleaner Stage	Pb Grade (% Pb)	
	With NaCN	H_2O_2 With NaBr
1	24	16
2	57	44
3	72	65

Initial testing reveals a very favorable recovery comparison (see Table 7) between the two methods.

However, the final concentrate grade was 7 percentage points less (72% Pb versus 65% Pb) when using the sodium bromide and hydrogen peroxide (see Table 8).

The feed for the tests was the combined concentrates from previous bench-scale continuous flotation operations, and all contained about 7% Pb. The collector used for the cleaner stages was a phosphine derivative that had previously been used in the cleaning sequence. The reagent dosages are shown in Table 9.

The initial cleaning test was performed with the same reagents and dosages as in Table 9, except that sodium cyanide (at 0.25

TABLE 9. REAGENTS FOR CLEANING TESTS (kg/mt)

Stage	Na_2CO_3	Phosphine Derivative	NaBr	H_2O_2	Frother
1 . .	To pH 9.0 . .	0.01	0.25	0.25	0.015
2 . .	NR . .	NR	NR	NR	NR
3 . .	To pH 9.0 . .	0	0.04	0.04	0

NR No reagents.

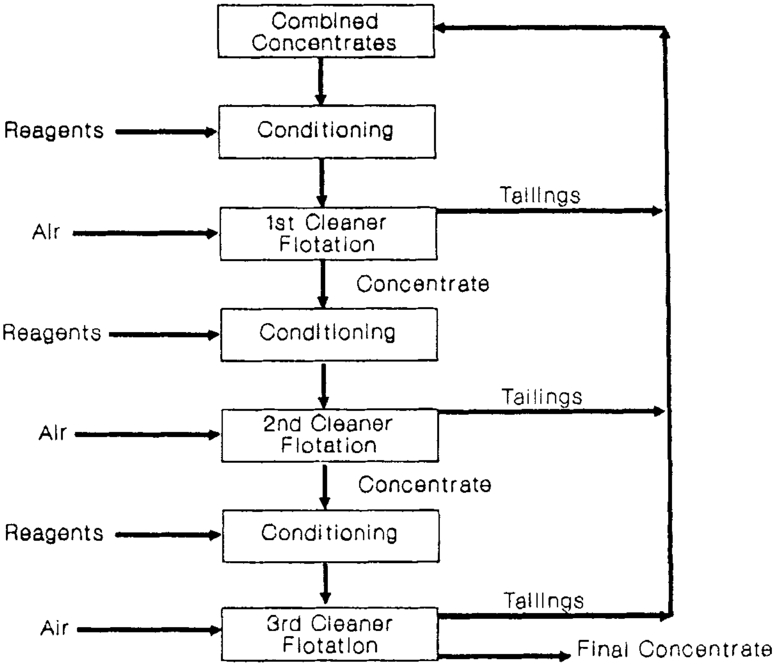


FIGURE 5. Typical Flow Schematic for the Cleaner Flotation Process.

TABLE 10. SINGLE-COLLECTOR COMPARISON FROM SINGLE-STAGE FLOTATION TESTS

	Metal Value Recovery (%)			
Collector Type	Pb	Cu	Zn	Fe
Xanthate	65	19	15	6
Dithiophosphate	65	33	26	4
Mercaptan	14	5	6	2
Mercaptobenzothiazole . .	68	51	44	5
Canola Oil	89	61	52	8

kg/mt for Stage 1 and 0.04 kg/mt for Stage 3) was used. In another cleaning test, the hydrogen peroxide was omitted, which lowered both the final cleaner concentrate grade (to 60% Pb) and the final cleaner concentrate recovery to 69% of the Pb values. These initial results for the elimination of cyanide from the cleaning stages appear to be very promising. A typical flow schematic for the cleaner flotation process is shown in Figure 5.

Comparison to Previous Flotation Testing

A comparison of single-stage flotation testing, using the Canola oil without the sodium sulfide reagent scheme, to previous single-collector single-stage flotation tests is shown in Table 10.

The Canola oil does improve recoveries of the Pb, Cu, and Zn values while maintaining some selectivity against the flotation of the Fe values in the single-stage flotation.

CONCLUSIONS

The use of Canola oil in froth flotation shows great potential for recovery of Pb and other heavy metals from lead mill tailings. Froth flotation testing lowered the amount of Pb remaining in the

National tailings to ≤500 ppm using Canola oil as the galena collector, and scavenging with either soya lecithin or cod liver oil. The Canola oil is an inexpensive, less-toxic food additive, which can be used as an alternative to classic galena collectors. Sodium bromide and hydrogen peroxide may be substituted as a less-toxic replacement for sodium cyanide in froth flotation, with little effect on recovery and a small drop in concentrate grade.

ACKNOWLEDGMENTS

The author would like to thank Cominco American, Inc., Magmont Operations, and Dresser Minerals Division of Dresser Industries for providing sample chemical analyses.

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