RI 8757

Bureau of Mines Report of Investigations/1983

Hydrometallurgical Treatment of Electronic Scrap Concentrates Containing Precious Metals

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UNITED STATES DEPARTMENT OF THE INTERIOR

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ERRATA

Page 5, table 1: First two entries should read as follows:

Al, Cu.....	>10	
Mg.....	1	-10

Page 6, table 2: Fifth entry should be Cu, not Au.

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Robert C. Horton, Director

This publication has been cataloged as follows:

Hilliard, H. E. (Henry E.)

Hydrometallurgical treatment of electronic scrap concentrates containing precious metals.

(Report of investigations / United States Department of the Interior, Bureau of Mines ; 8757)

Bibliography: p. 15.

Supt. of Docs. no.: I 28.23:8757.

1. Hydrometallurgy. 2. Precious metals–Recycling. 3. Electronic materials–Recycling. I. Dunning, B. W. II. Makar, H. V. (Harry V.). III. Title. IV. Series: Report of investigations (United States. Bureau of Mines) ; 8757.

TN23.U43 [TN688] 622s [669'.2] 82-600399

CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

° C	degree centigrade	pct	percent
g	gram	ppm	part per million
hr	hour	rpm	revolution per minute
L	liter	tr	troy
lb	pound	wt-pct	weight-percent
oz	ounce		

HYDROMETALLURGICAL TREATMENT OF ELECTRONIC SCRAP CONCENTRATES CONTAINING PRECIOUS METALS

By H. E. Hilliard,[1] B. W. Dunning, Jr.,[2] and H. V. Makar[2]

ABSTRACT

The Bureau of Mines investigated hydrometallurgical procedures for removing base metals from mechanically processed fractions of obsolete military electronic scrap. Feed material was a minus 1/4-in nonmagnetic metallic concentrate produced by high-tension separation. Aluminum was extracted from the feed material in the first-stage ambient temperature, 20-wt-pct sodium hydroxide leach, which was followed by incineration to remove organic matter. A portion of the soluble nickel was extracted in the second-stage oxidizing dilute sulfuric acid leach. Copper and the remainder of the soluble nickel were extracted in the third-stage oxidizing concentrated sulfuric acid leach; copper was recovered from the spent leachate by cementation with an iron-base magnetic fraction. The third-stage leach residue and leachate contained essentially all of the precious metal values.

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INTRODUCTION

Scrap from a variety of sources represents an important component of domestic requirements for gold and silver, as well as other metals. Bureau of Mines statistics show that U.S. refinery production of gold and silver in 1981 totaled 4.6 and 95.0 million tr oz, respectively (6).[3] Of this amount, 83 and 53 pct, respectively, was reclaimed from scrap. The same source also shows that net import reliance for gold in 1981 was 7 pct of apparent consumption, and net import reliance for silver in 1981 was estimated at 50 pct. Obsolete electronics is one example of scrap that contains significant amounts of gold and silver. Although gold and silver use in electronics is a substantial amount of consumption, 37 and 29 pct, respectively, recovery of these metals from obsolete electronic scrap is difficult and expensive owing to the complexity and heterogeneity of such scrap.

Through an agreement with the Defense Property Disposal Service (DPDS), the Bureau of Mines, at its Avondale Research Center, initiated a research program to mechanically process electronic scrap. The DPDS, an agency in the Department of Defense, is responsible for the disposal of millions of pounds of obsolete military electronic scrap annually; 12 million lb from aircraft avionics alone is a typical example. Some of the equipment is sold to scrap dealers who specialize in the recovery of base and precious metals, and some is sold to surplus

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

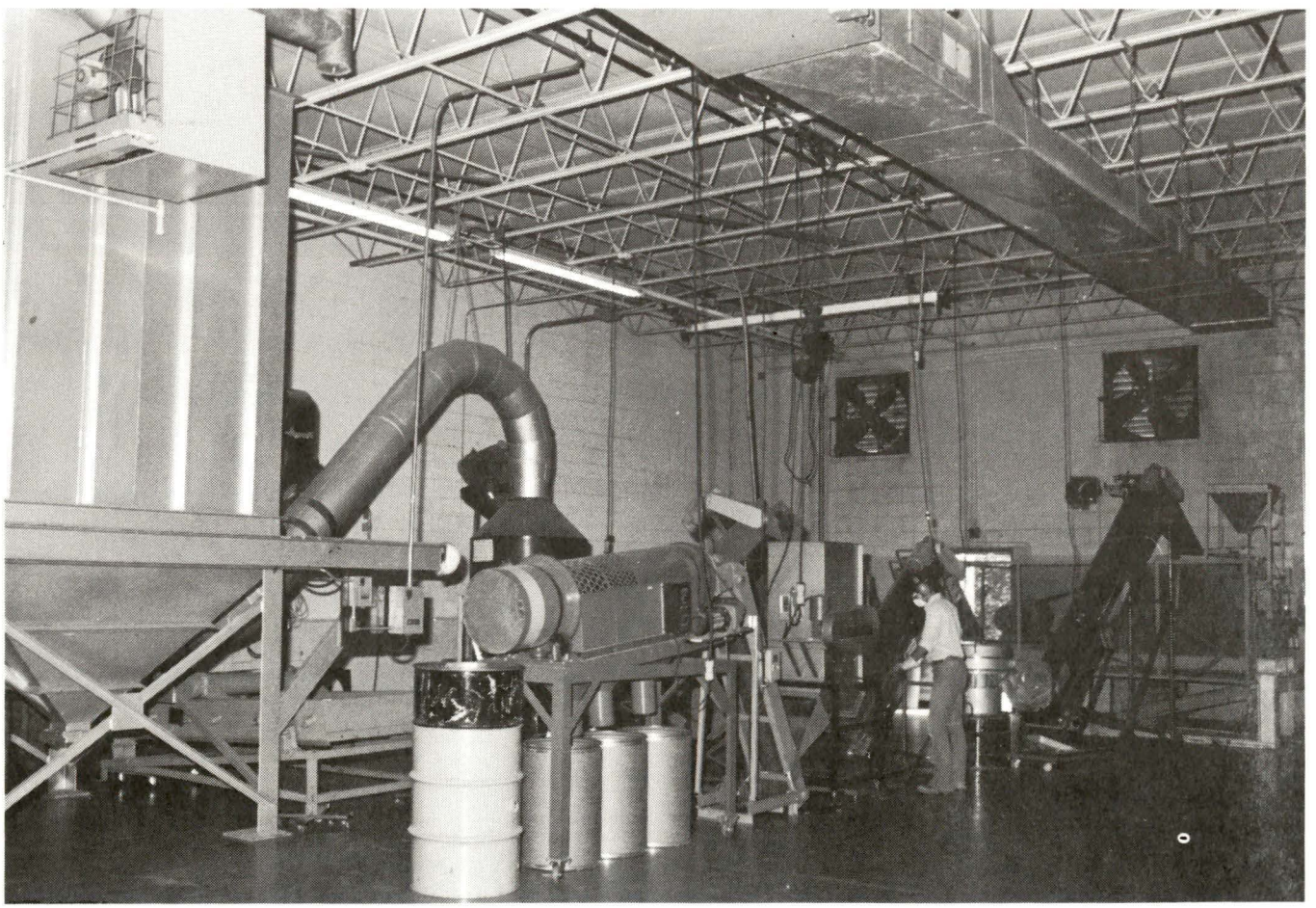

FIGURE 1. - Continuous portion of scaled-up research unit for mechanical beneficiation of electronic scrap.

electronic dealers who resell functional equipment and component parts to electronic experimenters. As military electronic equipment becomes more complex and expensive, getting a fair value for this material has become a pressing problem for DPDS. Precious metals can be found throughout electronic equipment in components such as pin connectors, contact points, silver-coated wire, terminals, capacitors, plugs, and relays. Some equipment may have relatively high concentrations of precious metals, and some may have little or no precious metal.

In an effort to estimate the distribution of precious metals in obsolete electronic equipment, a minerals processing concept was first developed and demonstrated on a laboratory scale. Based on the laboratory model, a scaled-up unit was assembled for upgrading scrap into valuable metal concentrates at feed rates up to 500 lb/hr. Details of the unit have been described elsewhere (1-2). Briefly, the unit operations consist of shredding, air classification, wire picking, magnetic separation, and sizing, all operated in a continuous sequence. These are followed by magnetic precleaning and eddy-current and high-tension separations, which are batch operations. Figure 1 is an overall view of the continuous portion of the process. Figure 2 shows the batch operations.

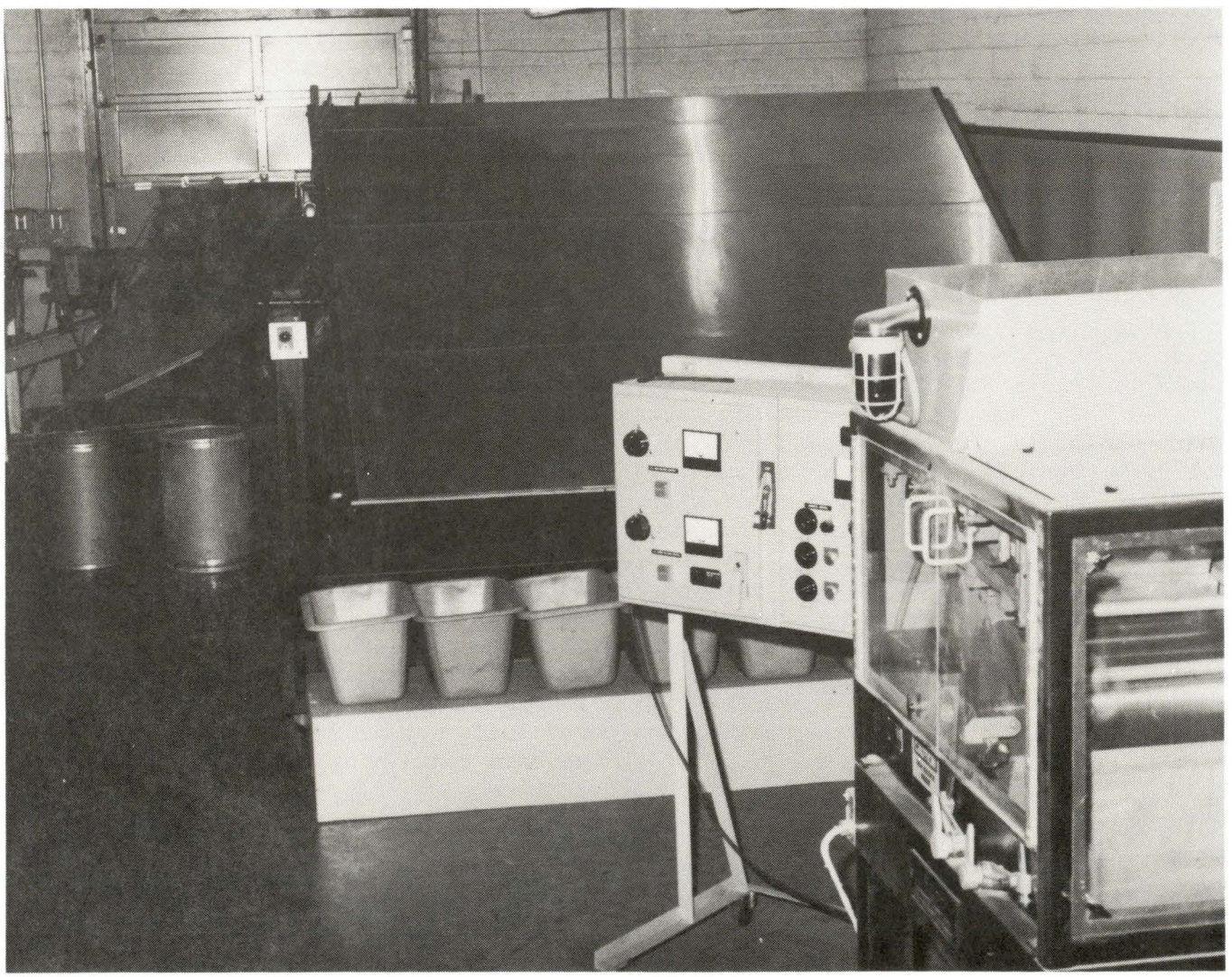

FIGURE 2. - Batch operations of scaled-up research unit for mechanical beneficiation of electronic scrap.

Products obtained by this process include an iron-base fraction, an aluminum fraction, a mixed metal fraction, a wire fraction, air classifier lights, and a minus 1/4-in nonmagnetic metal fraction. The latter is recovered by high-tension separation and is hereafter referred to as the "HTS fraction." The HTS fraction represents about 25 pct of the total input for certain types of mixed scrap, yet contains more than one-half of the total gold and silver. Air classifier lights and tangled wire bundles account for most of the remainder of gold and silver in the nonmagnetic portions of shredded scrap. The small particle size of the HTS fraction makes it ideal for hydrometallurgical treatment to remove the base metals (for subsequent recovery) and further concentrate the precious metals. Traditional treatment of hand-segregated electronic modules (circuit cards, cannon plugs, connectors, etc.) by a toll refiner consists of burning, rod milling, and screening. The fines (sweeps) and the coarse materials (prills) are treated by separate pyrometallurgical procedures to produce copper anodes for electrorefining. Finally, the precious metals are recovered in a regular copper tankhouse circuit from the slimes. Precious metals toll refiners charge by the pound of scrap treated, and shipping this material to the toll refiner is an added expense. The purpose of the mechanical unit operations was to concentrate precious metals in smaller fractions and thus reduce the weight of the material going to the toll refiner. A further weight savings could be made by the hydrometallurgical removal of the base metals from the HTS fraction. This report describes the results of the current ongoing research to demonstrate the technical feasibility of applying hydrometallurgical techniques for removal of base metals from the HTS fraction and to further concentrate the precious metals.

EXPERIMENTAL PROCEDURE AND RESULTS

DESCRIPTION AND ANALYSIS OF HTS FRACTION

Typical test material from the HTS fraction used for this investigation is shown in figure 3. This fraction is recovered from the high-tension separator (HTS) shown in the foreground of figure 2. Typical metallics consist of small pieces of aluminum, copper wire, copper strips, plated gold connectors, fine pieces of stainless steel, and many particles too fine to identify. Nonmetallics are in such forms as lacquer coatings on wire, plastic wire insulation, hard plastics from cannon plugs, bakelite and fiberglass from printed circuitboards, and bits of glass, paper, and film plastic.

The analysis and character of this material vary depending on the initial scrap treatment. Earlier tests with a particular lot of avionic scrap, for example, showed gold and silver concentrations in the HTS fraction equivalent to 42.37 and 505.8 tr oz/ton, or 0.145 and 1.73 pct, respectively (1). The HTS fractions used in the studies described in this report contained gold and silver concentrations ranging from approximately 0.081 and 0.78 pct up to 0.193 and 2.47 pct, respectively. The avionic scrap from which this fraction was recovered consisted of such items as radio receivers, amplifiers, transmitters, tuners, and decoders. Many of the items had been partially stripped of easily removed components containing precious metals.

FIGURE 3. - Typical HTS fractions (minus 1/4-in nonmagnetic metallic concentrates) from processed electronic scrap.

Table 1 is a semiquantitative optical spectrographic analysis of the HTS fractions used in this study. Table 2 shows quantitative analysis for various samples of HTS fractions. A very apparent characteristic of this material, visually and analytically, is its extreme heterogeneity. A single representative head analysis for the test lot was not practically feasible for small randomly selected analytical samples. An accurate "head" analysis for each test sample (tests 1, 2, and 3) was obtained, however, by using the product assays after hydrometallurgical processing. Table 2 also shows assays for gold and silver determined by a commercial refiner for separate samples of HTS fractions. In each case (200 g, 75.5 lb, and 295 lb) the head sample was the total sample. Considering that a wide variety of electronic units were processed to produce the HTS fractions reflected by these analyses, the variation in analysis is not at all surprising.

TABLE 1. - Semiquantitative analysis of HTS fraction (minus 1/4-in nonmagnetic metallic concentrates)

Element	Spectrographic analysis, wt-pct
Al, Cu	>10 -10
Mg	1
Cr, Fe	.3 - 3.0
Ag, Ca, Ni, Pb, Si, Sn, Ti, Zn	.1 - 1.0
Au, Cd, Mg	.03- .3
Na	.01- .1
Ba, Be, K, Li, Mo	<.04

TABLE 2. - Quantitative analyses of HTS fractions

Element	Analysis,[1] wt-pct					
	Test 1	Test 2	Test 3	Commercial assays[2]		
				A	B	C
Ag.....	2.47	.78	.93	1.73	1.07	2.25
Al.....	15.7	19.1	19.2	NA	NA	NA
Au.....	.193	.114	.081	.145	.061	.108
Cr.....	NA	NA	.5	NA	NA	NA
Au.....	25.6	32.0	24.3	NA	NA	NA
Fe.....	NA	NA	2.3	NA	NA	NA
Ni.....	2.0	.9	.6	NA	NA	NA
Pb.....	NA	NA	.6	NA	NA	NA
Si.....	NA	NA	2.3	NA	NA	NA
Sn.....	NA	NA	1.6	NA	NA	NA

NA Not available.

[1]Tests 1, 2, and 3 were all 1,000-g samples. Analyses were calculated from analysis of solutions and residues after leaching tests were completed.

[2]Gold and silver assays were determined by a commercial refiner. Sample sizes were A--200 g, B--75.5 lb, C--295 lb. In each case, the assays were conducted on the total sample.

EXPERIMENTAL APPROACH

Initial laboratory experiments were performed on the HTS fraction as screening tests to assess the behavior of the major base-metal constituents under a few selected leach conditions. Maximum extraction of aluminum was sought first, followed by removal of other base metals such as nickel and copper. Information available from the literature also aided in selecting a process scheme without extensive preliminary testing. The overall objective of the various leaching steps was to concentrate the bulk of the precious metals in a final insoluble residue. A process scheme was thus developed for further study. The process steps consisted of (1) dissolution of aluminum in sodium hydroxide, (2) destruction of organic materials by incineration, (3) dissolution of soluble nickel in dilute sulfuric acid, (4) dissolution of silver and copper by hot concentrated sulfuric acid, (5) cementation of copper with ferrous magnetic fraction, (6) recovery of silver from leach solution, and (7) concentration of gold and remaining silver in a final residue.

Leaching tests were conducted in glass reaction flasks of up to 4-L capacity. Tops for the flasks contained four necks for (1) an air dispersion tube, (2) a thermometer, (3) a blade-type stirrer, and (4) venting. During the second- and third-stage leach, the flask was heated with a heating mantle controlled by a variable transformer. Residue from the previous leach was added to the stirred leach solution (approximately 300 rpm). After the charge was added, the solution was heated to the reaction temperature in the absence of air. Air was added when the desired reaction temperature was attained. On completion of the test, the charge was cooled, filtered, and washed with distilled water. The various products were then weighed and analyzed.

First-Stage Leach (20 wt-pct NaOH)

Leaching studies were conducted on the HTS fraction. Based on published data, it was recognized that aluminum can be readily dissolved in NaOH. Preliminary tests were conducted with stoichiometric amounts of NaOH for aluminum dissolution (approximately 10 wt-pct NaOH). Although aluminum dissolved, a precipitate formed before the solution could be filtered to separate the insolubles. With further testing, approximately twice the stoichiometric amount, i.e., 20 wt-pct NaOH

under ambient temperature conditions--was found to be satisfactory. In the first-stage leach, 3 L of 20-wt-pct-NaOH solution was used for each 1,000-g sample. The first-stage leach was conducted at room temperature in a 3-L reaction kettle equipped with a blade-type stirrer. The dissolution of aluminum by aqueous NaOH can be represented by the following equation:

$$2NaOH + 2Al^\circ + 2H_2O \rightarrow 2NaAlO_2 + 3H_2O. \quad (1)$$

The resulting NaOH solution was filtered, and the residue washed with distilled water. Table 3 shows the variation in extraction efficiency with time. Typical leach liquors produced by the NaOH leach are shown in table 4. Use of a stirred reactor achieved optimum extraction at 8 hr.

TABLE 3. - Extraction of aluminum from minus 1/4-in metallics (HTS fraction) with 20 wt-pct NaOH

Extraction time	Al extraction, pct	
	Beaker tests	Stirred reactor
4 hr.....	23.9	72.2
8 hr.....	72.8	95.3
12 hr.....	95	ND

ND Not determined.

TABLE 4. - Typical leach liquors produced by leaching HTS fractions with 20 wt-pct NaOH

Element	Beaker tests		Stirred
	4 hr	8 hr	reactor, 8 hr
Ag.....ppm..	0.1	0.1	ND
Al.....g/L..	16	38	51
Cu.....ppm..	0.2	0.3	ND
Fe.....ppm..	0.3	0.3	ND
Ni.....ppm..	0.3	0.2	ND
Si.....ppm..	217	417	1,280

ND Not determined.

Incineration of the residue from the NaOH leach at 400° C destroys the combustibles.

Second-Stage Leach (Dilute H_2SO_4, 90° C)

Spectrographic analysis of the HTS fraction indicated that nickel concentration was 0.1 to 1.0 pct. The second-stage leach was designed to dissolve nickel and at the same time produce a solution low in copper. Removal of nickel is important because the copper refiners who eventually receive the precious metals in copper ingots must use extra processing steps for the electrolytes when nickel concentrations are excessive, thus raising process costs. The second-stage leach can be represented by the following equations:

$$2Ni^\circ + 2H_2SO_4 + O_2 \rightarrow 2NiSO_4 + 2H_2O, \quad (2)$$

$$2Cu^\circ + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O, \quad (3)$$

$$Ni^\circ + CuSO_4 \rightarrow Cu^\circ + NiSO_4, \quad (4)$$

$$Fe^\circ + CuSO_4 \rightarrow Cu^\circ + FeSO_4. \quad (5)$$

Equations 2 and 3 represent copper and nickel dissolution by H_2SO_4 and oxygen; equations 4 and 5 represent copper cementation by nickel and iron that are present in the leach residue. Copper cementation by undissolved nickel and iron, equations 4 and 5, must be carried out in the absence of oxygen to allow the cementation of copper and prevent the dissolution of additional copper. Screening tests were run with 20-vol-pct-H_2SO_4 solution at 50° and 90° C using retention times of 2 and 4 hr. Best nickel extraction was achieved at 90° C and 4 hr with a solution low in copper.

Thus, the process test conditions selected for the second-stage leach consisted of leaching in 20-pct H_2SO_4 for 4 hr at 90° C under oxidizing (bubbling air through the solution), followed by an additional 4 hr under nonoxidizing conditions. Heating was accomplished with a heating mantle. Actual test temperature varied between 90° and 95° C.

Third-Stage Leach (Concentrated H_2SO_4, 150° C)

The objective of the third-stage leach was to produce a final residue with a volume and weight of just a fraction of the original feed yet containing most or all of the precious metals. The dissolution rate of copper and silver in concentrated H_2SO_4 is temperature dependent. Copper, for example, begins to dissolve slowly at about 55° C, with dissolution becoming rapid at about 150° C. Kunda (3) studied the dissolution of silver in hot concentrated acid by heating silver metal and concentrated H_2SO_4 at 160° to 200° C. The results showed that the rate of dissolution was characterized by a short period of rapid dissolution after which the reaction stabilized and proceeded at a constant rate. Upon cooling, silver sulfate crystallized from solution. Kunda suggested 200° C for a reasonable dissolution rate of silver in concentrated H_2SO_4. This appeared to be the ideal temperature for the third-stage leach, permitting high extraction rates for both copper and silver. However, since Kunda's data showed that most of the silver crystallizes from solution upon cooling, a lower temperature that would minimize silver dissolution while dissolving maximum copper was considered more desirable. Thus, for the third-stage leach, 150° C was selected for leaching second-stage residue in excess concentrated H_2SO_4. Actual test temperatures ranged between 150° and 160° C. Copper dissolved rapidly at this temperature, while silver dissolved more slowly. Air was sparged through the solution during the entire 6-hr leach period. Essentially all of the copper and soluble nickel not extracted in the second-stage leach were dissolved in this third-stage leach. The nickel present in stainless steel was virtually unattacked in all of the leaching stages. Copper formed insoluble salts that were later washed from the third-stage leach residue with distilled water.

The reactions occurring in the third-stage leach can be represented by the following equations:

$$2Cu^\circ + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O, \quad (6)$$

$$2Ni^\circ + 2H_2SO_4 + O_2 \rightarrow 2NiSO_4 + 2H_2O, \quad (7)$$

$$2Ag^\circ + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O. \quad (8)$$

In equations 6 and 7, nickel and copper are dissolved by H_2SO_4 and oxygen, and in equation 8 silver is dissolved by H_2SO_4. On completion of the third-stage leach, the charge was allowed to cool and then filtered. The solid residue was washed with distilled water to dissolve soluble metal salts. The water-insoluble residue was dried, weighed, and screened through a 50-mesh sieve, and the minus and plus screen fractions were assayed.

Results

Three separate tests of the overall hydrometallurgical process were conducted under the test conditions described above using 1,000-g samples in each test. Data for tests 1 and 2 are summarized in tables 5 and 6. These show the materials distribution in the filtrates and final residue. Data for test 3 are summarized in tables 7, 8, and 9. Tables 7 and 8 show the solution and residue analyses, respectively; table 9 summarizes the overall materials distribution. Figure 4 shows the overall process flow and also includes data from test 3. Filtrate volumes are different because different amounts of wash waters were used. This does not affect the results since actual leach conditions were the same. The filtrate and wash from the first-stage leach contained approximately 137, 180, and 183 g of aluminum for tests 1, 2, and 3, respectively. These represented 87-, 94-, and 95-pct aluminum extractions, respectively. No attempt was made to recover an aluminum product. However, the first-stage leach solution was diluted with water, seeded with

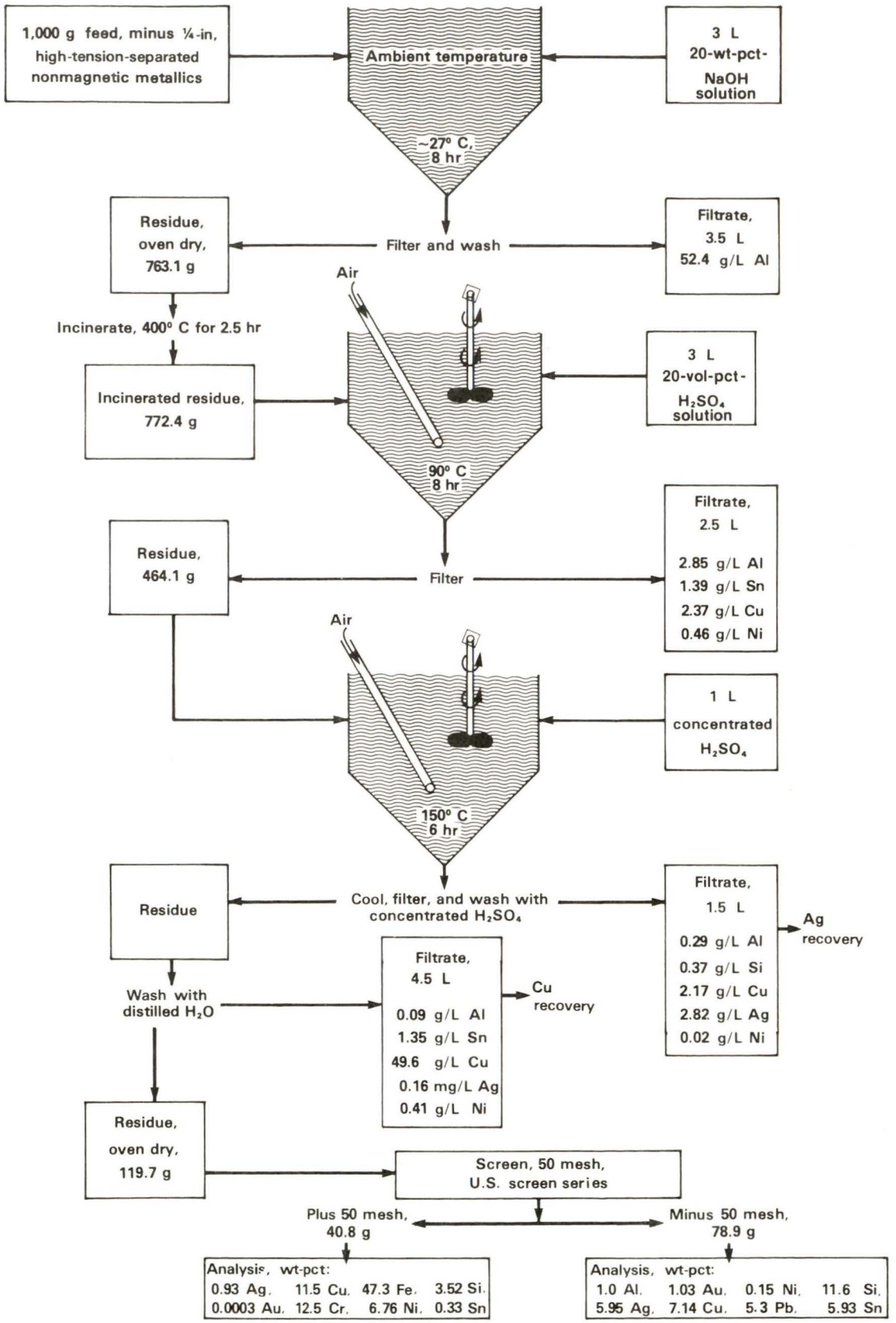

FIGURE 4. - Flowsheet for hydrometallurgical processing of HTS fractions.

TABLE 5. - Materials distribution for test 1, g

	Ag	Al	Au	Cu	Ni
Filtrate:					
1st stage (3.5 L).....	0.0004	136.5	ND	0.011	0.0002
2d stage (2.5 L).....	.0004	6.5	ND	.29	.65
3d stage (2.5 L).....	12.570	.13	ND	6.56	.0002
3d stage wash (7.5 L).....	.0008	.41	ND	235.0	.59
Total.....	12.57	143.54	NAp	241.86	1.24
Final residue:					
Plus 50 mesh (35.0 L).....	.21	.22	0.035	1.32	.13
Minus 50 mesh (110.0 g).....	11.90	13.10	1.892	12.87	.59
Total.....	12.11	13.32	1.93	14.19	.72
Grand total.....	24.68	156.86	1.93	256.05	1.96

NAp Not applicable.
ND Not detected.

TABLE 6. - Materials distribution for test 2, g

	Ag	Al	Au	Cu	Ni
Filtrate:					
1st stage (11.1 L).....	0.0001	179.8	ND	0.0002	0.0003
2d stage (7.0 L).....	.0005	11.2	ND	7.35	.213
3d stage (2.0 L).....	3.200	.0002	ND	6.30	.02
3d stage wash (8.0 L).....	.0002	.01	ND	296	.01
Total.....	3.20	191.0	NAp	309.7	.24
Final residue:					
Plus 50 mesh (35.3 g).....	.19	.3	0.23	1.02	.2
Minus 50 mesh (142.2 g).....	4.649	.1	1.116	9.26	.5
Total.....	4.84	.4	1.35	10.28	.7
Grand total.....	8.04	191.4	1.35	319.98	.94

NAp Not applicable.
ND Not detected.

TABLE 7. - Filtrate analyses[1] (test 3)

	Leach			Stage 3
	Stage 1	Stage 2	Stage 3	wash solution
Analysis, g/L:				
Ag.....	0.0001	0.0002	2.82	0.0002
Al.....	54.2	2.85	0.29	0.09
Au.....	<0.0001	<0.0001	<0.0001	ND
Cr.....	ND	0.13	0.71	0.05
Cu.....	0.0002	2.37	2.17	49.6
Fe.....	0.0003	0.46	0.31	0.29
Ni.....	0.0002	0.46	0.02	0.41
Pb.....	ND	0.004	0.004	0.003
Si.....	0.97	0.65	0.56	1.35
Sn.....	0.29	1.39	0.37	1.35
Residue weight.....g..	763.1	464.1	119.7	NAp

NAp Not applicable.
ND Not determined.
[1]Volumes are shown in table 9.

TABLE 8. - Analysis of final residue (third-stage leach, test 3)

	Screen size, mesh	
	Plus 50	Minus 50
Analysis, wt-pct:		
Ag.....	0.93	5.95
Al.....	0.25	1.0
Au.....	0.0028	1.03
Cr.....	12.5	0.3
Cu.....	11.5	7.1
Fe.....	47.3	0.9
Ni.....	6.8	0.2
Pb.....	0.2	7.9
Si.....	3.5	11.6
Sn.....	0.3	5.9
Fraction weight....g..	40.8	78.9

aluminum hydroxide crystals, and set aside for several weeks. Crystalline aluminum hydroxide separated according to the equation

$$2NaAlO_2 + 4H_2O = 2Al(OH)_3 + 2NaOH. \quad (9)$$

NaOH is regenerated by this reaction and can be used to leach more aluminum.

The second-stage leach was designed to preferentially extract nickel. The filtrates from the second-stage leach for tests 1, 2, and 3 contained 0.65, 0.21, and 1.15 g of nickel, respectively. These were equivalent to 52, 88, and 38 pct, respectively, of the soluble nickel. Most of the copper remained in the residue. The differences in nickel extraction are believed to reflect the presence of various forms of copper-nickel alloys that exhibit different degrees of solubility in 20-pct H_2SO_4. This is a reasonable assumption considering the heterogeneity of the HTS fraction. Stainless steel did not dissolve, and the nickel contained therein reported to the final residue. The remainder of the soluble nickel was dissolved along with copper during the third-stage leach with concentrated H_2SO_4. The percentage of nickel extracted in the second stage could probably be increased by increasing the time of the oxidative leach. Tests to improve extraction efficiency through use of ultrasonics and pressure leaching are in progress.

TABLE 9. - Materials distribution for test 3[1]

	Ag	Al	Au	Cr	Cu	Fe	Ni	Pb	Si	Sn
Filtrate:										
1st stage (3.5 L).....	0.00035	183.4	ND	NA	0.0007	0.0011	0.0007	NA	3.40	1.02
2d stage (2.5 L).....	.0005	7.13	ND	0.33	5.93	1.15	1.15	0.01	1.63	3.48
3d stage (1.5 L).....	4.23	.44	ND	1.07	3.26	.47	.03	.01	.84	.56
3d stage wash (4.5 L).....	.0007	.41	ND	.23	223.2	1.30	1.85	.01	6.08	6.08
Total.....	4.23	191.38	NAp	1.63	232.39	2.92	3.03	.03	11.95	11.14
Final residue:										
Plus 50 mesh (40.8 g).....	.379	.10	0.0011	5.10	4.69	19.30	2.76	.08	1.44	.14
Minus 50 mesh (78.9 g).....	4.695	.79	.8127	.22	5.63	.72	.12	6.25	9.15	4.68
Total.....	5.07	.89	.814	5.32	10.32	20.02	2.88	6.33	10.59	4.82
Grand total	9.30	192.3	.814	6.95	242.71	22.94	5.91	6.36	22.54	15.96

NA Not available. NAp Not applicable. ND Not detected.

[1]Determined from analyses shown in tables 5 and 6.

In the third-stage leach, copper and silver sulfate are formed when copper and silver metal are dissolved by hot concentrated H_2SO_4. Copper sulfate, once formed, is insoluble in concentrated H_2SO_4 and becomes part of the residue on filtering. Silver sulfate begins to crystallize out of hot H_2SO_4 solution upon cooling, at the filtering temperature used to collect the copper sulfate solids (25° C), more than 50 pct of the silver sulfate had crystallized. A few techniques were tried for recovering silver from the third-stage leach filtrate. Addition of water and sodium chloride precipitated all the silver as sulfate and chloride. Tests showed that silver could be recovered by cementation using iron or zinc. With the latter, typical constituents in the product analyzed, in wt-pct, 73.9 Ag, 6.2 Pb, 2.5 Cu, 1.4 Zn, 0.11 Fe, and 0.02 Ni. With further testing, an improved recovery process for silver was applied (4). This consisted of heating the silver sulfate-silver chloride with sodium carbonate at 500° C. The recovered silver exceeded 97 pct purity.

The copper sulfate in the third-stage residue is soluble in water and is easily separated from the insoluble silver sulfate and other residual materials by washing with distilled water. The wash solution from the third-stage leach in tests 1, 2, and 3 contained 235, 296, and 223 g of copper, representing 92, 93, and 92 pct, respectively, of the total available copper. Copper powder was cemented from the wash solution with the magnetic iron-base fraction. Cementation proceeded over a 12-hr period, followed by washing and filtering. Chemical analyses of the cement copper and the filtrate are shown in table 10. For comparison purposes, analyses of cement copper from commercial operations (7) and other Bureau of Mines research (5) are shown in table 11. Based on these data, the quality of the cement copper shown in table 10 is acceptable for further commercial recovery operations, such as reverberatory smelting in a copper refinery.

TABLE 10. - Chemical analyses of cement copper and filtrate

Element	Cement Copper, wt-pct	Filtrate, g/L
Ag	0.01	0.00017
Al	<.01	ND
Cr	<.01	ND
Cu	88.0	.012
Fe	.03	11.9
Ni	.06	.31
Pb	.01	.004
Sn	.70	.068

ND Not detected.

TABLE 11. - Cement copper analyses reported by others, wt-pct

Element	Source A[1]	Source B[2]
Ag	0.1	0.04
Au	.0006	.01
Cu[3]	90	89
Fe	NA	1.1
Ni	.2	NA
Pb	.7	.32
Sn	NA	.36

NA Not available.

[1]Commercial cement copper (7, p. 193).

[2]Cement copper from other BuMines studies (6, p. 15).

[3]Van Arsdale (7, p. 171) gives 72.7 and 71.5 wt-pct Cu; values not given for other elements.

The final residue weights for the three tests represented 12 to 18 pct of the original weight of HTS fractions processed. Typical final residue is shown in figure 5. The gold in the residue represents essentially 100-pct recovery. Silver recovered in the residue represented 49, 60, and 55 pct of the total silver, respectively, for tests 1, 2, and 3. Almost all of the balance was in the third-stage leach filtrate and was recoverable as greater than 97 pct purity silver as described above.

The importance of this process in concentrating the precious metals in a small residue product can be illustrated by the following example. A recent lot of 1 ton

FIGURE 5. - Final residue produced after third-stage leach and wash.

of electronic scrap concentrates shipped from Avondale, Md., to a New England address cost $241 in freight charges. The toll refiner charged $1.50/lb to process the concentrates, or $3,000 for the 1-ton lot. Payments are made for the precious metal recovered and for copper. However, payment is made for copper only if it is present in the concentrate in an amount greater than 50 pct. The concentrates have analyzed 20 to 40 pct copper depending on the type of electronic scrap mechanically processed and are thus only borderline at best for copper value. If the concentrates were treated by the three-step leach procedure shown in figure 4, and assuming the average residue weight equivalent to 15 pct, the toll refiner would receive 300 lb of material instead of 1 ton and charge $450 to process it rather than $3,000. Freight charges would also be considerably less. The cement copper is, by this process, a separate product of direct commercial value. Current data are insufficient for a detailed process evaluation, but a preliminary analysis indicates that process costs would, at worst, be less than half the projected savings.

FUTURE WORK

Tests are in progress to further improve the procedure by increasing the efficiency of reactions at certain stages. For example, the dissolution of copper and nickel in aqueous H_2SO_4 solutions in the presence of oxygen takes place in four successive steps:

1. Dissolution of the oxygen in the aqueous solution.

2. Transport of the dissolved oxygen to the surface of the metal.

3. Oxygen-metal surface reaction.

4. Dissolution of the reaction products by the aqueous solution.

Step 3 is greatly influenced by surface area, and the concentration of dissolved oxygen is increased by pressure. For this reason, a well-agitated pressure leaching system offers considerable promise for achieving significant improvements in the overall efficiency. Appropriate pressure leaching equipment has been acquired and assembled, and tests are currently in progress. These studies are designed to optimize sequence of operation and process parameters such as pressure, temperature, retention time, and degree of extractions. Base metal recovery, recycling of leachants, effluent disposal, and process economics will also be evaluated.

CONCLUSIONS

Laboratory tests have demonstrated the technical feasibility of a proposed hydrometallurgical process for concentrating precious metals by removing base metals from an upgraded fraction of processed obsolete electronic scrap. The upgraded fraction consists of minus 1/4-in nonmagnetic metallics recovered by high-tension separation of mechanically processed electronic scrap. The main stages include (1) dissolution of aluminum in sodium hydroxide, (2) incineration of the resulting residue to destroy organic materials, (3) dissolution of nickel in dilute sulfuric acid, (4) dissolution of silver, copper, and the remainder of the soluble nickel in hot concentrated sulfuric acid, (5) cementation of copper with a magnetic fraction, (6) recovery of silver from leach solution, and (7) concentration of gold and remaining silver in a final residue.

This three-stage leach procedure produced a final residue which was only 12 to 18 pct of the initial feed weight, yet contained all the gold and 49 to 60 pct of the silver. This residue is amenable to precious metal recovery by toll refining, but at a fraction of the cost involved for the original feed material. The remaining silver was recoverable from the third-stage filtrate as cement silver (74 pct) or in a higher purity form (greater than 97 pct). Copper concentration in the feed (approximately 24 to 32 pct), though too low to receive credit by direct toll refining, was recovered as an 88-pct-grade cement copper, comparable to commercial grade. Copper extraction was approximately 92 pct. The results also demonstrated that aluminum extracted during the first-stage leach as sodium aluminate can be treated with water and aluminum hydroxide seed crystals to recover aluminum hydroxide crystals and fresh sodium hydroxide for recycle.

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INT.-BU.OF MINES,PGH.,PA. 26725