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Continuous Flotation Testing To Recover a Bulk Sulfide Concentrate From Missouri Lead Ore Tailings

By W. L. Cornell and D. C. Holtgrefe

BUREAU OF MINES



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

ft ³	cubic foot	min	minute
gal/min	gallon per minute	min/cell	minute per cell
lb/min	pound per minute	pct	percent
lb/st	pound per short ton	wt pct	weight percent
μm	micrometer		

CONTINUOUS FLOTATION TESTING TO RECOVER A BULK SULFIDE CONCENTRATE FROM MISSOURI LEAD ORE TAILINGS

By W. L. Cornell¹ and D. C. Holtgreffe²

ABSTRACT

The Missouri Pb ores are the only domestic Co resource being mined and processed for other metals; therefore, they present a viable short-term opportunity for Co production. Lead, zinc, and copper concentrates are produced from the ore. The Cu concentrate can contain up to 30 pct Co and the Pb concentrate up to 15 pct Co. Since Co is detrimental to the processing of the Zn concentrate; the remainder of the Co is rejected to the tailings. The tailings can contain as much as 50 pct Co originally present in the mined ore. Researchers at the U.S. Bureau of Mines have successfully tested on a continuous basis a process that recovers a bulk sulfide concentrate from mill tailings. The concentrate contains up to one-half of the Co and from 50 to 90 pct of the Pb, Zn, and Cu. Concentrate weight represents 10 pct or less of the total tailings.

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INTRODUCTION

The United States is dependent on foreign sources for virtually all of its Co. There are domestic occurrences of Co in Alaska, California, Minnesota, Idaho, and Missouri. These deposits are subeconomic regarding the Co values, and the only deposits that are being actively mined are the ores of the Missouri Lead Belt. Economic values of Pb, Zn, Cu, and Ag are mined and extracted. At present, Co is not recovered from the ores, in fact, as much as 50 pct is rejected into the mill tailings. Figure 1 represents the distribution of Co into the various concentrator streams. Any method that could economically recover this Co could lower U.S. dependency on foreign suppliers. Total Co contained in the yearly production of ore from the Missouri Lead Belt could supply 13 pct of the United States annual needs.³

The Co occurs mainly in the mineral siegenite, $(\text{Ni},\text{Co})_3\text{S}_4$. There are also minor occurrences of the mineral bravoite, $(\text{Ni},\text{Co},\text{Fe})\text{S}_2$. The $(\text{Ni},\text{Co})_3\text{S}_4$ is most frequently found as intimate replacement inclusions with the chalcopyrite (CuFeS_2) (fig. 2), and occurs in the mill streams as middled particles with the CuFeS_2 (fig. 3). The $(\text{Ni},\text{Co},\text{Fe})\text{S}_2$ occurs mainly as bands in host pyrite (fig. 4), and so is usually found middled with pyrite or marcasite. Bravoite can also occur as discrete grains in host gangue (fig. 5).

Earlier U.S. Bureau of Mines research concentrated on separating the $(\text{Ni},\text{Co})_3\text{S}_4$ from the CuFeS_2 in the Cu concentrates. The Cu concentrates contain 30 pct of the contained Co at an average grade of 0.50 pct, which represents an improvement ratio of 33 over the mill feed grade. Two separate flowsheets were developed using a regrind to a d_{50} of less than $10\ \mu\text{m}$ followed by reverse flotation to recover the Co, as $(\text{Ni},\text{Co})_3\text{S}_4$, into the tailings and the CuFeS_2 as an enriched concentrate. Combined Co and Ni grades exceeding 7 pct at recoveries of 80+ pct were possible.⁴

The tailings average 0.015 pct Co grade and represent as much as 50 pct of the total Co contained in the ore. Bench-scale testing by the Bureau resulted in the development of a method to recover a bulk sulfide concentrate from the mill tailings. This method used a primary amine as the main collector and was augmented by one or more enhancers. These enhancers included fuel oil, sodium sulfide (Na_2S), and creosote. The best overall results came when fuel oil was used as the enhancer, but the Na_2S also showed some promise. Amine dosages in the range of 0.30 to 1.00 lb/st were necessary depending on sulfide grade in the feed. Fuel oil additions in the range of 3.0 to 6.0 lb/st were also used.⁵ With this scheme as a starting point, continuous pilot-scale testing was initiated using the augmented amine flotation of a bulk sulfide concentrate from mill tailings.

⁵Cornell, W. L., D. C. Holtgreffe, and F. H. Sharp. Recovery of Cobalt and Other Metal Values From Missouri Lead Ore Concentrator Tailings. Paper in Recycle and Secondary Recovery of Metals, ed by P. R. Taylor, H. Y. Sohn, and N. Jarret. TMS-AIME, 1985, pp. 675-682.

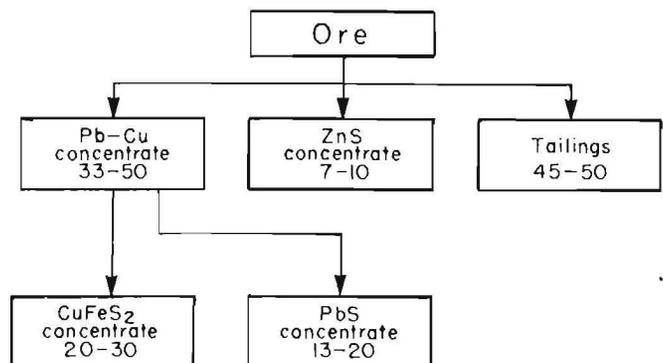


Figure 1.—Distribution of Co during the milling of Missouri Pb ores, in percent.

³Kirk, W. S. Cobalt. BuMines Mineral Commodity Profile, 1983, 16 pp.

⁴Clifford, R. K., and L. W. Higley, Jr. Cobalt and Nickel Recovery From Missouri Lead Belt Chalcopyrite Concentrates. BuMines RI 8321, 1978, 14 pp.

Cornell, W. L., A. M. Wethington, D. C. Holtgreffe, and F. H. Sharp. Continuous Flotation Testing To Recover Cobalt From Missouri Lead Ores. BuMines RI 9072, 1987, 11 pp.

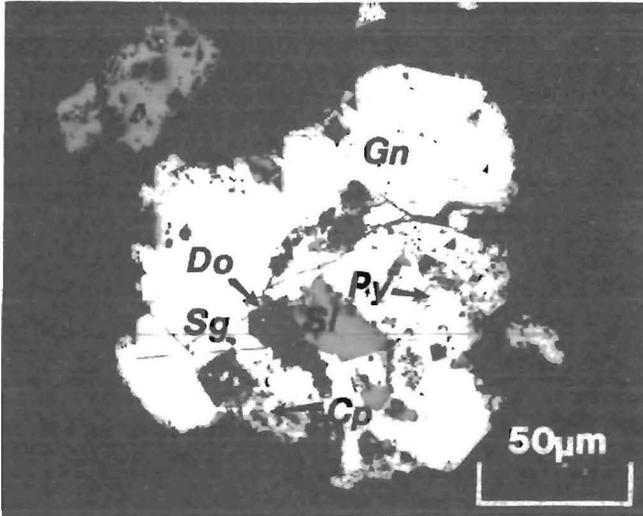


Figure 2.—Chalcopyrite (Cp) with siegenite (Sg), dolomite (Do), galena (Gn), and pyrite (Py).

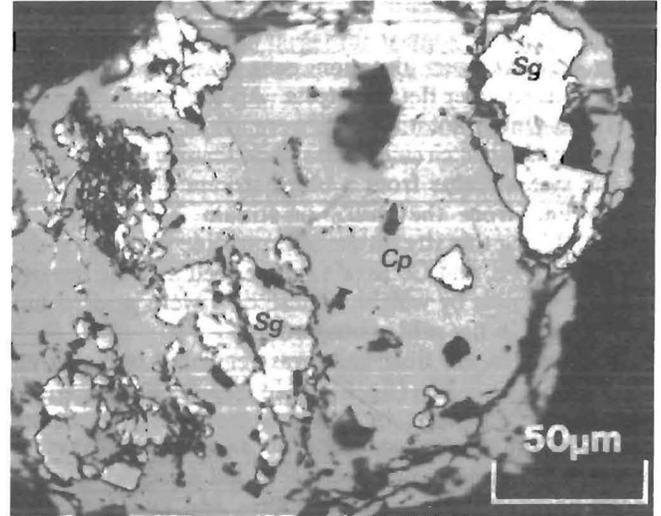


Figure 3.—Inclusions of siegenite (Sg) in chalcopyrite particle (Cp).

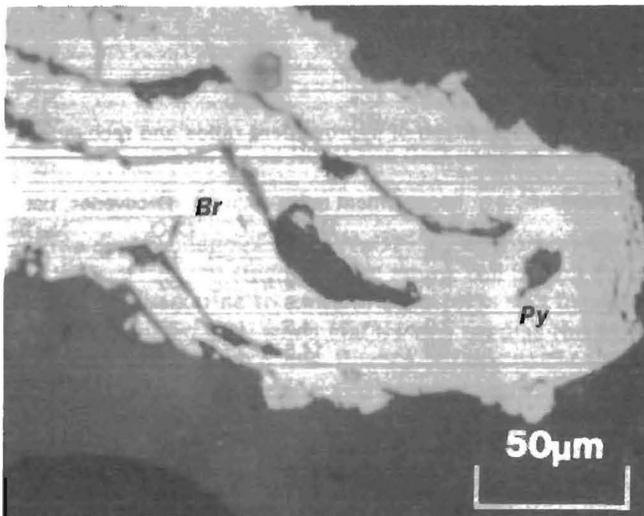


Figure 4.—Bravoite (Br) banded around pyrite (Py).

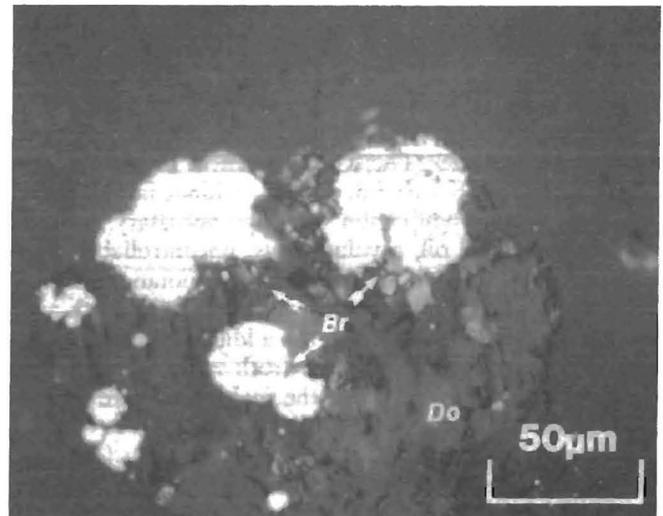


Figure 5.—Bravoite (Br) in dolomite (Do).

EQUIPMENT AND PROCEDURE

Six 1-ft³ Denver⁶ flotation cells were used for the continuous rougher flotation tests. An additional six, 0.25-ft³ Hazen-Quinn flotation cells were available for use as a two-stage cleaner circuit during the cleaning tests. Feed for the system came from a bleed stream off the tailings return line from the mill's on-stream X-ray analyzer system. Using this stream made it possible to monitor the Pb, Zn, Cu, Fe, and Co assays on the feed and the density in percent solids by weight. These data were printed out every 5 min in the mill control room.

The feed to the float cells was regulated by using an adjustable splitter box (fig. 6). Pulp transfer from cell unit to cell unit was done by utilizing the built-in pumping action of the Denver cells or by air-driven diaphragm pumps. Flotation reagents were added using adjustable-speed peristaltic pumps. Flow rates and densities were monitored at 10-min intervals to allow for reagent adjustment on a pound per short ton basis and to allow for adjustments in the feed rate to keep that parameter within the predetermined test limits.

In all tests, the volume and weight percent solids in the feed were checked at 15-min intervals. These figures were then averaged to give a weight of feed per minute over the

entire run. Samples of the feed, tailing, and concentrate streams were also taken at 15-min intervals, and these composite samples were assayed for Co, Cu, Fe, Ni, Pb, and Zn. Using these assays and the feed weight, concentrate weight was calculated with the two-product formula as follows:

$$R = \frac{100 c(f-t)}{f(c-t)},$$

where R = Recovery,

c = concentrate, pct,

f = feed, pct,

and t = tailing, pct.

The pivot element was chosen by using a statistical program, which predicts the most likely correct element assay. Distributions were then calculated using the actual feed weight and the calculated distribution of weight to the tailing.

ROUGHER FLOTATION

Continuous tests were planned using amine only and amine with fuel oil. These tests were to be run at the natural pH from 8.2 to 8.6. It was evident immediately that some froth modification would be necessary. In any test not using fuel oil, a voluminous, uncontrollable, and very persistent froth made control of the flotation impossible. Cells and launders were overflowed with froth and continually clogged. Although the addition of fuel oil was very successful in modifying the froth volume, there was some question as to the effect the fuel would have on the subsequent cleaning and separation steps.

The only other method of froth modification found to be very effective was the regulation of pH. When pH was regulated into a tight band between 9.8 and 10.2, the froth loading and volume became very manageable. It was necessary to use sodium hydroxide (NaOH) rather than lime (CaO) as a modifier. Earlier bench-scale tests using CaO resulted in both lower grades and recoveries than tests using NaOH. Table 1 shows this comparison.

This difference is probably due to the opposite effects of each of these reagents on slimes. While NaOH is a slime dispersant, CaO tends to flocculate the slimes and cause losses due to a slime coating on the larger particles of sphalerite (ZnS) and CuFeS₂, or the minus 37- μ m particles tend to flocculate and are collected indiscriminantly.

Table 1.—Comparison of improvement ratios and recoveries between CaO and NaOH as pH modifiers

Element	Improvement ratios		Recoveries, pct	
	CaO	NaOH	CaO	NaOH
Co	3.8	10.0	17	59
Cu	5.9	6.9	65	85
Fe	1.4	4.6	34	25
Pb	2.9	4.5	29	44
Zn	7.0	14.5	74	82

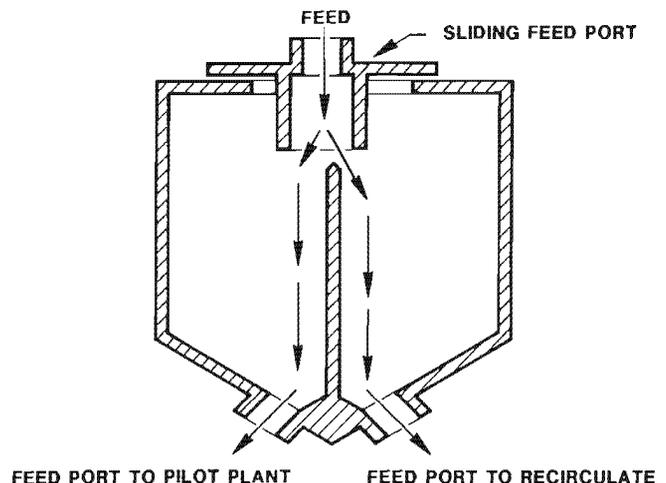


Figure 6.—Splitter box used in continuous test unit.

⁶Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Table 2 gives the results of typical tests using fuel oil and pH as the froth modifier.

Table 2.—Results of test at pH 10.0 with fuel oil and NaOH

	Feed	Conc	Tailing
FUEL OIL			
Wt pct	100	12	88
Assay, pct:			
Co	0.02	0.11	0.01
Cu	0.06	0.46	0.05
Fe	2.30	8.10	1.40
Ni	0.03	0.14	0.02
Pb	0.18	0.96	0.10
Zn	0.18	1.40	0.06
Distribution, pct:			
Co	100	66	34
Cu	100	92	8
Fe	100	42	58
Ni	100	56	44
Pb	100	64	36
Zn	100	93	7
NaOH			
Wt pct	100	10	90
Assay, pct:			
Co	0.02	0.08	0.01
Cu	0.06	0.50	0.04
Fe	2.00	6.90	1.20
Ni	0.03	0.13	0.01
Pb	0.15	1.10	0.11
Zn	0.22	2.10	0.04
Distribution, pct:			
Co	100	53	47
Cu	100	83	17
Fe	100	35	65
Ni	100	52	48
Pb	100	73	27
Zn	100	95	5

One disadvantage of using NaOH as the froth modifier was the necessity to stage add the amine cell by cell down the bank. The amine to mineral adsorption was found to be most tenuous; and, when NaOH was used as the froth modifier, any particles not floated in the earlier cells tended to desorb the amine and recovery suffered. This phenomenon was independent of reagent dosage. Reagent additions of up to 3 lb/st resulted in little or no increase in recovery. When fuel oil was used as a froth modifier following the amine addition, it had a natural attraction for the already hydrophobic sulfide particle. This secondary coating of the hydrophobic particle by fuel oil tended to lock the hydrophobicity throughout the circuit. It also tended to impart additional buoyancy to the larger particles of CuFeS_2 and ZnS .

Slurry density variances seemed to have very little effect on either grades or recoveries. The continuous test unit was operated directly off the tailings stream at whatever density the stream was at the time. These were from a low of 25 pct to a high of 35 pct solids by weight. This confirmed previous bench-scale testing, which had shown little or no variance in grade or recovery with pulp density variances.

A more important parameter was retention time. Preliminary bench-scale testing had indicated that a retention time of 20 to 24 min would be necessary. Under plug-flow

conditions, this would represent a feed rate of 0.25 gal/min. This became the target for testing. With the natural variations in pulp densities, actual solids flow ranged between 6 and 11 lb/min.

Figure 7 plots the cumulative recovery and concentrate grade versus retention time down the cell bank for Co, Cu, Zn

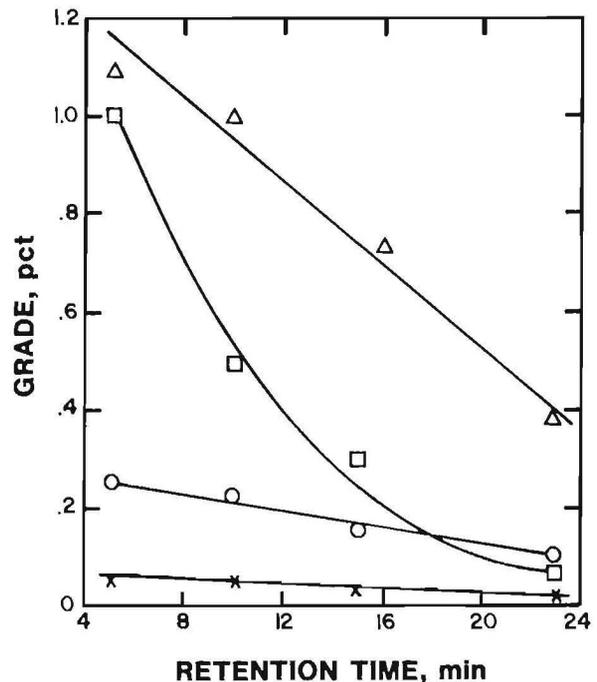
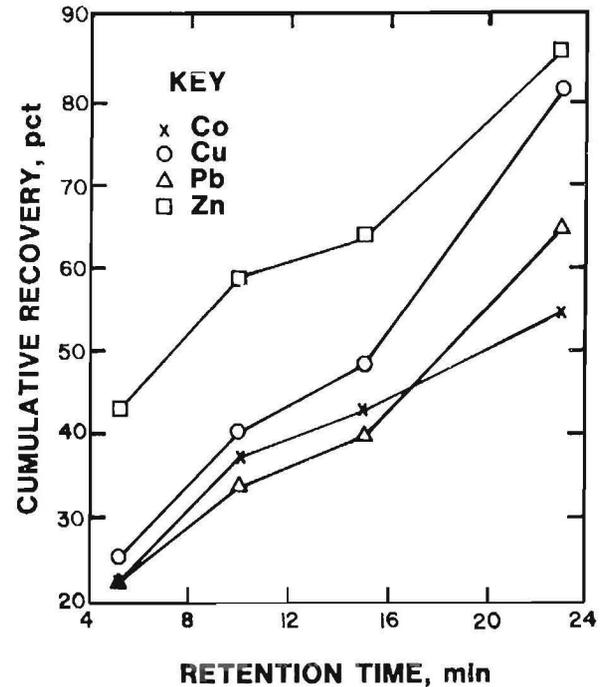


Figure 7.—Plot of recovery and grade versus retention time.

Pb, and Zn. The recovery versus retention time curves are very similar in shape. The upward slope from 16 to 22 min following the plateau from 10 to 16 min represents the stage addition of the amine. The upslope is not apparent in the grade versus retention time plot. This is because of the lowered amount of minerals available when the stage addition is made. At 16 min, two-thirds to three-fourths of each mineral's final recovery has been met. The grade curves show a straightline relationship for Pb, Cu, and Co, with the Zn trend better suited to an exponential fit. This seems to reflect a faster flotation rate for ZnS. ZnS is the most responsive mineral to the amine. In almost every test run, ZnS recoveries approached or exceeded 90 pct. ZnS also consistently showed the highest improvement ratios of all the minerals.

CLEANER FLOTATION

Two types of cleaner flotation were tested, the first used a continuation of the cationic collection scheme used in the rougher stage and the second used an anionic collection scheme more common to sulfide flotation. When the actual tests were run, four rather than the six available 1-ft³ cells were used as roughers. This change was necessary due to overloading of the cleaners. When all six of the 1-ft³ cells were used to rough, the concentrate volume overwhelmed the cleaner circuit. By taking two of the 1-ft³ cells out of service, the rougher concentrate volume was lowered to a more manageable level. Since it was very important to maintain a retention time from 4 to 5 min/cell in the cleaning stage, the reduction by one-third of rougher volume meant an increase of one-third in the cleaner retention time. This translated to an increase in recoveries as follows, in percent: 25 Co, 40 Cu, and 60 Pb. Zinc recoveries were not affected nor were grades of the metals.

Of the two cleaning methods, the cationic cleaning was less involved. In this method, the only reagent addition was 0.2 to 0.3 lb/st of amine into the first cleaning stage.

Anionic cleaning was more involved as to reagent additions. Sulfur dioxide (SO₂) was added as sulfurous acid (H₂SO₃), and the pH dropped to 6.0. Sodium aerofloat was then added along with methyl isobutyl carbonol (MIBC) frother and the cleaner flotation was carried out. In order to accomplish this, the two extra 1-ft³ cells were used as conditioners. The SO₂ was added to the first and the Na aerofloat to the second. Final results for the two methods were relatively close, although the cationic cleaning gave overall higher grades. In fact, one test resulted in a Zn grade exceeding 18 pct at a recovery of 80+ pct. More common are the results given in table 3. This represents long-term mean results over a series of 20+ tests.

The following parameters represent the optimum for the roughing tests as conducted:

Reagents

- Amine, 1 lb/st added equally down the cell bank.
- NaOH to pH 10.0±0.2 added down the cell bank.

Slurry parameters

- 25 to 35 pct solids by weight.
- 20- to 24-min total retention time.

Figure 8 is representative of the typical flowsheet during a combined rougher-cleaner run, and table 4 gives material balances. These are long-term mean values for over 20+ tests. In actual practice, the cleaner tailings would be recycled back into the feed stream.

Table 3.—Long-term results of cationic and anionic cleaning averaged over several tests

Element	Grades		Recoveries	
	Cationic	Anionic	Cationic	Anionic
Co	0.12	0.14	50	40
Cu	1.00	.65	60	40
Fe	25.00	12.50	40	35
Ni15	.18	40	35
Pb	5.00	3.00	75	60
Zn	7.5	4.80	90+	90+

Table 4.—Typical material balance for roughing and cleaning

	Feed	Rougher conc	Cleaner conc ¹	Cleaner tailing ¹	Final tailing
Wt pct	100	15	6	9	85
Grade, pct:					
Co	0.02	0.06	0.14	0.03	0.01
Cu	0.05	0.40	0.90	0.15	0.02
Fe	2.10	6.00	19.50	6.00	1.80
Ni	0.03	0.08	0.18	0.08	0.02
Pb	0.20	1.00	3.20	0.80	0.12
Zn	0.25	1.70	5.80	0.57	0.10
Recovery, pct:					
Co	100	60	40	20	40
Cu	100	75	50	25	25
Fe	100	43	40	3	57
Ni	100	55	31	24	45
Pb	100	75	68	7	25
Zn	100	96	92	4	4

¹From rougher concentrate.

2 - stage recirculation

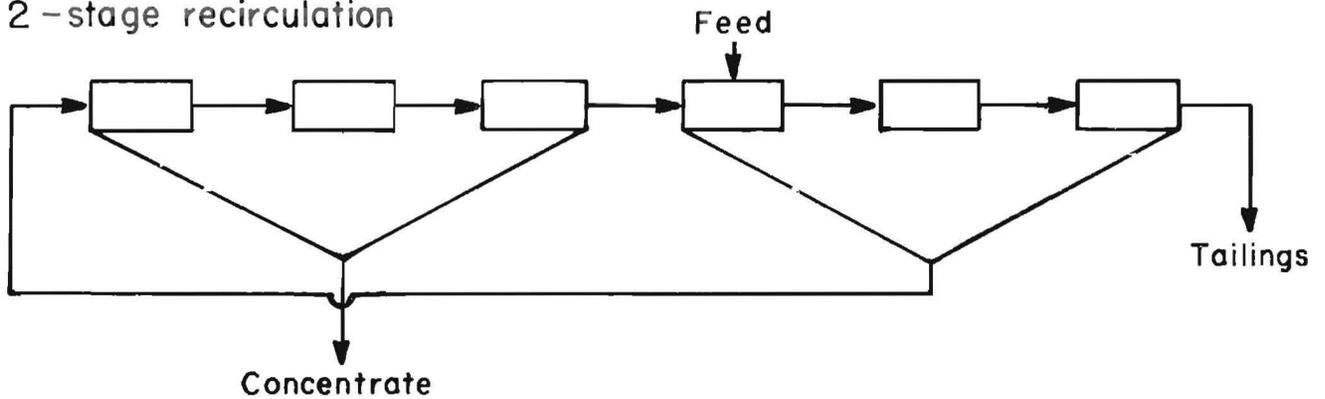


Figure 8.-Schematic for material balance data in table 4.

CONCLUSIONS

It has been shown that a bulk sulfide concentrate can be recovered from Missouri Pb mill tailings on a continuous, pilot scale, using froth flotation. An amine collector is used in the rougher stage and either the amine or Na

aerofloat are used as collectors in the cleaner stage. A final concentrate is produced from the cleaner stage, which contains over half of the valuable metals in less than 10 pct of the total tailing weight.