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Recovery of Principal Metal Values From Electrolytic Zinc Waste

By T. L. Hebble, V. R. Miller, and D. L. Paulson

UNITED STATES DEPARTMENT OF THE INTERIOR

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RECOVERY OF PRINCIPAL METAL VALUES FROM ELECTROLYTIC ZINC WASTE

by

T. L. Hebble,[1] V. R. Miller,[2] and D. L. Paulson[3]

ABSTRACT

The Bureau of Mines investigated a hydrometallurgical procedure to recover Co, Ni, and Cu from an electrolytic zinc industrial copper filter cake. The copper filter cake is presently unmarketable or of low value because economic and environmentally acceptable processing technology is lacking.

Research by the Bureau of Mines has developed a multistage process for recovering or recycling over 93 pct of the Zn, Cd, Cu, Co, and Ni from this material. The stages involved are (1) wet sizing, (2) H_2SO_4 leaching of undersized material, (3) H_2SO_4-MnO_2 leaching of H_2SO_4 leach residue, (4) selective precipitation of As, Cu, and Co-Ni products, and (5) precipitation of manganese for recycling to the leach circuit. The final process residue is only 1.6 wt-pct of the initial cake and consists of lead sulfate.

INTRODUCTION

It is the goal of the Bureau of Mines to help maintain an adequate U.S. supply of minerals to meet economic and strategic needs to avoid dependence on foreign supplies. That goal makes it necessary to accomplish complete utilization of all domestic mineral resources. One domestic source of metal is copper filter cake, a byproduct of the electrolytic zinc industry. This cake is produced during one of the process steps designed to remove impurities such as Cu, Co, and Ni from the zinc electrolyte (2-3, 5, 9-10).[4] The composition of the cake varies from plant to plant depending on the types of the zinc concentrates being processed. Typical cake contains As, Cd, Ni, Co, and Zn in addition to Cu. The residue from one plant, which produces approximately 1,800 tpy copper filter cake, contains 439 tons Cu, 195 tons Zn,

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

210 tons Cd, 50 tons Co, and 19 tons Ni. Current metal market values indicate this single residue has an estimated annual value of $5.2 million.

The copper filter cake has, in the past, been processed pyrometallurgically to recover copper with little or no attempt to recover the contained cobalt and nickel. Current economic and environmental restraints discourage domestic smelters from processing this filter cake. The cake is exported or stockpiled for future processing.

The object of the Bureau of Mines research described in this report was to develop a suitable hydrometallurgical method for recovering the metals contained in electrolytic zinc plant copper filter cake.

MATERIALS

A copper filter cake was obtained from a commercial electrolytic zinc plant. The as-received material was oven dried 16.0 hr at 105° C and analyzed for chemical composition and compound identification. The elemental analysis of the dried copper cake is shown in table 1. Preliminary X-ray diffraction data indicate the possible presence of β-Cu_3As, $ZnSO_4$, $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O$, $6Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$, $CoSO_4$, Cu-Ni, and/or Co. All chemicals used in the experimental work were reagent-grade chemicals, and the water was distilled.

TABLE 1. - Chemical analysis of copper filter cake, weight-percent

Copper	24.4
Arsenic	11.9
Cadmium	11.7
Zinc	10.9
Cobalt	2.8
Nickel	1.1
Lead	.9
Magnesium	.5
Iron	.02
Moisture, trace elements	Balance

EQUIPMENT AND PROCEDURES

Screening

As-received copper filter cake (38.4 wt-pct moisture) was wet sieved on a series of 8-in-diam stainless steel screens. The wet shaking screen analysis unit consists of the vibrator mechanism and suspended rack containing five screens ranging from 150 μm to 38 μm. A small sample was placed on the top screen, the vibrator mechanism was activated, and water was sprayed on the top screen. The water was turned off when the last screen's discharge was clear. The minus 38-μm solids and wash water were pressure filtered through a

33.0-cm-diam No. 50 Whatman[5] filter paper. Each size fraction was oven dried for 16 hr at 104° C and analyzed. The wash water volume was measured, and an aliquot was collected for analysis.

Sulfuric Acid Leaching

The acid leaching experiments on minus 75-μm material were conducted to solubilize the cadmium and zinc values in this fraction. The experiments were carried out in a 500-ml, four-necked Pyrex glass reaction kettle. The kettle top was equipped with a stirrer assembly, a West condenser, and a dual iron-constantan thermocouple. The H_2SO_4 solution was poured into the reactor and heated to temperature with the aid of a heating mantle connected to a 5-amp proportioning controller. The temperature was monitored with a digital readout meter; once the temperature stabilized, the appropriate solids were fed into the reactor and agitated for a specific time. On completion of the experiment, the leach slurry was vacuum filtered through a 9.0-cm-diam porcelain Buchner funnel lined with No. 50 Whatman filter paper. The filtrates were cooled to room temperature, where their volume and final pH were measured and aliquots collected for analyses. Residues were oven dried at 105° C for 16 hr, weighed, crushed to minus 840 μm, and analyzed.

Oxidative Leaching

The remaining metals, Cu, Co, Ni, and As, were solubilized by oxidative leaching with H_2SO_4 and MnO_2. The leaching experiments were conducted using the same equipment and procedures described for H_2SO_4 leaching. The variables investigated in the oxidative leaching experiments were H_2SO_4 and MnO_2 quantities, time, and temperature.

Metal Precipitation

Arsenic was removed from the oxidative leach liquor by adding iron (III) sulfate to precipitate iron arsenate. The precipitation was accomplished by adjusting the Fe:As molar ratio to 1.4 to 1.0, heating the solution to 50° C, and raising the solution pH to 4 with 400 gpl NaOH. After 30 min, H_2SO_4 was added to the slurry to reduce the pH to 3 in order to redissolve coprecipitated copper. The mixture was held at pH 3 and 50° C for 45 min, then filtered. The solids were oven dried at 105° C for 16 hr, ground, and sampled for analyses. The filtrate was cooled to room temperature, the volume and pH measured, and sampled for analyses.

The filtrate from the As removal stage was next treated to precipitate copper by bubbling H_2S through 500 ml of solution in a 1,000-ml beaker. Platinum and reference electrodes were used to monitor the reduction-oxidation potential to determine the end point of the reaction. The beaker was heated and stirred by a combination magnetic stirrer. The gas delivery tube was removed when a reading of plus 200 mv was reached, that indicating the end

[5]Reference to specific trade names is meant for identification only and does not imply endorsement by the Bureau of Mines.

precipitation (9). The solution was then filtered and the solids oven dried at 105° C for 16 hr.

The cobalt and nickel were precipitated as sulfide by returning the filtrate from the copper precipitation stage to the reaction vessel and adding 60-pct Na_2S flakes to the 50° C solution until a reduction-oxidation potential reading of minus 300 Mv was reached. The solution was filtered and the solids oven dried at 105° C for 16 hr.

Manganese was precipitated from the remaining filtrate by the addition of Na_2CO_3. Products from each precipitation stage were analyzed to determine purity and recovery.

RESULTS AND DISCUSSION

Screening

As-received copper filter cake was wet screened on 150-, 75-, 53-, 45-, and 38-μm screens. The cumulative weights and metal distributions of the different size fractions are shown in table 2. The associated wash water solubilized 63.0 pct of the cadmium and 15.0 pct of the zinc contained in the initial copper filter cake. Analysis of the wash water indicated Co, Ni, Cu, and As are insoluble in the tap water (pH = 5 to 6) used for the wet screening. In one case, the wash water was evaporated to dryness to identify the cadmium compound present. The recovered crystalline material contained 24.0 pct Cd and 1.5 pct Zn. The principal compound identified by X-ray diffraction was cadmium sulfate hydrate ($CdSO_4 \cdot H_2O$), which agrees with the literature (7).

TABLE 2. - Screen analysis of copper filter cake, percent

Particle size, μm	Weight fraction	Cumulative weight fraction	Cumulative metals distribution			
			Zn	Cd	Co	Cu
Plus 150	7.77	7.77	35.4	8.7	4.7	4.8
Plus 75	4.94	12.71	54.7	12.7	9.1	8.7
Plus 53	1.93	14.64	61.8	14.6	11.3	10.8
Plus 45	1.26	15.90	66.8	15.9	12.8	11.9
Plus 38	1.26	17.16	71.4	17.1	14.1	13.2
Minus 38	42.23	59.39	85.0	37.0	99.9	99.9
Water-soluble[1]	40.61	100.0	100.0	100.0	100.0	100.0

[1]Water-soluble material determined by weight difference.

The plus 75-μm fraction contained 54.7 pct of the zinc, ≤12.7 pct of the cadmium, and <10 pct of the other metals in the starting material. The fraction is mostly zinc metal; and, although it is coarser than the zinc dust normally added during zinc electrolyte purification, it appears feasible to recycle the plus 75-μm fraction directly to the purification circuit. Consequently, no additional experimentation was conducted on this fraction.

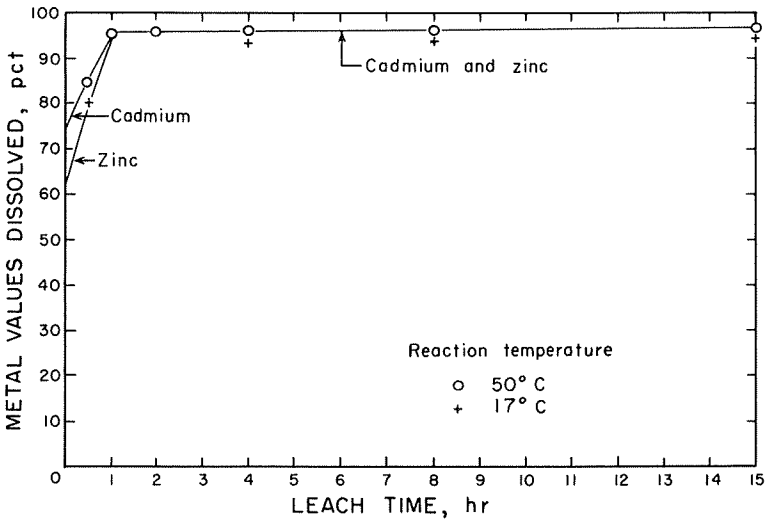

FIGURE 1. - Effect of leach time on the percentage of cadmium and zinc solubilized from minus 75-μm copper filter cake at 17° and 50° C.

Sulfuric Acid Leaching

In a series of tests to improve the zinc and cadmium recovery, acid leaching tests were conducted on the minus 75-μm screened fraction, which contained 30.5 pct of the zinc and 24.3 pct of the cadmium in the as-received copper filter cake. Several fresh samples of the copper filter cake were screened, and the dried minus 75-μm fractions were leached in 200 ml of 10-gpl H_2SO_4 from 0.5 to 15.0 hr at temperatures of 17° and 50° C. The data are listed for tests 1 to 11 in table 3. The data plotted in figure 1 show that the cadmium and zinc dissolution after 1 hr is independent of temperature up to 50° C. A small 1- to 3-pct gain is attained at longer leaching times than 1 hr at 17° C. The average dissolutions of cadmium and zinc for 1.0 hr over the 17° to 50° C range are 92.0 and 94.2 pct, respectively. The metals are solubilized between a pH of 2.20 to 5.70 with a maximum 2.8 pct of the copper solubilized at the lower pH.

TABLE 3. - Results of H_2SO_4 leaching of minus 75-μm copper filter cake

Test	Leach parameters			Metal dissolution, pct			Test	Leach parameters			Metal dissolution, pct		
	Time, hr	Temp, ° C	pH	Cd	Zn	Cu		Time, hr	Temp, ° C	pH	Cd	Zn	Cu
1	0.50	50.0	4.25	85.4	85.4	ND	10	4.00	17.0	2.60	95.0	98.4	2.85
2	1.00	50.0	5.70	93.9	92.1	0.30	11	15.00	17.0	5.60	92.0	94.9	2.74
3	2.00	50.0	5.45	94.2	96.0	.31	12	1.00	50.0	6.05	84.4	28.8	ND
4	4.00	50.0	4.90	93.3	96.5	.94	13	1.00	50.0	4.95	90.1	94.2	ND
5	8.00	50.0	5.40	95.0	98.0	.31	14	1.00	50.0	3.90	93.5	94.4	ND
6	15.25	50.0	ND	94.1	95.2	.60	15	1.00	50.0	2.70	90.9	95.0	ND
7	.50	17.0	ND	79.7	79.9	ND	16	1.00	50.0	1.85	88.0	92.8	ND
8	.50	17.0	ND	76.9	72.3	ND	17	1.00	50.0	1.15	90.3	95.1	ND
9	1.00	17.0	2.20	90.1	96.2	0	18	1.00	50.0	.08	92.4	94.2	ND

ND Not determined.

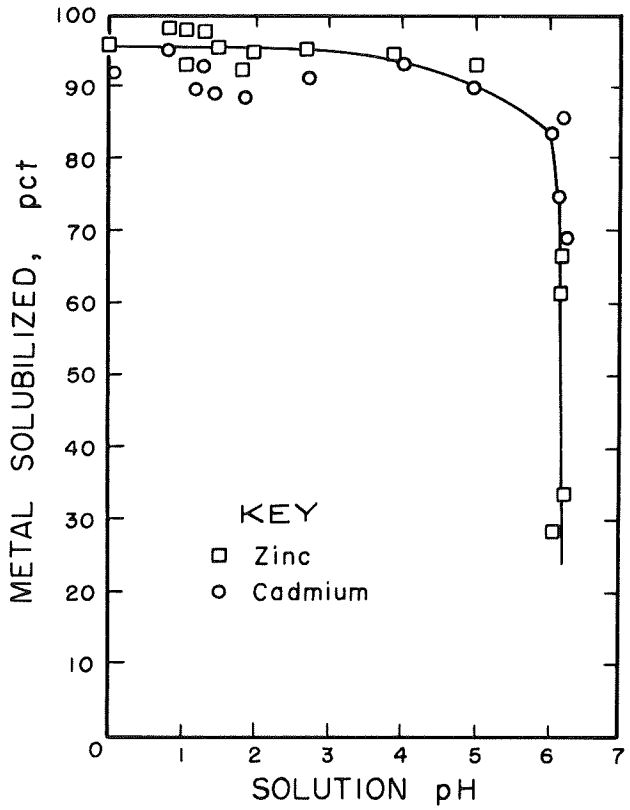

FIGURE 2. - Effect of pH on the percentage of cadmium and zinc solubilized from minus 75-μm copper filter cake at 50° C for 1 hr.

To determine the amount of H_2SO_4 required for leaching the minus 75-μm material, tests 12 to 18 shown in table 3 were conducted. Twenty grams of dry solids were mixed with 200 ml of distilled water at 50° C. Concentrated H_2SO_4 was added dropwise, while the pH was monitored over the 1-hr reaction time. The data represented in figure 2 indicate that a pH $\leq$3.95 will solubilize greater than 93.5 pct of the contained cadmium and zinc. The highest metal concentration obtained in the leach tests was 33.5 gpl Cd, 25.5 gpl Zn, and 0.001 gpl Cu, which represents extractions of 94.1, 97.1, and 0.30 pct, respectively. The average residue composition (in weight-percent) was 50.0 Cu 27.0 As, 5.0 Co, and 2.0 Ni. The major phase of the acid leached residue as determined by X-ray diffraction analysis was Cu_3As.

In the above tests, the sized material was wet screened and dried at 105° C for 16 hr. To determine if drying was necessary, a fresh sample of as-received moist copper filter cake was wet screened at 75 μm. The undersized solids and wash water were not separated. Instead, the slurry was heated to 50° C, and H_2SO_4 was added dropwise to maintain a pH of 3.0. After a 1-hr leach time, the acidic slurry was filtered and analyzed. The metal distribution of the various products is shown in table 4. The combination of screening and acid dissolution dissolved more than 92.4 pct of both the cadmium and the zinc from the initial material. The oversized material contained 39.4 pct of the zinc as a coarse metal agglomerate and contained approximately 7.0 pct of the copper and cobalt. The acid leach residue contained approximately 93 pct of the cobalt and copper in only 36 wt-pct of the original moist copper filter cake.

TABLE 4. - Products from combined screening and H_2SO_4 leaching of copper filter cake, percent

Product	Weight fraction	Metals distribution			
		Zn	Cd	Co	Cu
Plus 75-μm oversize.....	6.44	39.4	4.2	7.4	6.1
Acidified wash water...	57.11	56.6	88.2	.1	.1
Acid leach residue.....	36.45	4.0	7.6	92.5	93.8

Oxidative Leaching

Oxidative leaching tests were made on the insoluble residue remaining after leaching the minus 75-μm fraction of copper filter cake with H_2SO_4. The H_2SO_4 concentration, MnO_2 additions, time, and temperature were varied, with typical results shown in table 5.

TABLE 5. - Typical results of MnO_2-H_2SO_4 leaching of Cu_3As residue

Test	Leaching parameters				Metal solubilized, pct				
	H_2SO_4, g	MnO_2, g	Temp., ° C	Time, hr	Co	Ni	Cu	As	Mn
1	50	16.0	90	2.0	94.1	91.1	94.7	96.0	99.6
2	50	10.0	90	2.0	99.1	88.6	72.0	76.1	99.9
3	50	5.0	90	2.0	97.5	97.0	49.0	55.0	97.9
4	35	17.0	90	4.0	99.9	ND	98.5	97.8	ND
5	25	17.0	90	4.0	98.9	ND	76.5	66.7	50.3
6	15	17.0	90	4.0	96.7	ND	31.8	17.6	40.4
7	40	17.0	90	2.0	99.9	99.8	98.6	98.0	ND
8	40	17.0	50	2.0	98.0	98.5	98.3	97.9	ND
9	40	17.0	30	2.0	60.4	61.3	79.4	79.6	ND
10	20	8.5	80	1.0	99.8	99.7	99.9	99.9	ND
11	20	8.5	80	.5	99.8	99.4	99.9	99.9	ND
12	20	8.5	80	.25	96.0	95.6	79.0	81.9	ND
13	20	8.5	50	1.0	99.8	99.2	99.9	99.9	ND
14	20	8.5	50	.5	70.3	70.0	50.0	57.0	ND
15	40	17.0	90	1.0	98.9	98.4	97.8	98.3	98.2

ND Not determined.

Twenty-gram samples of the leach residue were leached with 0 to 17 g MnO_2 and 200 ml of 250-gpl H_2SO_4 solution at 90° C. When 16 g MnO_2 was added, the results of 2-hr and 4-hr leaching were so similar that other tests were run for 2 hr only.

The effect of MnO_2 additions on solubilizing Co, Ni, Cu, and As is shown in figure 3. The curves in figure 3 show that the cobalt dissolution increases from 63.5 to 99.1 pct by adding 10 g MnO_2 to the system. The nickel solubility reached a maximum with additions of 13 g MnO_2. The copper and arsenic dissolution increased linearly from 35 pct to 100 pct as MnO_2 additions increased from 0 to 17 g; therefore, 17.0 g MnO_2 is optimum for total metal dissolution with excess acid.

To determine the minimum amount of sulfuric acid required for plus 99-pct metal dissolution, the MnO_2 was held constant at 17.0 g as the H_2SO_4 additions were varied from 5.0 to 50.0 g in 200 ml aqueous solutions (50- to 250-gpl H_2SO_4). The results, summarized in figure 4, show cobalt and nickel solubilities increasing rapidly from approximately 0 to 98.9 pct with acid additions up to 18.0 g. The Cu-As dissolution increased linearly with acid concentrations up to 35.0 g, then became essentially constant at 98 pct while as much as 99.6 pct of the cobalt and nickel was solubilized. The leach residue contained $PbSO_4$ and unreacted MnO_2. The lead sulfate residue was typically less than 2 wt-pct of the initial cake weight.

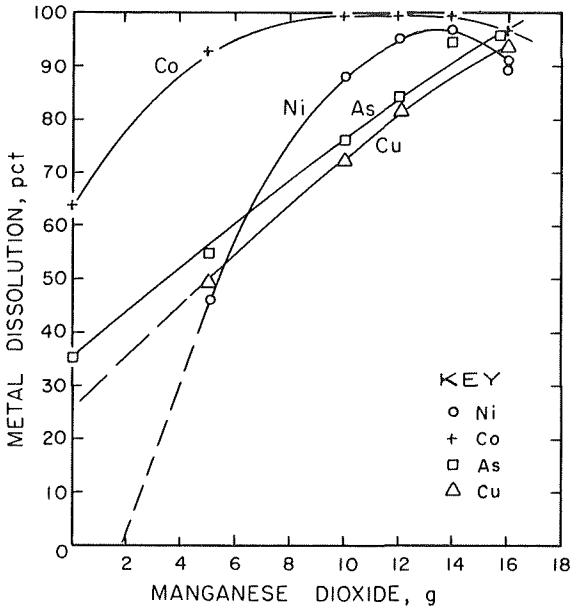

FIGURE 3. - Effect of manganese dioxide additions on the metal dissolution of Cu_3As residue at 90° C for 2 hr in 200 ml of 250 gpl H_2SO_4.

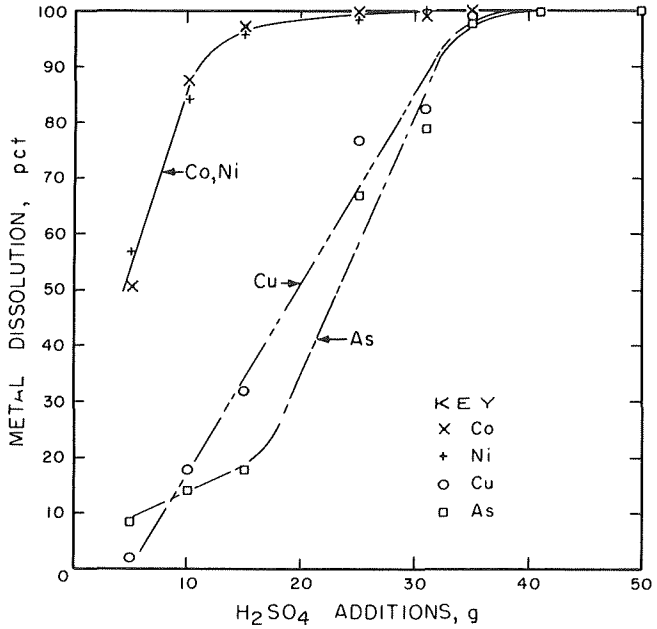

FIGURE 4. - Effect of sulfuric acid additions on the percent metal dissolution from Cu_3As residue at 90° C for 4 hr with 17.0 g MnO_2.

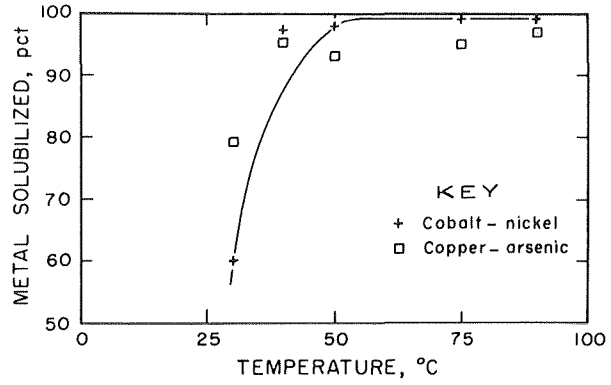

FIGURE 5. - Effects of temperature on the percent of metals solubilized from Cu_3As residue reacted with 200 ml of 200 gpl H_2SO_4 and 17.0 g MnO_2 for 2 hr.

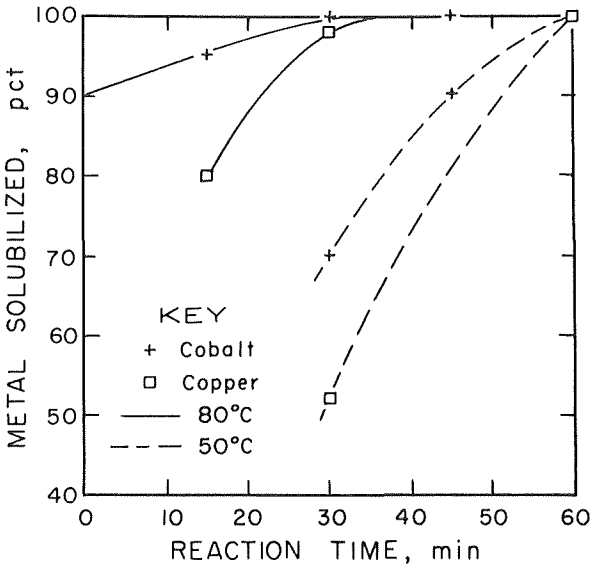

FIGURE 6. - Effect of leaching time at 50° and 80° C on the percent cobalt and copper solubilized from the Cu_3As residue with 100 ml of 200 gpl H_2SO_4 and 8.5 g MnO_2.

Thus, the optimum amounts of MnO_2 (17.0 g) and H_2SO_4 (35.0 g) per 20 g of solids were established. To further define the leaching variables for favorable metal dissolution, the effect of temperature was studied between 30° and 90° C. The tests were conducted with 20 g solids, 17.0 g MnO_2, and 40.0 g

H_2SO_4 in 200 ml of aqueous solution (240 gpl) for 2 hr at the specific temperature. Figure 5 contains the curve for Co, Ni, Cu, and As dissolution at the various temperatures. The temperature effect was similar in each case. The metals dissolution rate increased rapidly from 30° to 40° C, going from 60 to 97 pct. From 40° to 90° C there was only a slight increase in dissolution.

The effect of various reaction times between 15 and 60 min was studied in a system containing 10 g solids, 8.5 g MnO_2, and 20 g H_2SO_4 at 50° or 80° C. The results are summarized in figure 6. The cobalt dissolution increased from 96.0 pct to 99.9 pct when the reaction time was lengthened from 15 to 60 min at 80° C. When the same experimental conditions were used at 50° C, the cobalt dissolution increased from 70.0 pct in 30 min to 99.8 pct in 60 min. Behavior of the nickel dissolution was very similar to that of the cobalt. The copper dissolution rate is also shown in figure 6 at 80° and 50° C. The copper dissolution increased linearly from 79.0 pct to 99.9 pct at 80° C as the time was lengthened from 15 to 60 min. At 50° C, the copper dissolution increased much faster from 50.0 pct at 30 min to 99.9 pct at 60 min. The arsenic solubility followed a curve parallel to the copper solubility curve in figure 6.

To determine the effect of using less leaching water, the solution volume to acid leach residue weight was lowered from 10:1 to 5:1 for test 15, (table 5). The test included 20 g residue, 17.0 g MnO_2, 40.0 g H_2SO_4 in 100 ml of aqueous solution, and a reaction time of 1 hr at 90° C. The filtrate contained 7.1 gpl Co, 3.5 gpl Ni, 51.0 gpl Cu, 33.3 gpl As, and 61.3 gpl Mn. A slight decrease in overall metal dissolution was accounted for by the formation of dark blue crystals ($CuSO_4 \cdot 6_2O$) in the filtrate after standing and cooling overnight (16 hr). Therefore, the volume of leach solution to acid leach residue weight ratio must be maintained above 5:1 for efficient metal solubilization.

Metal Precipitation

The oxidative leaching of the copper filter cake acid residue results in a liquor containing As, Cu, Co, Ni, and Mn sulfates. The leach liquor contains arsenic but lacks iron (III) to remove the arsenic as an iron-arsenate. The molar ratio of iron to arsenic was increased to 1.4:1.0 by adding iron (III) sulfate to the solution. The iron-arsenate precipitation tests produced a solid containing 99.7 pct of the iron and 90.1 pct of the arsenic. This represents a grade of 30.5 pct As, 30.1 pct Fe, 1.0 pct Cu, and 0.7 pct Co. The arsenic recovery could be increased by increasing the Fe:As ratio and adding a small amount of lime (CaO) for scavenging the solution, as shown in similar Bureau research (11).

Sulfide precipitation is an effective chemical method to recover the remaining metal values in solution (9). The addition of near stoichiometric amounts of H_2S to the oxidative leach liquors resulted in the precipitation of 98.3, 0.9, and 1.0 pct of the Cu, Co, and Ni, respectively. The precipitation product contained 59.0 pct Cu and 0.06 pct combined Co-Ni. The copper-depleted leach liquor was treated with stoichiometric amounts of 60 pct Na_2S flakes to recover 97.0 pct of the cobalt and 98.0 pct of the nickel. The precipitate metal grade was 19.3 pct Co, 9.2 pct Ni, and 0.6 pct Cu.

The manganese in industrial leach liquors is recovered as a $MnCO_3$ by precipitation with soda ash and converted to recyclable manganese dioxide by calcining at 350° C (8, 12-15). In the laboratory, a $MnCO_3$ solid was precipitated from the liquor after sulfide processing to verify the feasibility of this approach for recovering manganese. The solid was 37.0 Mn as compared to reagent grade $MnCO_3$, which has a minimum grade of 43.0 pct Mn. The brines from the manganese precipitation had a final pH of 9.3 and contained <0.01 gpl metal values.

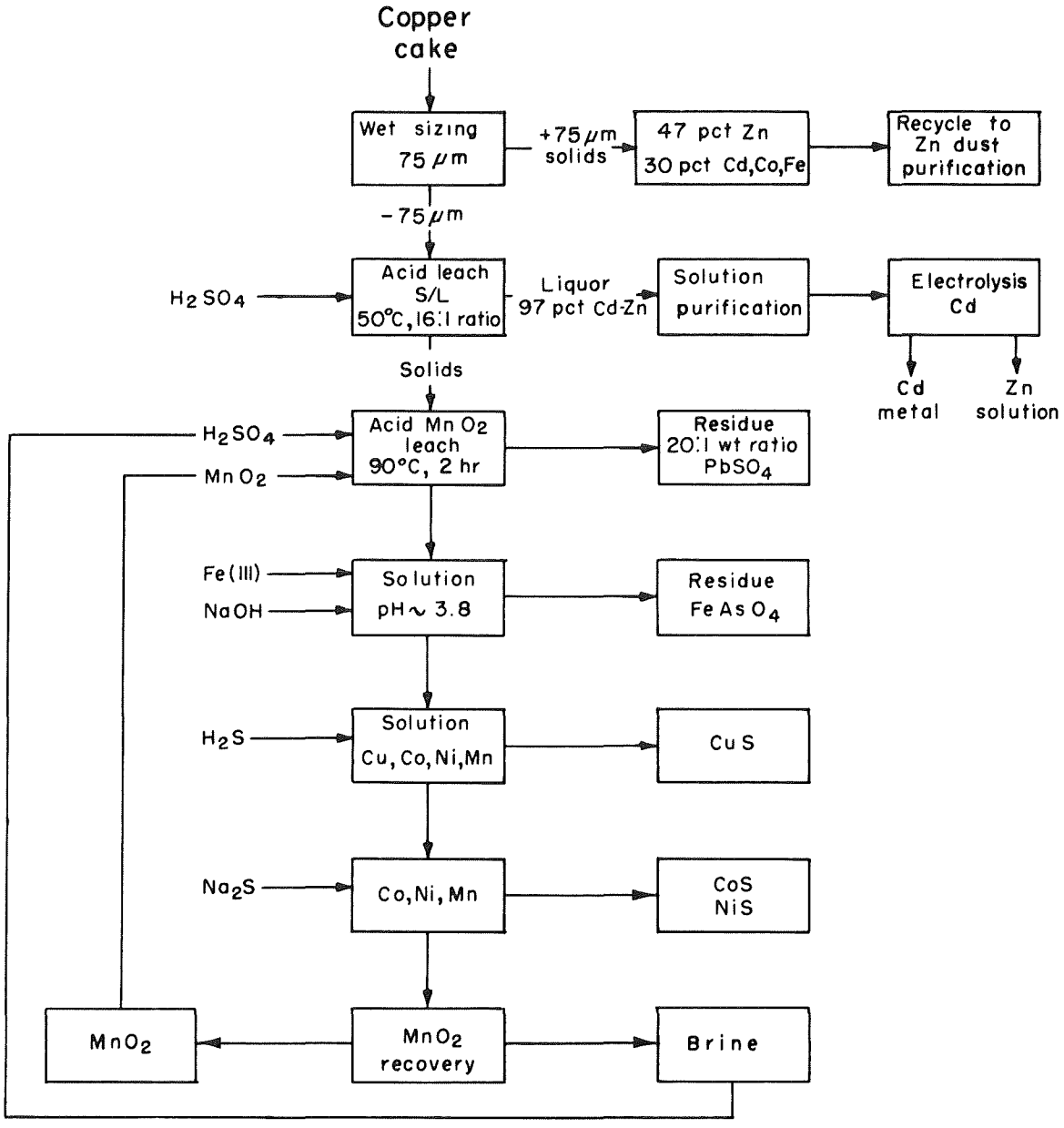

FIGURE 7. - Flowsheet for recovery of principal metals from copper filter cake.

CONCLUSIONS

This investigation has identified a method for recovering the metal values from electrolytic zinc plant copper filter cake, as outlined in figure 7. Wet screening at 75 μm produced an oversized fraction containing 40 to 55 pct of the zinc as metal. This fraction was set aside for recycle back to the initial zinc purification stage of an electrolytic zinc plant. The undersized minus 75-μm material and the screening wash water are repulped with sulfuric acid to decrease the pH to the range of 4.0 to 2.0 for dissolution of the remaining cadmium and zinc. Greater than 97.0 pct of the remaining cadmium and zinc is solubilized. The cadmium can be commercially recovered by electrowinning or cementation-caustic pyrorefining methods (1, 4, 6). The remaining zinc solution can be blended back to the main electrolytic plant's process for zinc metal production.

The residue from the acid dissolution is approximately 77.2 pct Cu_3As, and oxidative leaching of this material for 30 to 60 min at temperatures above 50° C solubilizes $\geq$99.0 pct of the contained Co, Ni, Cu, and As metal values. Arsenic is removed from solution by selective precipitation with iron (III) sulfate. Ninety-eight percent of the copper is recovered from the arsenic-free filtrate by sulfide precipitation with H_2S. Following copper removal, over 97 pct of the cobalt and nickel is precipitated as a sulfide product using Na_2S. Manganese dioxide can be recovered by adding soda ash to precipitate $MnCO_3$ which can be calcined to produce MnO_2 for recycling to the oxidative leach circuit.

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