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Cobalt and Nickel From Lead-Smelter Matte: Purification of Leach Liquor

By R. B. Prater, Jr., and Robert M. Doerr



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
cm	centimeter	mL/min	milliliter per minute
g	gram	mm	millimeter
g/l	gram per liter	mm/s	millimeter per second
h	hour	MMlb/yr	million pound per year
K	Kelvin	MMst	million short tons
L	liter	pct	percent
lb	pound	s	second
lb/st	pound per short ton	st	short ton
m	meter	st/yr	short ton per year
mg	milligram	vol pct	volume percent
min	minute		

COBALT AND NICKEL FROM LEAD-SMELTER MATTE: PURIFICATION OF LEACH LIQUOR

By R. B. Prater, Jr.,¹ and Robert M. Doerr²

ABSTRACT

Research by the Bureau of Mines includes efforts to devise means for maximum recovery of critical and strategic metals from primary and secondary domestic resources. As part of that effort, the Bureau developed a hydrometallurgical process to recover Co, Ni, and Cu from Missouri lead-smelter matte.

The process includes leaching with H_2SO_4 plus MnO_2 as an oxidizing agent, liquor purification, selective precipitation of CuS , $(Co,Ni)S$, and $MnCO_3$, and crystallization of Na_2SO_4 . This report is concerned primarily with liquor purification, in which As and Fe are removed from the leach liquor by pH adjustment and filtration. Two variations of the purification step are described. One variation provides liquor containing <1 mg/L As and Fe but requires two solid-liquid separations. The other is achieved with only one solid-liquid separation but leads to a lower degree of purification.

¹Metallurgist.

²Supervisory metallurgist (retired).

Rolla Research Center, Bureau of Mines, Rolla, MO.

INTRODUCTION

About 9 MMst of lead ore are mined annually from Missouri's New Lead Belt. The estimated ore reserves of 300 MMst (1)³ contain about 16 MMst Pb at an average grade of 5.4 pct. Although these ores could supply significant quantities of Co (2.5 MM lb/yr) and Ni (3.4 MM lb/yr), current recoveries include no Co and very little Ni. About 48 pct of the Co and Ni contained in the ore remains with the Pb-Cu bulk concentrate through the conventional milling process. Subsequent pyrometallurgical treatment of the Pb concentrate (2-3) produces about 13,000 st/yr of mattes containing 190,000 lb Co, 260,000 lb Ni, and 4,000 st Cu. The production rates and metal contents of matte furnace slags are similar. Missouri processors often export the matte furnace products under severe financial penalties.

As part of its continuing effort to maximize mineral and metal recovery from primary and secondary domestic resources, the Bureau of Mines performed research directed toward the recovery of Co, Ni, and Cu from these lead-smelter mattes (4-5). The research objective was to develop an environmentally sound and economic hydrometallurgical process for treating Missouri lead-smelter mattes that is compatible with existing milling and smelting operations. The resulting process, as shown in figure 1, begins with a previously described H₂SO₄-MNO₂ oxidative leaching step (6). This report is primarily a presentation of the research on removal of the main impurities, As and Fe, from the leach liquor. In general, this was achieved by controlled partial neutralization of acid in the raw leach liquor at moderate temperatures.

A representative lead-smelter matte assay is presented in table 1. All data presented in this report are derived from work on mattes similar to this. Subsequent to the research reported here, the matte practice was substantially changed at the two Missouri smelters that produce

TABLE 1. - Representative lead-smelter matte assay, percent

Ag.....	0.033	Na.....	1.0
As.....	1.42	Ni.....	4.58
Cd.....	.029	Pb.....	12.3
Co.....	1.10	S.....	13.2
Cu.....	43.6	Sb.....	.14
Fe.....	5.43	Zn.....	1.05

TABLE 2. - Typical new matte assay from one smelter, percent

Ag.....	0.0016	Na.....	21.6
As.....	.51	Ni.....	.55
Cd.....	.52	Pb.....	3.6
Co.....	.68	S.....	21.1
Cu.....	29.2	Sb.....	.13
Fe.....	3.08	Zn.....	2.6

matte. In consequence, the matte assays for one smelter were changed to those shown in table 2.

The principal impact of the changed matte composition is thought to be on the leaching and purification steps. Note that 21.6 pct Na is equivalent to 36.7 pct Na₂S, the principal form present in the matte. The other smelter changed matte practice in a manner that does not result in a high Na content but does lead to a much higher concentration of sulfate.

Lead-smelter matte compositions vary greatly, both between smelters and between lots from the same smelter. The chief difference between mattes from different smelters is in the Pb content. The chief difference between matte lots from the same smelter is that some contain a relatively high proportion of Cu and Fe while others contain relatively high levels of Co, Ni, Pb, and As. In the purification step, the molar ratio of Fe to As was found to be important; it ranged from 0.21 to 19.3 for the leach liquor samples assayed, and from 0.2 to 8.1 for mattes from the Missouri lead smelters.

For mattes similar in composition to that given in table 1, the typical approximate analysis of the leach liquor, in g/L, was As, 3 to 5; Cd, 0.01 to 0.04;

³Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

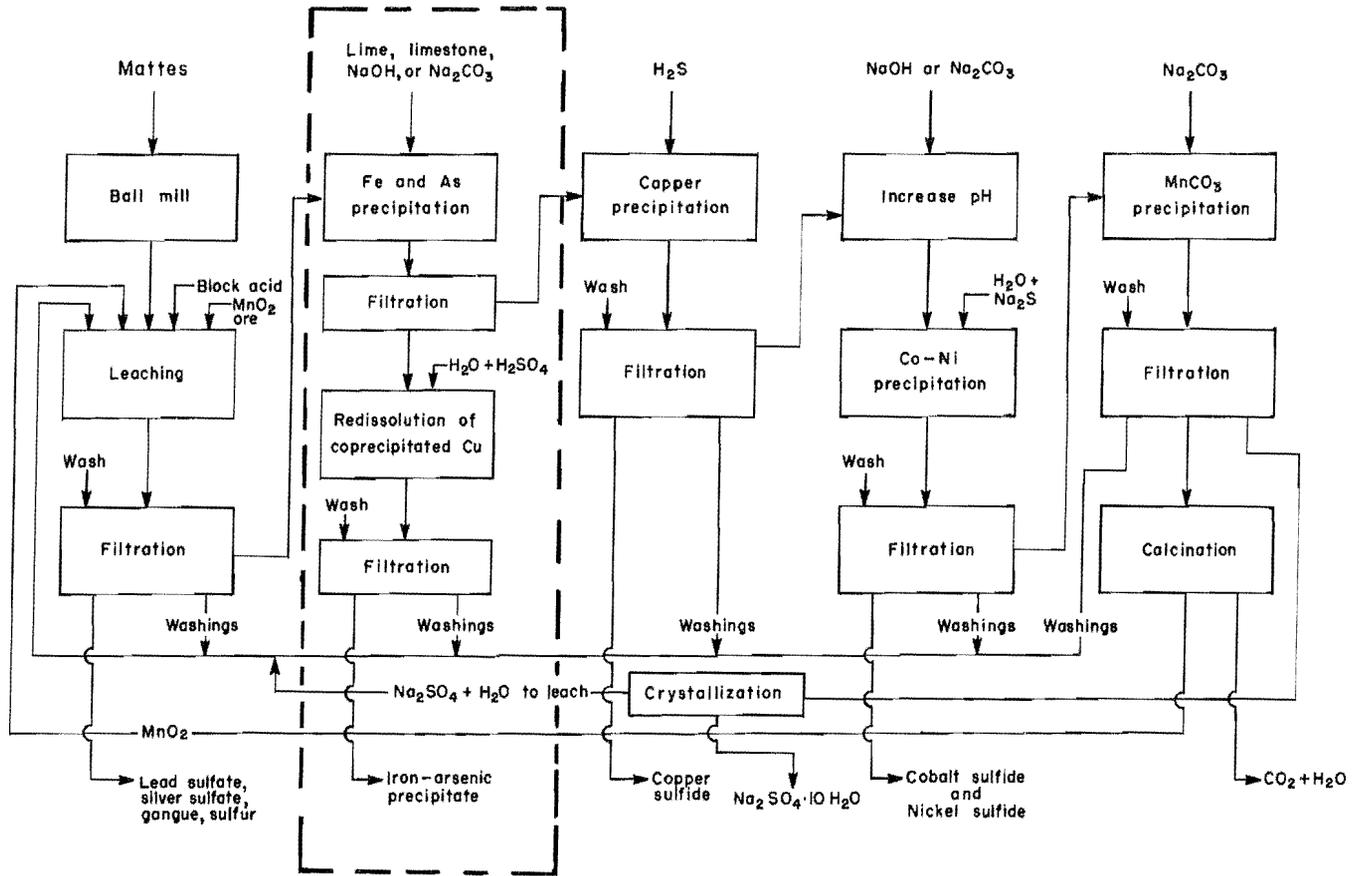


FIGURE 1.—Overall process flowsheet, with double-filtration liquor purification. This report addresses development of process enclosed by dashed lines.

Co, 1 to 2; Cu, 40 to 50; Fe, 3 to 5; Mn, 40 to 50; Ni, 5 to 15; and Zn, 1 to 2. The acidity was about pH 0.

Shelton (7) reported on precipitation tests based on a solution containing Co, As, Cu, and Fe. As the pH was increased from 0.03 to 1.33, 92 pct of the Fe and lesser fractions of the other elements were precipitated. As the pH was then increased to pH 2.38, the remaining Fe was precipitated. However, the pH was increased to 6.62 before 96.6 pct of the As was precipitated; and in the course of this treatment, 95.8 pct of the Cu and 42.7 pct of the Co were also precipitated. The solution did not contain sufficient Fe to precipitate the As as FeAsO_4 . When the Fe concentration was increased so that the Fe-As molar ratio was 2.21, in a different solution apparently containing no Cu, essentially none of the Co, 99.9 pct of the As, and 86 pct of the Fe were precipitated by

raising the pH to 3.45. The remaining As was precipitated in the range pH 3.45 to 6.45, during which treatment only 2.2 pct of the Co was precipitated. Reacidification of the precipitates from pH 6.45 to 1.0 caused redissolution of the coprecipitated Co.

Shelton (8) reported that, when removing As from leach liquor, with sufficient Fe present for the formation of FeAsO_4 , lime or calcite was the preferred precipitating agent for reasons of filtering speed. Shelton also reported that filtering speed is about four times faster at 95° C than at 25° C.

Patterson (9) stated that when polyvalent metallic ions, particularly Fe, Al, and Zn, are present in a waste water that contains As, they complex with the As ions and are coprecipitated at the pH of metal hydroxide formation. This author also mentioned that the oxidation of AsO_3^{3-} to AsO_4^{3-} is necessary for

effective precipitation. Erdey (10) showed that $\text{Fe}(\text{OH})_3$ is precipitated substantially in the range pH 2.2 to 3.2.

Monhemius (11) presented a graph of $\log [M^{n+}]$ (metal ion activity) and pH versus $\log [\text{AsO}_4^{3-}]$ for various metal ions in solution at 25° C. In the pH range of 3 to 4, only Ba^{2+} leads to a lower activity of AsO_4^{3-} in solution at equilibrium than does Fe^{3+} . At a total As activity of 10^{-5} M at pH 3, the indicated equilibrium activities are $10^{-17.5}$ M for AsO_4^{3-} and $10^{-2.7}$ M for Fe^{3+} .

Robins (12) showed that in the $\text{FeAsO}_4\text{-H}_2\text{O}$ system there is a minimum in the solubility of FeAsO_4 at about pH 2.2 with a corresponding As activity of approximately 10^{-3} M.

Tozawa (13), based on the solubility data of Chukhlantsev (14-15), reported relations between As concentration in solution and pH, in equilibrium with various arsenates. However, for FeAsO_4 , Tozawa's test results indicate a minimum equilibrium As concentration of 0.02 g/L at pH 3.3 and 25° C.

Tozawa also presented the results of tests of the precipitation of As^{5+} with Fe^{3+} ; for an Fe-As molar ratio of 2,

precipitation of As^{5+} from a 0.005M solution at 25° C was essentially complete in 1 h at pH 2, compared with only about 90 pct at pH 2.5 when the Fe-As molar ratio was 1. For comparison, leach liquor containing 1.3 g/L As has an As concentration of 0.017M. The ion As^{3+} was effectively precipitated only at pH 8 and then only with an Fe-As molar ratio of 2. In each case, there was a pH value for which the As remaining in solution was at a minimum. Tozawa showed that the precipitation of As is more nearly complete at 25° C than at 80° C, at Fe-As ratios of 2 to 5 and at pH 3 to 6.

Bloom (16), who dealt with lead-smelter flue dusts, referred to the coprecipitation of As with Fe^{3+} as simple and economically attractive, reporting that "selectivity for precipitation of As is best in a pH range of 3.1 to 3.4 and at an iron-arsenic ratio above 1.2." Higher pH improved the As rejection but led to greater coprecipitation of Zn and Cd values. Bloom achieved almost 100-pct rejection of As, and minimal coprecipitation of Zn, Cd, and In, at 90° C by sulfide precipitation, but the sulfide was "slimy and difficult to filter."

ACKNOWLEDGMENT

Appreciation is expressed to Dr. Gary J. Long of the chemistry faculty of the University of Missouri - Rolla for the

Mossbauer results presented in this report and for their interpretation.

PROCEDURE

Leach liquor purification tests were based on controlled partial neutralization of the residual acid in the liquor to effect precipitation of the main impurities, Fe and As, for removal by filtration. Various alkaline reagents were used for the neutralization tests. These included 400 g/L NaOH solution, NaOH solution with a little $\text{Ca}(\text{OH})_2$, $(\text{NH}_4)_2\text{CO}_3$, MnCO_3 , $\text{Ca}(\text{OH})_2$, Na_2CO_3 , $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, and pulverized limestone. All of the reagents were technical grade. The selected level of acidity, in the range pH 2.77 to 4.60, was maintained for 1 to 120 min for precipitation of the As and Fe. Test temperatures ranged from 20° to 80° C.

Test conditions that led to effective purification of the liquor were found

to lead also to the coprecipitation of some metal values, primarily Cu. Therefore, reacidification of the slurry, or acid treatment of the precipitate, was used in tests to redissolve the coprecipitated values.

The purification tests were of two modes, batch and continuous; a bench-scale process research unit (BSPRU) was used in the continuous tests. Each mode was followed by two test methods for reacidification, termed the single-filtration (6, 17) and double-filtration methods.

In the single-filtration method, shown in figure 2, after the precipitation treatment, the slurry in its entirety was treated with H_2SO_4 to increase the

series; the process material was pumped to the first reactor, and then carried from the first to the second by gravity overflow. The capacities of the reactors were 175 and 730 mL, respectively. The reactor contents, from the previous run, were heated to the temperature selected for the test. Then the liquor, also heated to the test temperature, was pumped continuously into the first reactor for the duration of the run, and most of the required 400-g/L NaOH solution was also pumped continuously into the first reactor. An additional 400 g/L NaOH solution was pumped into the second reactor at a rate adjusted to maintain the degree of acidity selected for the test. As the capacity of the second reactor to its overflow was about 730 mL, when the combined liquor and caustic solution addition rates amounted to a typical 18 mL/min, the nominal residence time in the second reactor was about 40 min.

When a batch precipitation test was combined with single-filtration reacidification, the procedure was to add sufficient H_2SO_4 to the slurry after the precipitation step and before flocculating and filtering.

When a continuous precipitation test was combined with single-filtration reacidification, an additional reactor, as described for the second precipitation reactor, was used after the second reactor. H_2SO_4 , diluted to 20 vol pct, was pumped continuously into the third reactor at a rate to maintain the degree of acidity selected. Overflow from the third reactor passed into a small stirred vessel into which was pumped the flocculant, and overflow from the flocculant mixer passed into a Buchner funnel filter.

When a batch precipitation test was the first part of a double-filtration

test, the precipitation slurry was filtered and the filter cake was repulped and stirred with dilute acid at the test temperature for a selected time and refiltered.

When a continuous precipitation test was the first part of a double-filtration test, the slurry from the second precipitation reactor passed directly into the flocculant mixer and thence to the filter. The filter cake was treated as for batch double-filtration precipitation tests.

Chemical analyses were performed on samples of raw leach liquors, on purified liquors, and on final precipitates. In the case of double-filtration reacidification tests, the second filtrates and wet first filter cakes were also analyzed. It was observed that Cu was more readily coprecipitated than was Co, Ni, or Mn, so the assays for Fe, As, and Cu were made for each step. For completeness, Co, Ni, and Mn assays were also made in some cases. Essentially none of the Zn or Cd coprecipitated, so these analyses were not normally performed.

For mass balances, the liquors retained in filter cakes were usually accounted for, either by combining the wash water with the filtrate or by calculating an adjustment from the wash water volume and the assays of the filtrate and the wash water.

In practice the leach temperature would be about 93° to 105° C, and other process steps would be effected at lower temperatures. Thus, the optimum point in the process for allowing the liquor to cool was to be determined. Purification tests were performed at 20° to 80° C.

Selected samples were evaluated by Mossbauer spectroscopy.

RESULTS AND DISCUSSION

SINGLE-FILTRATION BATCH TESTS

Eighty-three batch, single-filtration tests were made. The distributions of Cu to the precipitate and of Fe and As to the liquor were computed. The selectivity indices (geometrical mean of the

relative rejections and recoveries of two components being separated) for As versus Cu and for Fe versus Cu were also computed. Independently of the precipitation pH, the tests that exhibit As-Cu selectivity indices of 20 or greater, with a final (redissolution) pH of about 3,

include none of the tests at 80° C. Room-temperature tests led to indices of greater than 25 unless the final pH was ~1.0.

Only two tests led to an As-Cu selectivity index below 20 when the test temperature was 60° C or below. Selected test data are presented in table 3.

A low selectivity index is indicative of a poor separation, but a high selectivity index is not definitive. A high index can result from good grade and recovery results but also from either a very good grade or a very good recovery without respect to possible poor results for the other.

Little purification effect appears to be attributable to the different alkaline reagents used.

Five of the tests led to retention of less than 2 pct of the As and Fe in the liquor, and loss to the precipitate of less than 2 pct of the Cu. All of these tests were run with a precipitation pH in the range 3.6 to 3.9. Three of these tests were run with a final (redissolution) pH of 3.3, which is considered high for such low Cu losses. These three tests were made with liquor from a single batch having an Fe-As molar ratio of 3.72; the liquor was 14 to 21 days old when purified and is considered to have been relatively fresh.

Other tests led to retention of less than 2 pct of the As, but with higher retention of Fe. For these few tests and the five mentioned in the paragraph immediately above, when the final pH was 2.8 or lower, less than 1.0 pct of the Cu was lost; and except for two tests, this result always occurred. The Cu loss usually increased to about 5 pct when the final pH was 3.5.

Some tests run in the pH range 3.53 to 3.77 led to As retention between 2 and 5 pct but to extremely variable Fe retention and to Cu loss as high as 5.5 pct at a final pH of 3.

The loss of Cu to the precipitate, generally, appears to depend on the final pH, ranging typically from 5 pct for pH 3 to 3.5 to 0.4 pct for pH 2.8.

When the final pH for a single-filtration test was about 2.5, no temperature effect was apparent.

Figure 3 is a presentation of the As-Cu selectivity index values versus precipitation pH for redissolution at about pH 3. Figure 4 is a presentation of the Fe-Cu selectivity index versus precipitation pH for redissolution tests at about pH 3.

Figures 3 and 4 indicate that the poorest separations resulted with temperatures of 60° and 80° C and suggest little or no correlation between the selectivity indices and the precipitation pH used.

Using leach liquors having Fe-As molar ratios of less than 1.7 as feed materials, about 61 batch single-filtration tests were made. The resulting As-Cu selectivity indices depended principally on the test conditions used, but the index was less than 60 for all but one of these tests. Using leach liquors having Fe-As molar ratios of greater than 1.7 as feed materials, about 22 tests were made. The resulting As-Cu selectivity indices also depended primarily on the test conditions used, but the index exceeded 200 for 6 of these 22 tests. Thus, it appears that the As-Cu selectivity index is limited if the Fe-As molar ratio is less than about 1.7. These results are in

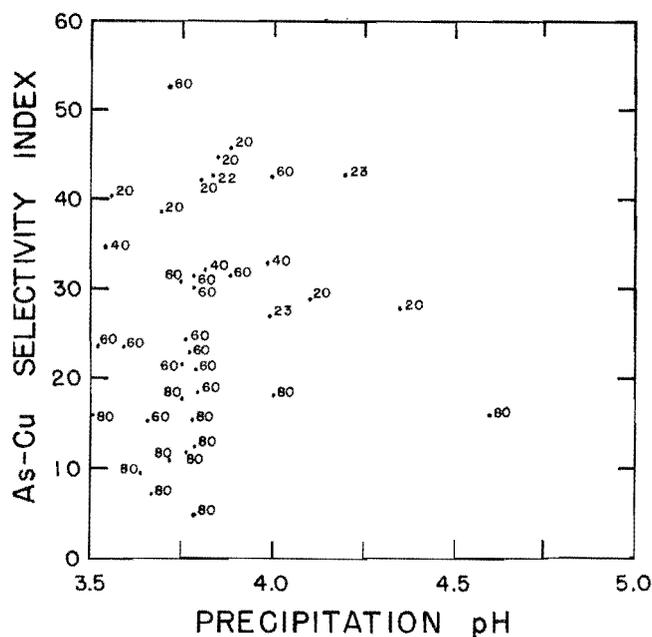


FIGURE 3.—As-Cu selectivity index versus precipitation pH for redissolution pH = 3 ± 0.04. Numbers by points are test temperatures, °C.

TABLE 3. - Single-filtration batch purification tests and results¹

Test	Test conditions					Fractional distribution			Fe-As molar ratio ²	Selectivity index	
	Precipitation				Final (redissolution) pH	To liquor		Cu to ppt		As-Cu	Fe-Cu
	Temp, °C	pH	Reagent(s)	Time, min		Fe	As				
7	20	3.55	Ca(OH) ₂ + NaOH.....	15	3.00	0.0215	0.1860	0.0027	1.19	40.2	129.6
45	20	3.80	NaOH.....	37	3.00	.0247	.1522	.0028	1.13	44.5	118.6
42	20	3.98	Ca(OH) ₂ + NaOH.....	10	3.00	.0249	.1735	.0065	1.17	27.0	77.4
23	40	3.52	...do.....	2	2.50	.1173	.2295	.0021	1.11	39.9	59.8
20	40	3.54	...do.....	2	3.00	.0411	.1879	.0036	1.17	34.6	80.4
24	40	3.80	...do.....	25	2.50	.1130	.2254	.0019	1.09	42.5	64.2
21	40	3.82	...do.....	2	3.02	.0455	.1682	.0047	1.10	32.4	66.6
22	40	3.98	...do.....	21	3.00	.0301	.1614	.0048	1.03	32.8	81.7
25	40	4.00	...do.....	52	2.50	.1003	.2044	.0043	1.08	30.0	45.6
73	52	3.23	Na ₂ CO ₃	70	2.74	.3446	.0988	.0003	1.34	174.3	79.6
11	60	3.52	Ca(OH) ₂ + NaOH.....	10	3.00	.0598	.1798	.0081	1.10	23.6	43.9
18	60	3.75	...do.....	8	2.46	.1284	.1935	.0026	1.03	40.0	51.0
51	60	3.76	NaOH, then Ca(OH) ₂	5	3.01	.0162	.0427	.0365	1.18	24.3	40.0
50	60	3.79	Ca(OH) ₂ , then NaOH.....	20	3.01	.0244	.1429	.0177	1.22	18.2	47.1
15	60	4.00	...do.....	10	3.00	.0113	.1468	.0032	1.34	42.6	165.1
16	60	4.05	...do.....	2	2.51	.0874	.2109	.0037	1.21	31.7	53.0
29	80	3.50	...do.....	9	3.00	.0907	.2044	.0151	1.07	15.9	25.6
33	80	3.75	...do.....	52	2.50	.1068	.2168	.0071	1.11	22.5	34.2
59	80	3.77	NaOH.....	15	2.96	.0115	.0771	.0465	1.20	15.7	42.0
34	80	4.00	Ca(OH) ₂ + NaOH.....	7	3.00	.0215	.1452	.0175	1.25	18.2	50.6
39	80	4.00	...do.....	22	2.50	.0585	.1589	.0084	1.10	25.0	43.6
2	80	3.53	NaOH.....	NR	2.50	.1371	.0417	.0043	2.52	73.0	38.2

NR Not recorded. ppt Precipitate.

¹For full data, see table A-1 in appendix.²Ratio calculated from product assays and quantities.

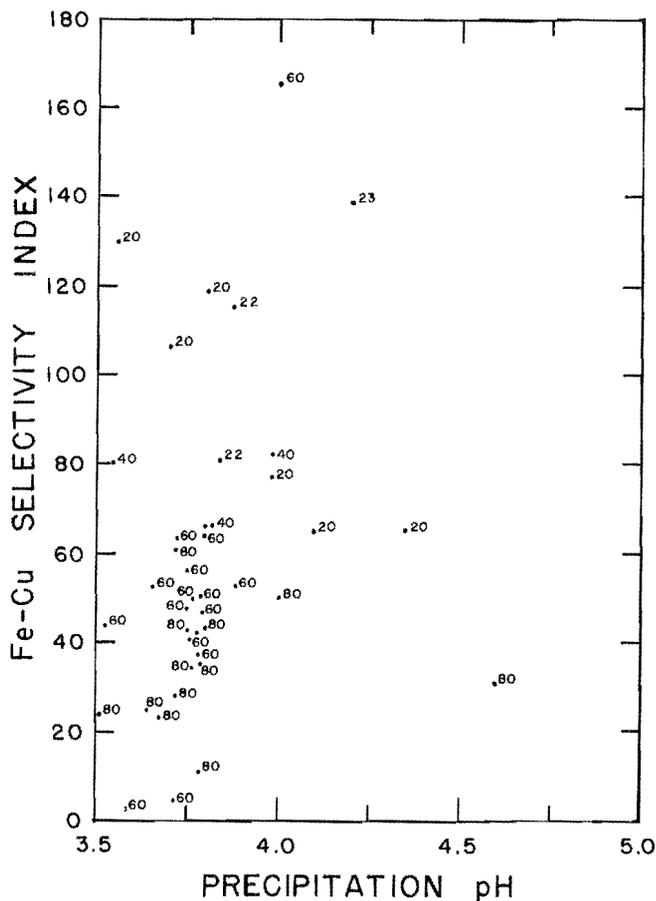


FIGURE 4.—Fe-Cu selectivity index versus precipitation pH for redissolution pH = 3 ± 0.04 . Numbers by points are test temperatures, °C.

essential agreement with Shelton (7) and Tozawa (13).

A total of 26 tests were conducted at 50° to 60° C with the precipitation pH in the range 3.52 to 3.88 and the final pH in the range 2.79 to 3.33. When the Fe-As ratio was 1.03 to 1.22 (13 tests), the resulting As-Cu selectivity indices were 15.4 to 42.6 with a mean of 26.1, and the As distribution to the filtrate was 4.3 to 18.7 pct with a mean of 12.3 pct. When the Fe-As ratio was 1.77 (4 tests), the As-Cu selectivity indices were 153.1 to 636.1 with a mean of 371.9, and the As distribution to the filtrate ranged from 0.1 to 7.9 pct with a mean of 2.1 pct.

Nine tests were conducted with a feed liquor Fe-As ratio of 3.44 to 3.79. The resulting As-Cu selectivity indices were 28.3 to 1010.4 with a mean of 304.3, and the As distribution to the filtrate was

0.01 to 3.3 pct with a mean of 1.5 pct. The best separations and As removals were obtained with Fe-As ratios of 1.77 to 3.79. The Fe-As ratio seems to have a greater effect than the test temperature in the ranges tested.

The effect of the Fe-As molar ratio on the As-Cu selectivity index in tests with appropriate pH appears to be explainable as follows. If the Fe-As ratio is low, the Fe is preferentially precipitated as FeAsO_4 and the excess As is precipitated preferentially as a Cu-As compound. If the Fe-As ratio is unity or slightly above unity, FeAsO_4 is the dominant species precipitated. If the Fe-As ratio is high, FeAsO_4 is preferentially precipitated until the As is depleted from the liquor; then the excess Fe may be precipitated as an iron hydroxide. The precipitate is a brownish-yellow powder, more brown when the Fe content is high.

DOUBLE-FILTRATION BATCH TESTS

Precipitation

Table 4 is a presentation of the data for selected batch tests of the precipitation part of double-filtration purification. Some of the tests listed are based on slurry samples drawn during single-filtration batch tests, after precipitation and before reacidification of the slurry.

The objectives of this step are the same as those in single-filtration purification, that is, to free the liquor of As and Fe and to generate a residue low in Cu. However, in the double-filtration mode, the emphasis for the precipitation step is on the purity of the liquor; co-precipitated metal values are subject to redissolution from the wet filter cake in the reacidification step.

Some of the tests, most of them involving short treatment times, exhibit anomalous results. Also, a number of the tests were based on aged liquor, which led to low levels of As in the liquor at pH 3.4. In the 16 tests at pH 3.6 to 3.9, 6 of which are included in table 4, the Fe and As were satisfactorily precipitated. Only 0.01 to 3.45 pct of

TABLE 4. - Results for first (precipitation) part of batch double-filtration purification tests¹

Test	Leach liquor assay, g/L			Precipitation test conditions				Fractional distribution			Fe-As molar ratio ²
				Temp, °C	pH	Reagent(s)	Time, min	To liquor		Cu to ppt	
	Fe	As									
26	4.40	1.40	49.80	55	3.39	Na ₂ CO ₃	120	0.0022	0.0088	0.0356	5.35
21	5.16	1.30	44.80	51	3.40	...do.....	120	.0022	.0012	.0286	7.17
28	4.40	1.36	50.20	53	3.40	NaOH.....	120	.0029	.0116	.0124	5.42
19	5.08	1.16	48.00	50	3.42	Ca(OH) ₂	120	.0019	.0010	.0572	5.96
34	4.96	1.20	42.60	49	3.42	...do.....	120	.0088	.0011	.1774	4.18
22	4.86	1.24	44.60	51	3.60	Na ₂ CO ₃	120	.0005	.0010	.0799	5.49
6	4.46	3.38	41.02	51	3.80	MnCO ₃ + Na ₂ CO ₃ .	60	.0003	.0017	.0034	2.17
10	3.88	1.40	37.39	50	3.80	Na ₂ CO ₃	60	.0208	.0021	.0335	3.68
12	4.10	1.45	42.03	51	3.80	...do.....	60	.0345	.0012	.1471	5.59
13	4.10	1.45	42.03	51	3.80	...do.....	60	.0001	.0024	.1399	5.33
11	4.10	1.45	42.03	51	3.81	...do.....	60	.0306	.0013	.0126	5.66
18	5.06	1.44	50.00	51	3.98	Ca(OH) ₂	120	.0002	.0009	.8238	6.59

ppt Precipitate.

¹For full data, see table A-2.²Ratio calculated from product assays and quantities.

the Fe and 0.01 to 0.24 pct of the As remained in the liquor. In these tests, the Cu precipitation was erratic and ranged from 0.06 to 65.71 pct. Also, some additional untabulated precipitation tests using Na₂CO₃ at pH 3.9 to 4.0 led to Cu losses of 13 to 21 pct.

A total of 14 different flocculants were tested on 670- to 900-mL samples of a large batch of slurry produced with soda ash as the precipitant. Each sample was subjected to three successive flocculant additions; each addition was followed by thorough mixing and a 20-min settling time. No settling was observed in most of the tests. Three of the tests produced 5 to 15 mL of clear liquid at addition rates of about 24 to 48 lb/st. No significant variations in filtering speed were observed for most flocculants; when a 15-cm funnel was used, an average of 47 min was required to recover 450 mL of filtrate. Much longer filtering times in two of the tests were probably the result of increased slurry viscosity caused by the flocculant. At low addition rates, the choice of flocculant was not critical; but the use of a flocculant did improve the filterability of the slurry.

Slurries formed by precipitation with lime as a reagent filtered faster, sometimes by orders of magnitude, than did those formed by precipitation with soda as the pH-adjusting agent. Some soda-precipitation test slurries filtered exceedingly slowly. Other than the impact on filtering rates, little effect appears attributable to the different alkaline reagents used.

Redissolution

Data on tests of the redissolution part of double-filtration purification are presented in table 5. These tests were run at 50° C for 120 min. The results are reported as distributions to the residue for As and Fe, the rejection of which is the object of purification, and to the liquor for Cu, Co, Ni, and Mn, whose recovery in solution is the object of the redissolution step. Because the liquor from this step is recycled in the process, recovery of the valuable elements in the liquor is somewhat more important than is the retention of a high fraction of the As and Fe in the solids; this liquor does, however, constitute a circulating load. The overall fractional

TABLE 5. - Redissolution part of double-filtration purification tests

Precipitation reagent	Test	Feed assays, pct						pH	Notes	Fractional distribution					
		Fe	As	Cu	Co	Ni	Mn			To residue			To liquor		
										Fe	As	Cu	Co	Ni	Mn
Na ₂ CO ₃	1	2.19	0.855	5.35	0.075	0.245	2.52	2.45	Minimum H ₂ O ¹ .	0.956	0.978	0.764	0.830	0.866	0.802
Do.....	2	2.19	.855	5.35	.075	.245	2.52	2.8	...do.....	.998	.986	.628	.717	.690	.700
Do.....	3	2.19	.855	5.35	.075	.245	2.52	2.6	...do.....	.989	.963	.693	.754	.784	.721
Do.....	4	2.19	.855	5.35	.075	.245	2.52	2.2	...do.....	.858	.964	.906	.929	.922	.920
Do.....	5	2.19	.855	5.35	.075	.245	2.52	2.4	Twice minimum H ₂ O.	.947	.990	.993	.934	.981	.980
Do.....	6	2.19	.855	5.35	.075	.245	2.52	2.2	...do.....	.998	.999	.983	.894	.960	.955
Do.....	7	2.19	.855	5.35	.075	.245	2.52	2.0	...do.....	.736	.896	.995	.928	.983	.974
Do.....	8	2.3	.58	3.87	.06	.30	2.69	2.3	...do.....	.925	.983	.927	.946	.941	.954
Do.....	9	2.3	.58	3.87	.06	.30	2.69	2.0	...do.....	.834	.930	.883	.894	.909	.904
Do.....	10	2.3	.58	3.87	.06	.30	2.69	2.4	...do.....	.954	.993	.850	.896	.881	.888
Do.....	11	2.3	.58	3.87	.06	.30	2.69	2.1	...do.....	.806	.936	.934	.943	.956	.946
Do.....	12	2.3	.58	3.87	.06	.30	2.69	2.2	...do.....	.852	.960	.978	.989	.995	.999
Do.....	² 13	27.6	6.89	9.10	.03	.08	.26	2.3	...do.....	.993	.999	.900	.443	.746	.989
Do.....	² 14	30.9	7.85	3.68	.01	.03	.005	2.1	...do.....	.982	.996	.828	.151	.348	.772
NaOH.....	² 15	29.5	7.25	3.87	.01	.03	.12	2.3	...do.....	.995	.999	.992	.460	.499	.885
Ca(OH) ₂	16	1.84	.5	1.1	.02	.025	.17	2.3	...do.....	.962	.997	.961	.129	.565	.548
Do.....	17	1.84	.5	1.1	.02	.025	.17	2.1	...do.....	.922	.990	.959	.276	.533	.509
NaOH.....	² 18	32.8	8.09	2.27	.02	.02	.05	2.1	...do.....	.989	.999	.984	.279	.218	.673
Ca(OH) ₂	19	1.36	.44	3.97	.09	.39	3.2	2.3	10-L batch, twice minimum H ₂ O.	.920	.988	.954	.964	.958	.959

¹Minimum water required to enable stirring of the resulting slurry.

²Feed was dried before the redissolution test.

distribution (FD) to the purified liquor is given by the equation

$$FD = PD + RD (1-PD), \quad (1)$$

where PD = distribution to the liquor in the precipitation step

and RD = distribution to the liquor in the redissolution step.

Although the level of acidity (set in the range pH 2.0 to 2.4) was the main independent variable in these tests, two levels of water addition were used, and one group of tests was based on the use of dried precipitate rather than wet filter cake. Because the liquor from this step would have to be returned to the leach step or to the precipitation step, one of the levels of water addition selected was just enough to enable good stirring of the slurry. The other was twice as much water. The dried precipitate tests were intended to indicate whether, in practice, accumulation of precipitates (and allowing their becoming dried) for batch redissolution for recovery of coprecipitated copper would be possible.

The results for tests in which dried residue was used as feed are that the As remained in the residue, as did a very large proportion of the Fe. Copper redissolution was generally high in these tests.

Successful precipitation tests led to the precipitation of very minor fractions of the contained Co and Ni but more significant fractions of the Cu, more or less in proportion to its concentration in the raw leach liquor. Manganese reported to the filter cake roughly in proportion to its concentration in the liquor, probably in retained liquor rather than as a precipitate. The concentrations in the feeds to the redissolution tests were 0.01 to 0.09 pct Co and 0.02 to 0.39 pct Ni. The fractional recovery of these elements fluctuated substantially but was very low only in tests with dried feeds or with the lean (high-gypsum) feed used in tests 13-15 and 16-18. The feeds, exclusive of dried feeds, typically contained about 2.5 pct Mn.

Manganese recovery fractions fluctuated substantially but were very low only for the tests that led to low fractional recovery of Co and Ni. Feed Cu ranged from 1.1 to 9.1 pct. Low Cu redissolution was encountered in two tests; this appears to be attributable to the relatively high pH (2.6 and 2.8) used for these two tests.

A substantial proportion of the iron is redissolved from the filter cakes if the treatment is made with pH below 2.3. At pH 2.3, 90 pct or more of the coprecipitated Cu is redissolved.

Comparison of the results for tests 1 with 5 and 4 with 6 (in table 5) indicates that increasing the water addition for the redissolution step increases the fractional redissolution of the valuable metals without seriously increasing the redissolution of As and Fe.

The As remaining in the residue ranged from 100 pct at pH 2.4 to 92 pct at pH 2.0; all tests at above pH 2.1 led to retention of more than 95 pct of the As in the residue. The Fe remaining in the residue ranged roughly linearly from 95 pct at pH 2.4 to 75 pct at pH 2.0 for the tests with sufficient water and excluding the tests with dried feed.

The redissolution of Cu and Mn appears to be roughly 95 pct for the tests with sufficient water, excluding the tests with dried or lean feed within the pH range 2.0 to 2.4. The two tests with lean feed (16 and 17 in table 5) led to 95-pct redissolution of Cu and 50-pct redissolution of Mn, but there was little Cu and Mn in the feeds. Possibly adsorbed Cu, Co, Ni, and Mn on particles of the primary precipitate may set a lower limit on the degree of separation of As and Fe from these values that is achievable, as indicated by Davey (18) for a similar purification process.

SINGLE-FILTRATION BSPRU TESTS

Data for selected single-filtration BSPRU tests are listed in table 6. The test temperatures were about 50° C. The precipitation pH ranged from 3.60 to 3.97. The redissolution pH ranged from 2.50 to 3.31. For about half the tests, separate data were collected for

TABLE 6. - Single-filtration BSPRU purification tests and results¹

Test	pH		Fe-Cu selectivity index	As-Cu selectivity index	Pre- dicted As in CuS, pct	Fractional distribution			Fe-As molar ratio ²
	Precipitation	Redissolution				To liquor		Cu to ppt	
						Fe	As		
³ 26	3.69	2.66	40.6	94.7	0.140	0.1764	0.0379	0.0028	2.32
12	3.70	2.57	37.2	69.6	.119	.1065	.0330	.0060	2.05
³ 27	3.79	2.78	44.2	95.5	.061	.0692	.0157	.0068	2.23
³ 39	3.79	2.92	10.6	23.7	.372	.2645	.0678	.0240	1.90
³ 29	3.80	2.72	13.2	26.7	.893	.5168	.2067	.0054	2.90
³ 34	3.80	3.02	8.8	19.2	.340	.2594	.0690	.0352	2.13
³ 36	3.80	2.83	11.0	23.4	.366	.2782	.0787	.0209	2.28
20	3.81	2.73	51.4	109.8	.037	.0519	.0119	.0069	2.04
21	3.82	2.80	40.6	111.6	.027	.0566	.0079	.0100	2.13
9	3.88	3.04	120.3	34.4	.105	.0018	.0213	.0374	1.36
10	3.90	2.95	59.8	61.8	.072	.0214	.0201	.0126	1.51
³ 24	3.90	2.70	32.7	51.1	.292	.1881	.0868	.0040	2.21
17	3.91	2.80	38.9	113.5	.033	.0569	.0070	.0108	1.99

ppt Precipitate.

¹For full data, see table A-3.

²Ratio calculated from product assays and quantities.

³Data are for entire test, not just the last interval.

successive intervals of, typically, 100 min. When the data were so collected, the values reported are for the last, usually the third, such interval, when the residual reactor contents from the previous run had been flushed to a maximum degree. For the remaining tests, the products from the intervals were combined before measurement and sampling for analysis.

Let a satisfactory single-filtration BSPRU test be defined as follows. It is one in which the As-Cu selectivity index exceeds 60, the predicted As content of the subsequent CuS product is less than 0.075 pct, the loss of Cu to the precipitate is less than 2 pct, and less than 13 pct of the Fe is retained in the liquor. Based on this definition, 13 of the 43 tests yielded satisfactory results, as listed in table 7. Nine other tests, listed in table 8, yielded results that were unsatisfactory in that they failed to meet one or more of the criteria defined above. The tests in tables 7 and 8 have the following test conditions in common. The Fe-As molar ratio lies in the range 1.51 to 3.73; the precipitation and redissolution pH values lie in the ranges 3.77 to 3.91 and 2.65 to 2.95, respectively; and the redissolution

pH is less than the precipitation pH by 0.9 to 1.2 units.

Nine tests made under the conditions that provided satisfactory results (table 7) actually led to unsatisfactory results (table 8). However, 11 of the 13 tests in table 7 versus only 1 of the 9 tests in table 8 have their results based on freshly produced precipitates. This indicates that prompt filtration of the process slurry may be necessary to obtain satisfactory results.

Twenty-one other single-filtration BSPRU tests also yielded results outside the range conservatively described as satisfactory. These were all tests with conditions outside the range that led to the satisfactory results. These tests served to establish the range of test conditions required to obtain satisfactory results.

DOUBLE-FILTRATION BSPRU TESTS

Two BSPRU tests of the precipitation part of double-filtration tests were made at pH 3.81 and 3.87. The degree of removal of As and Fe was highly satisfactory, despite Fe-As molar ratios in excess of 3.

TABLE 7. - Satisfactory single-filtration BSPRU tests

Test	pH		As-Cu selectivity index	Predicted As in CuS, pct	Cu loss to precipitate, pct	Fe retained in liquor, pct	Fe-As molar ratio ¹
	Precipitation	Redisso-lution					
41	3.77	2.84	72.1	0.05	0.8	11.6	3.73
² 27	3.79	2.78	95.5	.06	.7	6.9	2.23
18	3.80	2.65	117.0	.03	.6	6.3	2.47
20	3.81	2.73	109.8	.04	.7	5.2	2.04
11	3.82	2.79	74.9	.05	1.3	4.8	1.59
21	3.82	2.80	111.6	.03	1.0	5.7	2.13
15	3.83	2.67	131.4	.06	.3	10.3	2.14
19	3.83	2.82	144.4	.02	.8	5.2	2.38
22	3.83	2.73	110.9	.03	.9	6.0	2.28
² 28	3.85	2.81	135.8	.03	.7	6.3	2.23
16	3.86	2.76	102.2	.05	.5	12.2	1.77
10	3.90	2.95	61.8	.07	1.3	2.1	1.51
17	3.91	2.80	113.5	.03	1.1	5.7	1.99

¹Ratio calculated from product assays and quantities.

²Results reported are for entire products of test.

TABLE 8. - Unsatisfactory single-filtration BSPRU tests, with test conditions in the range of tests that yielded satisfactory results

Test	pH		As-Cu selectivity index	Predicted As in CuS, pct	Cu loss to precipitate, pct	Fe retained in liquor, pct	Fe-As molar ratio ¹
	Precipitation	Redisso-lution					
13	3.78	2.79	² 58.8	² 0.19	0.5	² 14.9	1.99
³ 32	3.78	2.86	29.5	² 2.12	1.5	² 69.0	2.50
³ 29	3.80	2.72	² 26.7	² 2.89	.5	² 51.7	2.90
³ 36	3.80	2.83	² 23.4	² 2.37	² 2.1	² 27.8	2.28
³ 37	3.82	2.80	² 27.0	² 2.49	.9	² 35.6	2.17
³ 38	3.82	2.91	² 22.9	² 2.34	² 2.6	² 25.0	2.08
³ 40	3.82	2.82	² 41.8	² 2.11	1.7	² 22.3	2.64
³ 35	3.85	2.94	² 23.9	² 2.37	2.0	² 31.4	1.90
³ 24	3.90	2.70	² 51.1	² 2.29	.4	² 18.8	2.21

¹Ratio calculated from product assays and quantities.

²Did not meet the criteria used to define satisfactory results.

³Results reported are for the entire products of test.

MOSSBAUER STUDIES

Attempts to identify precipitated species by X-ray diffraction analysis were unsuccessful. This is attributed to the exceedingly small crystal size of the precipitates. Mossbauer spectroscopy was selected as an alternative to X-ray diffraction for the characterization of these samples.

Mossbauer spectroscopy relates to the oxidation state of the Fe present, to the spin state of the Fe, and to any asymmetry of the electronic environment at

the lattice sites on which the iron ions are located. Mossbauer spectra were recorded at 78 K for various solid samples involved in the liquor purification. The basic energy unit is in millimeters per second relative to natural α -Fe foil at room temperature. Figure 5 is the spectrum recorded for the precipitate from the purification step. This spectrum is consistent with the presence of an Fe-containing molecule such as FeAsO_4 or a similar compound with Fe and another metal. Figure 6 is the spectrum recorded for the dried solute from evaporated

filtrate following reacidification of the precipitate for recovery of the coprecipitated Cu and is consistent with the presence of a species such as $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2(\text{SO}_4)_3$, or a mixture of such species. Figure 7 is the spectrum recorded for the residue from the reacidification of the purification precipitate and, like figure 5, is consistent with the presence of a molecule of the type FeAsO_4 . The measured Mossbauer spectral parameters, presented in table 9, tend to confirm the results reported from the spectra. Where the spectrum was resolved into two component spectra, the parameters for each component are given.

WASTE DISPOSAL

A safe disposal method for the Fe-As precipitate would be needed. To determine their suitability for disposal, a number of samples prepared by the double-filtration method were subjected to the EPA extraction procedure, a test for hazardous materials (19). In this 24-h agitated leach test, the pH is controlled

TABLE 9. - Mossbauer effect spectral parameters

Figure	δ^1	ΔE_q^2	Γ^3	Pct area	Total area ⁴
5	0.47	0.61	0.28	50	4.16
	.48	.93	.41	50	
6	.54	.26	.44	100	51.14
7	.48	.62	.34	52	
	.49	1.03	.45	48	9.33

¹Mossbauer chemical isomer shift, related to the electron density at the surface and to the oxidation state, in millimeters per second.

²Quadrupole interaction, related to asymmetry in electronic environment, in millimeters per second.

³Full line width at half maximum, in millimeters per second.

⁴Roughly indicates the amount of Fe present but cannot be directly compared because the sample thickness was not closely controlled, in millimeters per second*percent effect.

⁵This sample had lower Fe content than did the other two.

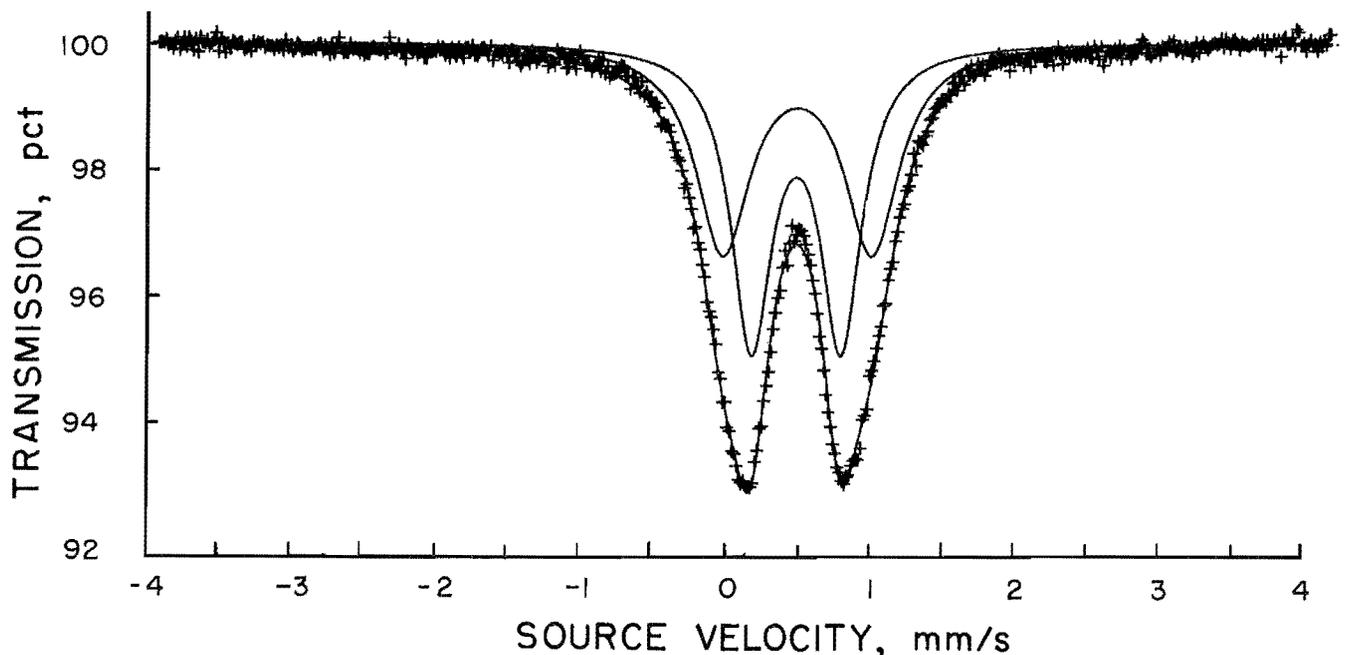


FIGURE 5.—Mossbauer spectrum at 78 K for precipitate from purification step.

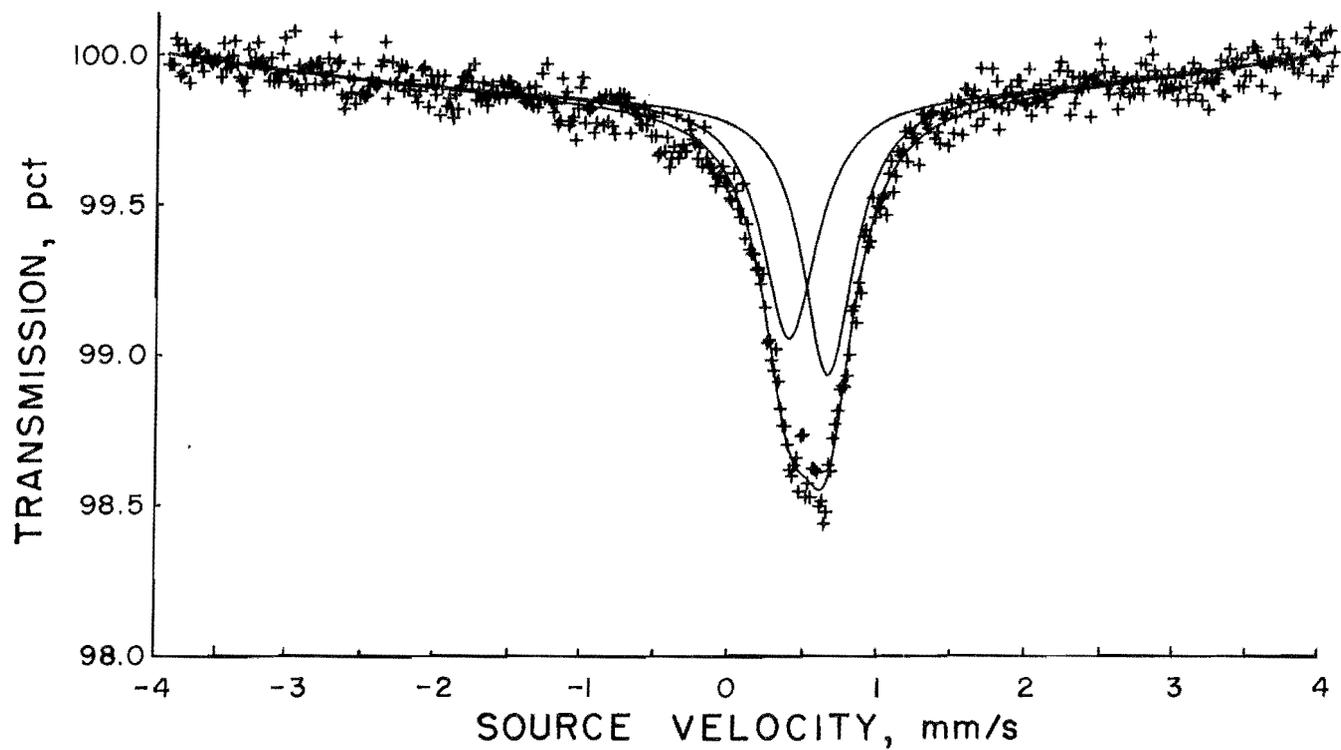


FIGURE 6.—Mossbauer spectrum at 78 K for residue from evaporation of liquor from redissolution step.

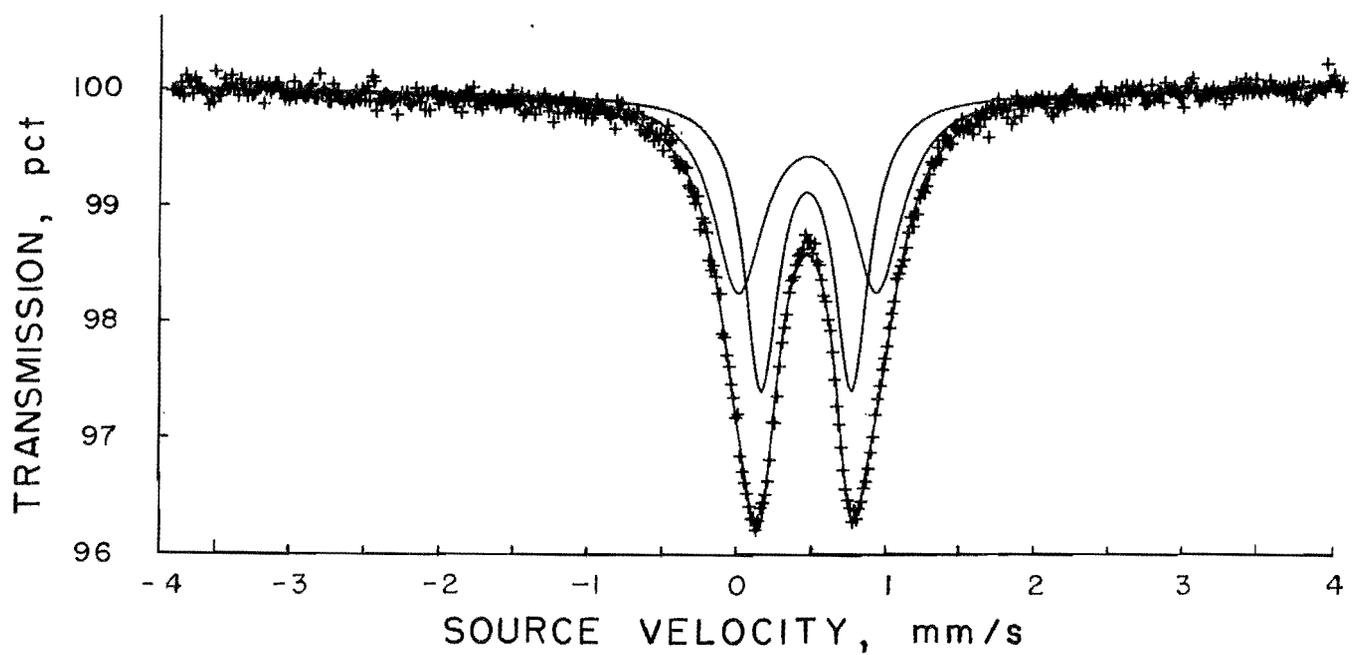


FIGURE 7.—Mossbauer spectrum at 78 K for residue from redissolution step.

at 5 ± 0.2 by additions of $0.5N$ acetic acid. If the natural pH of the slurry is 5 or less, no acetic acid is added. At the end of the test, the slurry is diluted and filtered; and the filtrate is analyzed for Ag, As, Ba, Cd, Cr, Hg, Pb, and Se. The analyses for Hg and Se were not performed because these elements were known to be absent in these samples. For a sample to be classified as nonhazardous by this test, the filtrate must contain no more than 1.0 mg/L Cd and 5.0 mg/L As or Pb. Significant levels of Ag, Ba, or Cr were not present in any of these samples.

Three samples of precipitates prepared with $\text{Ca}(\text{OH})_2$ in the precipitation step of the double-filtration method were washed, dried, and tested. All three samples passed the test with filtrates that contained less than 1 mg/L As, 0.74 to 0.85 mg/L Cd, and 0.5 to 1.63 mg/L Pb. Samples of precipitates prepared with both $\text{Ca}(\text{OH})_2$ and Na_2CO_3 were subjected to the redissolution step of the double-filtration method, and the residues were

washed, dried, and tested. The filtrates from both samples contained less than 1 mg/L of all of the elements, resulting in a classification of nonhazardous.

A brief reference (20) to the removal of As from solution by precipitation with Fe salts referred to Fe arsenates as "nontoxic" and "fit for safe ultimate disposal." However, Mehta (21) recommended that FeAsO_4 be dissolved in slag for long-term stability. Robins (22) presented stability diagrams for a number of metal arsenates. The arsenates of Pb, Cu, Cd, Zn, and Ni would provide lower As activity than Fe^{3+} in the pH range of 4 to 9. However, the increased metal cost and the possibility that the Pb and Cd arsenates would not pass the EPA extraction test reduce their usefulness as alternatives to FeAsO_4 . Tozawa (13) found that the stability of FeAsO_4 could be substantially improved by calcining the precipitate at 600°C . Additional research on methods of As disposal and recovery may provide a solution that is both effective and fully acceptable.

CONCLUSIONS

Precipitation of As and Fe is hindered by treatment temperatures above 60°C . Therefore, cooling of the liquor from leaching temperature should precede precipitation of As and Fe.

In single-filtration batch purification tests, the best results were achieved at 50° to 60°C , with the precipitation at about pH 3.8 and redissolution at about pH 2.8 with Fe-As molar ratios of 1.77 to 3.79. These conditions led to tests in which more than 98 pct of the As and Fe were rejected, with more than 98 pct of the Cu retained in solution.

Single-filtration, continuous-feed tests led to satisfactory results when the Fe-As molar ratio was 1.51 to 3.73; the precipitation and redissolution pH values were 3.77 to 3.91 and 2.65 to 2.95, respectively; the redissolution pH was less than the precipitation pH by 0.9 to 1.2 units; and the process slurry was filtered as it was produced.

The appropriate acidity for precipitation of As and Fe in double-filtration purification appears to range from pH 3.8 for fresh leach liquor to 3.4 for aged liquor.

The redissolution step in double-filtration purification was effective. Reacidification to acidity levels below pH 2.3 led to excessive redissolution of precipitated Fe; higher pH led to increased loss of Cu. Adequate water addition is necessary for the redissolution step.

The As-Cu separation index was higher when the Fe-As atomic ratio in the leach liquor exceeded 1.7, moderately in excess of the ratio in FeAsO_4 , than when the ratio was lower.

The alkaline reagent selected had little effect on the degree of liquor purification. However, when lime was used, filtration was often substantially more rapid.

The residues from double-filtration processing passed the EPA extraction procedure test.

Mossbauer analysis suggests that the predominant purification precipitate is FeAsO_4 or a like molecule.

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APPENDIX

TABLE A-1. - Single-filtration batch purification tests and results

Test	Test conditions					Fractional distribution			Fe-As molar ratio ¹	Selectivity index	
	Precipitation				Final (redissolution) pH	To liquor		Cu to ppt		As-Cu	Fe-Cu
	Temp, °C	pH	Reagent(s)	Time, min		Fe	As				
6	20	3.52	Ca(OH) ₂ + NaOH.....	3	2.02	0.2855	0.3803	0.0005	1.11	57.1	70.7
7	20	3.55	...do.....	15	3.00	.0215	.1860	.0027	1.19	40.2	129.6
43	20	3.69	NaOH, then Ca(OH) ₂	40	2.98	.0222	.1550	.0039	1.25	37.3	106.1
41	23	3.78	...do.....	10	3.50	.0152	.1305	.0104	1.24	25.2	78.5
5	20	3.80	Ca(OH) ₂ , then NaOH.....	5	2.00	.3214	.3934	.0004	1.15	62.1	72.6
8	20	3.80	...do.....	5	3.00	.0220	.1871	.0024	1.20	42.5	135.9
45	20	3.80	NaOH.....	37	3.00	.0247	.1522	.0028	1.13	44.5	118.6
47	22	3.83	Ca(OH) ₂ + NaOH.....	10	3.01	.0599	.1872	.0024	1.18	42.5	80.8
46	22	3.87	NaOH, then Ca(OH) ₂	5	3.02	.0317	.1718	.0023	1.15	45.7	115.1
9	20	3.98	Ca(OH) ₂ + NaOH.....	14	.95	.9892	.9812	.0001	1.17	13.8	10.4
10	20	3.98	...do.....	5	2.00	.2713	.3509	.0005	1.18	60.8	73.3
42	20	3.98	...do.....	10	3.00	.0249	.1735	.0065	1.17	27.0	77.4
44	20	4.10	...do.....	2	3.00	.0453	.1924	.0050	1.14	28.9	64.8
40	23	4.20	...do.....	6	3.00	.0195	.1737	.0026	1.33	42.7	138.9
4	20	4.35	NaOH.....	40	3.00	.0370	.1765	.0060	1.28	27.8	65.7
23	40	3.52	Ca(OH) ₂ + NaOH.....	2	2.50	.1173	.2295	.0021	1.11	39.9	59.8
20	40	3.54	...do.....	2	3.00	.0411	.1879	.0036	1.17	34.6	80.4
26	40	3.58	...do.....	5	2.00	.3049	.3624	.0006	1.16	54.1	61.6
27	40	3.79	...do.....	43	2.00	.3185	.3357	.0007	1.20	53.2	55.3
24	40	3.80	...do.....	25	2.50	.1130	.2254	.0019	1.09	42.5	64.2
21	40	3.82	...do.....	2	3.02	.0455	.1682	.0047	1.10	32.4	66.6
22	40	3.98	...do.....	21	3.00	.0301	.1614	.0048	1.03	32.8	81.7
28	40	3.98	...do.....	93	1.98	.3687	.3780	.0019	1.13	29.4	30.0
25	40	4.00	...do.....	52	2.50	.1003	.2044	.0043	1.08	30.0	45.6
72	52	2.75	Na ₂ CO ₃	75	2.30	.4881	.1608	.0006	1.64	93.2	41.8
73	52	3.23	...do.....	70	2.74	.3446	.0988	.0003	1.34	174.3	79.6
68	51	3.81	...do.....	60	2.80	.2542	.0786	.0005	1.23	153.1	76.6
66	51	2.77	Na ₂ CO ₃ · 1H ₂ O.....	60	2.31	.4638	.5290	.0010	2.89	29.8	34.0

67	51	3.31	Na ₂ CO ₃ ·1H ₂ O.....	60	2.71	0.3267	0.3305	0.0192	3.22	10.2	10.3
69	51	3.64	MnCO ₃	60	2.80	.0004	.0010	.0095	2.57	322.7	510.4
70	51	3.75	MnCO ₃ + Na ₂ CO ₃	240	2.80	.0004	.0016	.0044	2.68	375.8	752.0
81	50	3.77	Na ₂ CO ₃	60	2.85	.1114	.0300	.0388	5.94	28.3	14.1
82	50	3.77	...do.....	60	3.31	.0250	.0284	.0075	5.61	67.3	71.8
71	51	3.80	MnCO ₃ + Na ₂ CO ₃	60	2.80	.0300	.0041	.0006	2.00	636.1	232.1
77	52	3.80	Na ₂ CO ₃ ·1H ₂ O.....	60	3.30	.0153	.0006	.0102	2.16	402.0	79.0
79	50	3.80	(NH ₄) ₂ CO ₃	60	2.82	.1556	.0161	.0036	3.18	130.1	38.8
76	50	3.80	Na ₂ CO ₃	60	2.80	.0978	.0117	.0040	3.54	145.0	47.9
80	50	3.82	(NH ₄) ₂ CO ₃	60	3.29	.0099	.0001	.0097	2.38	1010.4	101.1
78	50	3.85	NaOH.....	60	2.81	.1305	.0161	.0032	3.59	138.0	45.6
75	50	3.88	...do.....	60	3.33	.0058	.0001	.0168	4.34	765.0	100.2
74	51	3.90	...do.....	60	2.82	.0852	.0170	ND	4.42	ND	ND
14	60	3.50	Ca(OH) ₂ + NaOH.....	30	2.00	.2225	.3804	.0012	1.07	36.8	53.9
11	60	3.52	...do.....	10	3.00	.0598	.1798	.0081	1.10	23.6	43.9
53	60	3.72	NaOH, then Ca(OH) ₂	10	2.79	.0212	.1189	.0114	1.16	25.4	63.3
12	60	3.75	Ca(OH) ₂ + NaOH.....	10	1.98	.2435	.3893	.0011	1.05	37.7	53.1
13	60	3.75	...do.....	5	3.00	.0447	.1869	.0093	1.28	21.5	47.7
18	60	3.75	...do.....	8	2.46	.1284	.1935	.0026	1.03	40.0	51.0
56	60	3.75	...do.....	5	2.99	.0292	.0920	.0104	1.18	30.6	56.2
49	60	3.76	...do.....	20	2.98	.0158	.1582	.0220	1.19	15.4	52.6
51	60	3.76	NaOH, then Ca(OH) ₂	5	3.01	.0162	.0427	.0365	1.18	24.3	40.0
54	60	3.77	Ca(OH) ₂ , then NaOH.....	25	3.01	.0297	.1252	.0129	1.09	23.1	50.0
48	60	3.78	NaOH.....	13	3.00	.0897	.1231	.0072	1.20	31.3	37.4
52	60	3.78	NaOH, then Ca(OH) ₂	15	3.00	.0265	.1297	.0145	1.26	21.4	50.0
55	60	3.78	...do.....	10	3.00	.0179	.0758	.0133	1.22	30.1	63.8
50	60	3.79	Ca(OH) ₂ + NaOH.....	20	3.01	.0244	.1429	.0177	1.22	18.2	47.1
63	60	3.88	...do.....	NR	3.00	.0296	.0781	.0117	1.12	31.6	52.6
15	60	4.00	...do.....	10	3.00	.0113	.1468	.0032	1.34	42.6	165.1
16	60	4.05	...do.....	2	2.51	.0874	.2109	.0037	1.21	31.7	53.0
17	61	4.06	...do.....	35	2.00	.4009	.3966	.0011	1.19	37.2	36.8

See footnotes at end of table.

TABLE A-1. - Single-filtration batch purification tests and results--Continued

Test	Test conditions					Fractional distribution			Fe-As molar ratio ¹	Selectivity index	
	Precipitation				Final (redissolution) pH	To liquor		Cu to ppt		As-Cu	Fe-Cu
	Temp, °C	pH	Reagent(s)	Time, min		Fe	As				
19	60	4.06	Ca(OH) ₂ + NaOH.....	20	1.50	0.9521	0.9473	0.0003	1.10	13.6	13.0
65	60	3.58	NaOH, then Ca(OH) ₂	30	3.00	.7112	.0296	.0545	11.44	23.8	2.6
64	60	3.71	...do.....	16	3.00	.7957	.0330	.0106	4.89	52.3	4.9
30	80	3.48	Ca(OH) ₂ + NaOH.....	28	2.48	.1009	.2260	.0054	1.20	25.1	40.5
29	80	3.50	...do.....	9	3.00	.0907	.2044	.0151	1.07	15.9	25.6
35	80	3.50	...do.....	21	2.00	.3411	.3908	.0018	1.11	29.4	32.7
60	80	3.63	NaOH, then Ca(OH) ₂	84	2.99	.0109	.0712	.1247	1.25	9.6	25.2
1	80	3.65	NaOH.....	NR	2.50	.0953	.0646	.0091	1.42	39.7	32.2
62	80	3.65	NaOH, then Ca(OH) ₂	NR	3.22	.0059	.0567	.4007	1.17	5.0	15.9
61	80	3.67	...do.....	16	3.00	.0064	.0604	.2248	1.05	7.3	23.1
32	80	3.72	Ca(OH) ₂ + NaOH.....	60	2.00	.3592	.4089	.0024	1.13	24.5	27.2
36	80	3.72	...do.....	27	3.00	.0219	.1316	.0527	1.08	10.9	28.3
33	80	3.75	Ca(OH) ₂ + NaOH.....	52	2.50	.1068	.2168	.0071	1.11	22.5	34.2
57	80	3.76	...do.....	40	2.99	.0106	.0829	.0737	1.16	11.8	34.2
59	80	3.77	NaOH.....	15	2.96	.0115	.0771	.0465	1.20	15.7	42.0
31	80	3.78	Ca(OH) ₂ + NaOH.....	7	3.00	.0329	.1533	.1846	1.16	4.9	11.4
58	80	3.78	...do.....	13	2.98	.0112	.0838	.0683	1.18	12.2	34.7
34	80	4.00	...do.....	7	3.00	.0215	.1452	.0175	1.25	18.2	50.6
38	80	4.00	...do.....	34	2.00	.2739	.3329	.0027	1.17	27.2	31.3
39	80	4.00	...do.....	22	2.50	.0585	.1589	.0084	1.10	25.0	43.6
37	80	4.60	...do.....	27	2.98	.0488	.1626	.0200	1.15	15.9	30.9
83	80	3.40	NaOH.....	120	2.50	.5300	.2735	.0014	6.32	43.5	25.2
3	80	3.42	...do.....	NR	2.50	.3019	.0943	.0019	5.58	71.0	34.8
2	80	3.53	...do.....	NR	2.50	.1371	.0417	.0043	2.52	73.0	38.2

ND Not determined. NR Not recorded. ppt Precipitate.

¹Ratio calculated from product assays and quantities.

TABLE A-2. - Results for first (precipitation) part of batch double-filtration purification tests

Test	Leach liquor assay, g/L			Precipitation test conditions				Fractional distribution			Fe-As molar ratio ¹
	Fe	As	Cu	Temp, °C	pH	Reagent(s)	Time, min	To Liquor		Cu to ppt	
								Fe	As		
2	3.44	3.83	18.60	20	3.50	Ca(OH) ₂	60	0.4652	0.0797	0.2443	1.07
1	3.44	3.83	18.60	20	4.40	...do.....	NR	.4204	.0288	.3726	1.19
3	3.44	3.83	18.60	20	4.80	...do.....	60	.3297	.0130	.3591	1.06
7	4.46	3.38	41.02	52	2.75	Na ₂ CO ₃	60	.3671	.1244	.0011	1.35
8	4.46	3.38	41.02	52	3.23	...do.....	60	.2796	.0514	.0003	1.23
31	5.18	1.58	48.80	54	3.19	NaOH.....	120	.0109	.0001	.0071	5.49
20	5.22	1.30	44.60	50	3.20	Na ₂ CO ₃	120	.0140	.0010	.0114	5.34
23	4.10	1.24	46.20	53	3.20	...do.....	120	.0117	.0012	.0136	6.88
27	5.00	1.36	48.60	54	3.20	...do.....	120	.0024	.0093	.0114	5.24
30	5.18	1.58	48.80	55	3.26	Ca(OH) ₂	120	.0047	.0001	.0512	5.06
32	4.80	1.60	47.20	51	3.30	Na ₂ CO ₃	120	.0520	.0844	.0423	4.35
33	4.50	1.40	45.00	54	3.30	...do.....	120	.0278	.0915	.0265	4.42
26	4.40	1.40	49.80	55	3.39	...do.....	120	.0022	.0088	.0356	5.35
21	5.16	1.30	44.80	51	3.40	...do.....	120	.0022	.0012	.0286	7.17
28	4.40	1.36	50.20	53	3.40	NaOH.....	120	.0029	.0116	.0124	5.42
19	5.08	1.16	48.00	50	3.42	Ca(OH) ₂	120	.0019	.0010	.0572	5.96
34	4.96	1.20	42.60	49	3.42	...do.....	120	.0088	.0011	.1774	4.18
29	4.40	1.36	50.20	53	3.43	...do.....	120	.0024	.0001	.0692	4.96
22	4.86	1.24	44.60	51	3.60	Na ₂ CO ₃	120	.0005	.0010	.0799	5.49
24	5.30	1.00	46.20	55	3.61	Ca(OH) ₂	120	.0015	.0010	.0978	7.38
4	4.46	3.38	41.02	51	3.64	MnCO ₃	60	.0002	.0006	.0006	1.85
5	4.46	3.38	41.02	51	3.75	MnCO ₃ + Na ₂ CO ₃	60	.0002	.0008	.0161	1.80
16	5.34	1.28	46.00	51	3.76	Limestone.....	120	.0003	.0009	.6571	7.10
37	3.88	1.40	37.39	50	3.80	(NH ₄) ₂ CO ₃	60	.0085	.0006	.0073	2.67
6	4.46	3.38	41.02	51	3.80	MnCO ₃ + Na ₂ CO ₃	60	.0003	.0017	.0034	2.17
36	3.88	1.40	37.39	52	3.80	Na ₂ CO ₃ ·1H ₂ O.....	60	.0051	.0006	.0455	2.28
10	3.88	1.40	37.39	50	3.80	Na ₂ CO ₃	60	.0208	.0021	.0335	3.68
12	4.10	1.45	42.03	51	3.80	...do.....	60	.0345	.0012	.1471	5.59
13	4.10	1.45	42.03	51	3.80	...do.....	60	.0001	.0024	.1399	5.33
11	4.10	1.45	42.03	51	3.81	...do.....	60	.0306	.0013	.0126	5.66
14	4.10	1.45	42.03	51	3.84	MnCO ₃ + Na ₂ CO ₃	60	.0005	.0003	.2142	5.64
15	4.10	1.45	42.03	51	3.87	...do.....	60	.0006	.0012	.2193	5.50
9	3.88	1.40	37.39	50	3.88	NaOH.....	60	.0026	.0001	.0130	4.34
17	5.50	1.12	45.20	49	3.88	Na ₂ CO ₃	120	.0009	.0008	.5011	4.62
25	5.25	1.32	39.18	50	3.93	NaOH.....	120	.0006	.0010	.3007	4.90
35	4.91	1.28	45.00	51	3.96	Limestone.....	120	.0230	.0001	ND	5.28
18	5.06	1.44	50.00	51	3.98	Ca(OH) ₂	120	.0002	.0009	.8238	6.59

ND Not determined. ppt Precipitate. NR Not recorded

¹Ratio calculated from product assays and quantities.

TABLE A-3. - Single-filtration BSPRU purification tests and results

Test	pH		Fe-Cu selec- tivity index	As-Cu selec- tivity index	Pre- dicted As in CuS, pct	Fractional distribution		Fe-As molar ratio ¹	
	Precipi- tation	Redisso- lution				To liquor			Cu to ppt
						Fe	As		
3	3.71	3.00	11.0	9.1	1.378	0.0975	0.1374	0.0710	0.66
6	3.75	2.78	26.5	10.2	1.113	.0249	.1467	.0528	.57
5	3.82	2.90	13.1	13.7	.420	.0478	.0437	.1038	.66
7	3.83	2.53	45.2	43.1	.162	.0187	.0205	.0250	1.29
8	3.85	2.94	78.4	28.6	.188	.0041	.0300	.0381	.95
1	3.93	3.15	4.5	8.1	1.579	.5215	.2489	.0438	.87
4	3.93	3.09	5.6	9.2	1.014	.2071	.0875	.1097	.65
2	3.97	3.14	2.7	4.4	3.437	.5571	.3184	.0989	.71
² 25	3.60	2.60	34.8	59.0	.368	.2421	.1002	.0026	2.36
² 31	3.63	2.82	5.8	9.9	2.038	.6919	.4330	.0132	2.61
² 26	3.69	2.66	40.6	94.7	.140	.1764	.0379	.0028	2.32
12	3.70	2.57	37.2	69.6	.119	.1065	.0330	.0060	2.05
² 33	3.73	3.10	8.1	20.6	.245	.2434	.0473	.0455	2.08
² 30	3.74	2.84	8.1	16.1	1.436	.5973	.2729	.0102	2.68
14	3.75	2.61	32.1	57.6	.137	.0858	.0284	.0102	1.76
41	3.77	2.84	30.0	72.1	.047	.1156	.0221	.0084	3.73
13	3.78	2.79	33.1	58.8	.186	.1486	.0525	.0052	1.99
² 32	3.78	2.86	5.4	9.5	2.124	.6896	.4162	.0152	2.50
² 27	3.79	2.78	44.2	95.5	.061	.0692	.0157	.0068	2.23
² 39	3.79	2.92	10.6	23.6	.372	.2645	.0678	.0240	1.90
² 29	3.80	2.72	13.2	26.7	.893	.5168	.2067	.0054	2.90
² 34	3.80	3.02	8.8	19.2	.340	.2594	.0690	.0352	2.13
² 36	3.80	2.83	11.0	23.4	.366	.2782	.0787	.0209	2.28
18	3.80	2.65	47.7	117.0	.034	.0628	.0110	.0065	2.47
20	3.81	2.73	51.4	109.8	.037	.0519	.0119	.0069	2.04
11	3.82	2.79	38.2	74.9	.046	.0482	.0130	.0133	1.59
21	3.82	2.80	40.6	111.6	.027	.0566	.0079	.0100	2.13
² 37	3.82	2.80	14.0	27.0	.490	.3565	.1291	.0092	2.17
² 38	3.82	2.91	10.5	22.9	.343	.2499	.0661	.0263	2.08
² 40	3.82	2.82	14.4	41.8	.108	.2230	.0328	.0166	2.64
15	3.83	2.67	51.0	131.4	.056	.1029	.0170	.0033	2.14
19	3.83	2.82	47.8	144.4	.018	.0518	.0060	.0080	2.38
22	3.83	2.73	42.0	110.9	.030	.0604	.0091	.0087	2.28
² 42	3.84	3.31	25.7	151.6	.001	.0138	.0004	.0979	4.12
² 43	3.84	3.31	24.3	43.4	.008	.0122	.0039	.1208	5.31
² 23	3.85	2.50	36.1	66.4	.165	.1451	.0477	.0045	2.18
² 28	3.85	2.81	47.0	135.8	.033	.0634	.0080	.0066	2.23
² 35	3.85	2.94	10.5	23.9	.367	.3135	.0804	.0196	1.90
16	3.86	2.76	36.4	102.2	.054	.1217	.0172	.0054	1.77
9	3.88	3.04	120.3	34.4	.105	.0018	.0213	.0374	1.36
10	3.90	2.95	59.8	61.8	.072	.0214	.0201	.0126	1.51
² 24	3.90	2.70	32.7	51.1	.292	.1881	.0868	.0040	2.21
17	3.91	2.80	38.9	113.5	.033	.0569	.0070	.0108	1.99

¹Ratio calculated from product assays and quantities.

²Data are for entire tests, not just the last interval.