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Scale-Up Study Using 20-Liter Multielectrode Cell

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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere
A/m^2	ampere per square meter
°C	degree Celsius
cm	centimeter
cm^2	square centimeter
g	gram
g/L	gram per liter
h	hour
in	inch
kg	kilogram
kW	kilowatt
kW•h	kilowatt hour
kW•h/kg	kilowatt hour per kilogram
L	liter
lb	pound
m	meter
m^2	square meter
min	minute
pct	percent
tpd	metric ton per day
$\mu g/m^3$	microgram per cubic meter
µg/mL	microgram per milliliter
V	volt
W	watt
wt pct	weight percent

ELECTROLYTIC METHOD FOR RECOVERY OF LEAD FROM SCRAP BATTERIES

Scale-Up Study Using 20-Liter Multielectrode Cell

By A. Y. Lee,[1] E. R. Cole, Jr.,[2] and D. L. Paulson[3]

ABSTRACT

Prior work at the Bureau of Mines resulted in the successful development of a bench-scale, combination electrorefining-electrowinning method for recycling the lead from scrap batteries using waste fluosilicic acid (H_2SiF_6) as electrolyte. This paper describes larger scale experiments.

Anodes cast from scrap battery lead were electrorefined in a 20-L multielectrode cell for 3 to 7 days. The anodes, containing 2 to 2.5 pct antimony, were ideal for obtaining firm and adherent slime blankets. Cathode deposits, assaying 99.99 pct Pb, were obtained, with current efficiencies near 99 pct.

Sludge leaching was done in 100-L tanks followed by filtering in 61 cm square vacuum pan filters.

Lead of greater than 99.99-pct purity was recovered from the filtrate by electrowinning in a 20-L multielectrode cell using insoluble PbO_2-Ti (lead dioxide-coated titanium) anodes and pure lead cathodes. The fluosilicic acid electrolyte depleted in lead was repeatedly recycled to leach more sludge, and there was no problem with impurity buildup.

The amount of PbO_2 formed on the anodes during electrowinning was less than 1 pct of the total lead deposited on the cathodes, as long as the phosphorus concentration in the electrolyte was greater than 1.3 g/L.

Emissions of lead in air were less than 10 $\mu g/m^3$, well below the proposed OSHA limit of 50 $\mu g/m^3$.

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INTRODUCTION

The Bureau of Mines has investigated an electrolytic recycling process to recover lead from scrap batteries as part of the effort to improve secondary recovery of metals, minerals, and other values from waste products. This process, eliminating sulfur dioxide (SO_2) generation and minimizing particulate lead emissions, is an acceptable alternative to the pyrometallurgical processes currently used by the secondary lead industry. The lead recovered by electrolysis is free of antimony and suitable for producing maintenance-free batteries.

In previous bench-scale studies (1-3)[4] lead was recovered from grids and lugs by electrorefining and from battery sludge by leaching-electrowinning. The process, based on the bench-scale data, has been considered to have economic potential (4).

In commercial practice, scrap batteries are first drained, then crushed in a hammer mill and separated into four fractions: plastic, rubber, large pieces of metallic lead, and a fine sludge. Plastics are recycled, and rubber is buried. In this work the large metallic fraction of the crushed batteries is melted and cast as anodes for electrorefining in lead fluosilicate electrolyte. The sludge is leached with ammonium carbonate [$(NH_4)_2CO_3$] and ammonium bisulfite (NH_4HSO_3) to convert the lead sulfate ($PbSO_4$) and lead dioxide (PbO_2) into lead carbonate ($PbCO_3$), which is acid soluble. Leaching the carbonate sludge with fluosilicic acid or spent electrolyte produces an electrolyte from which lead is electrowon.

The objective of this investigation was to identify possible problems in the scale-up. Specific areas of concern were impurity buildup in the electrolyte, generation of wastes, lead levels in the workplace, and worker health hazards.

ACKNOWLEDGMENTS

Thanks for furnishing materials used in this investigation are due to RSR Corp., Dallas, TX; AGRICO, Donaldsonville, LA; Georgia-Pacific Co., Bellingham, WA; Peter Cooper Corp., Oak Creek, WI; and Eagle Picher Industries, Inc., Cincinnati, OH.

The helpful suggestions by Dr. R. C. Kerby, senior development metallurgist with Cominco, Ltd., Trail, British Columbia, Canada, and Dr. R. D. Prengaman, Vice President--R&D, with RSR Corp., Dallas, TX, are sincerely appreciated.

MATERIALS, EQUIPMENT, AND PROCEDURES

BATTERY SCRAP

All of the lead metal and battery sludge used in this investigation was obtained from a large domestic secondary smelter in three different lots. Lot 1 contained shredded battery grids, terminals, and plastic-rubber materials. Lot 2 contained mostly finer shredded battery grids, mixed with some sludge and plastic-rubber materials. The lead grid samples were cleaned and sorted to remove the nonmetallic waste and melted to pour into lead pigs for later use in making anodes for electrorefining (1). About 90 kg of lead-antimony metal was recovered from lot 1 and 180 kg from lot 2.

Lot 3, a sludge sample, weighed about 520 kg and contained 84.4 pct sludge powder and 15.6 pct H_2O. Partial analyses of the battery sludge and lead pigs are given in table 1. The sludge contained mainly $PbSO_4$, PbO_2, and fine lead metal.

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

TABLE 1. - Composition of battery sludge and lead pigs, percent

Materials	Pb	Sb	Sn	As	Cu	SO_4	H_2O	Zn
Sludge................	59.2	0.35	0.05	<0.03	<0.006	15.61	15.6	ND
Pb pigs from lot 1....	97.9	2.08	<.06	.07	.06	ND	ND	<0.01
Pb pigs from lot 2....	97.2	2.40	.07	.19	.04	ND	ND	<.01

ND Not determined.

ELECTRODES

For electrorefining, impure anodes were prepared by melting the lead pigs at 425° to 450° C and pouring into a carbon or steel mold. A $ZnCl_2$-NaCl flux was used as a cover on the molten bath to prevent oxidation and loss of antimony to the dross. Each anode weighed about 7 kg, was 2.3 cm thick by 10 cm wide by 24 cm high, and had a 2- by 18-cm integrally cast bus bar, making a T-shape (fig. 1).

For electrowinning, insoluble PbO_2-Ti anodes, developed and patented by the Bureau (5), were used. The PbO_2-Ti anodes were approximately the same width and height as the lead anodes but only about 1/2 cm thick. Also the PbO_2-Ti anodes had evenly spaced holes throughout the surface to aid adherence of the PbO_2 coating (fig. 2).

Cathodes, which measured 12.5 cm wide by 28 cm long, were cut from 0.16-cm thick corroding-grade lead sheet.

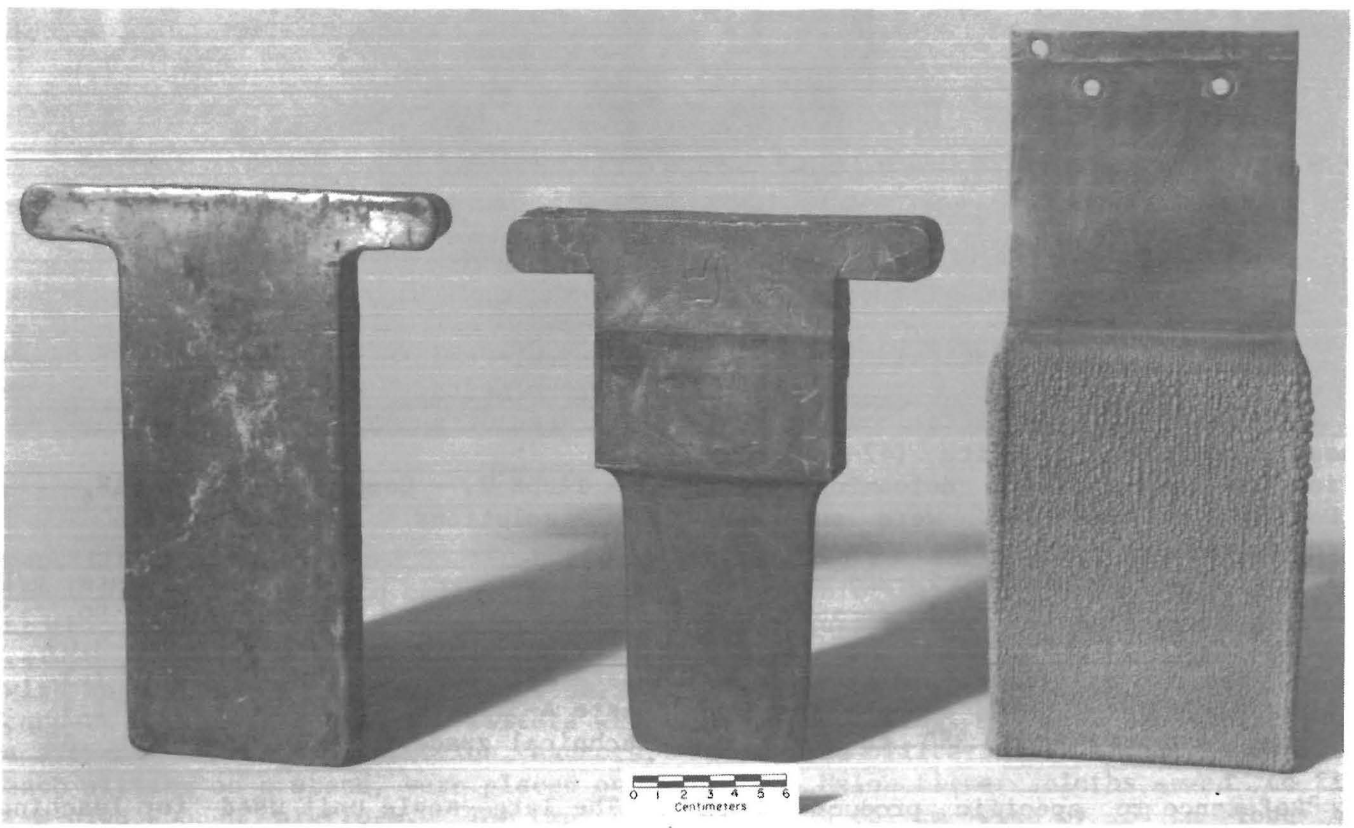

FIGURE 1. - Electrodes used in electrorefining. Impure lead anode before electrorefining (left), anode after electrorefining (center), and pure lead cathode deposit (right).

FIGURE 2. - Electrodes used in electrowinning. PbO_2-Ti anode before electrowinning (left), anode after electrowinning (center), and pure lead cathode deposit (right).

SLUDGE LEACHING UNIT

Ammonium carbonate, lead powder (200 mesh), ammonium bisulfite (47-pct solution by weight), and defoaming agent (Dow-Corning DB-110A)[5] were purchased from commercial sources. A sample of filter aids (Diatomite, FW-20) was obtained from an industrial company. A large quantity of waste H_2SiF_6 was supplied by a fertilizer company in three batches (A-1, A-2, and A-3); batch volumes ranged from 380 to 570 L. Technical-grade H_2SiF_6 was also purchased for some tests. Partial analyses of the H_2SiF_6 solutions are given in table 2.

TABLE 2. - Composition of H_2SiF_6 solutions

	Major constituents, g/L		
	H_2SiF_6	P	SO_4
Waste A-1.......	312.0	6.18	2.09
Waste A-2.......	269.0	.67	1.3
Waste A-3.......	304.8	.53	1.3
Technical grade.	393.6	.57	.82

The large-scale unit used for leaching consisted of two 100-L cylindrical reactors (fig. 3), two polypropylene vacuum

[5]Reference to specific products does not imply endorsement by the Bureau of Mines.

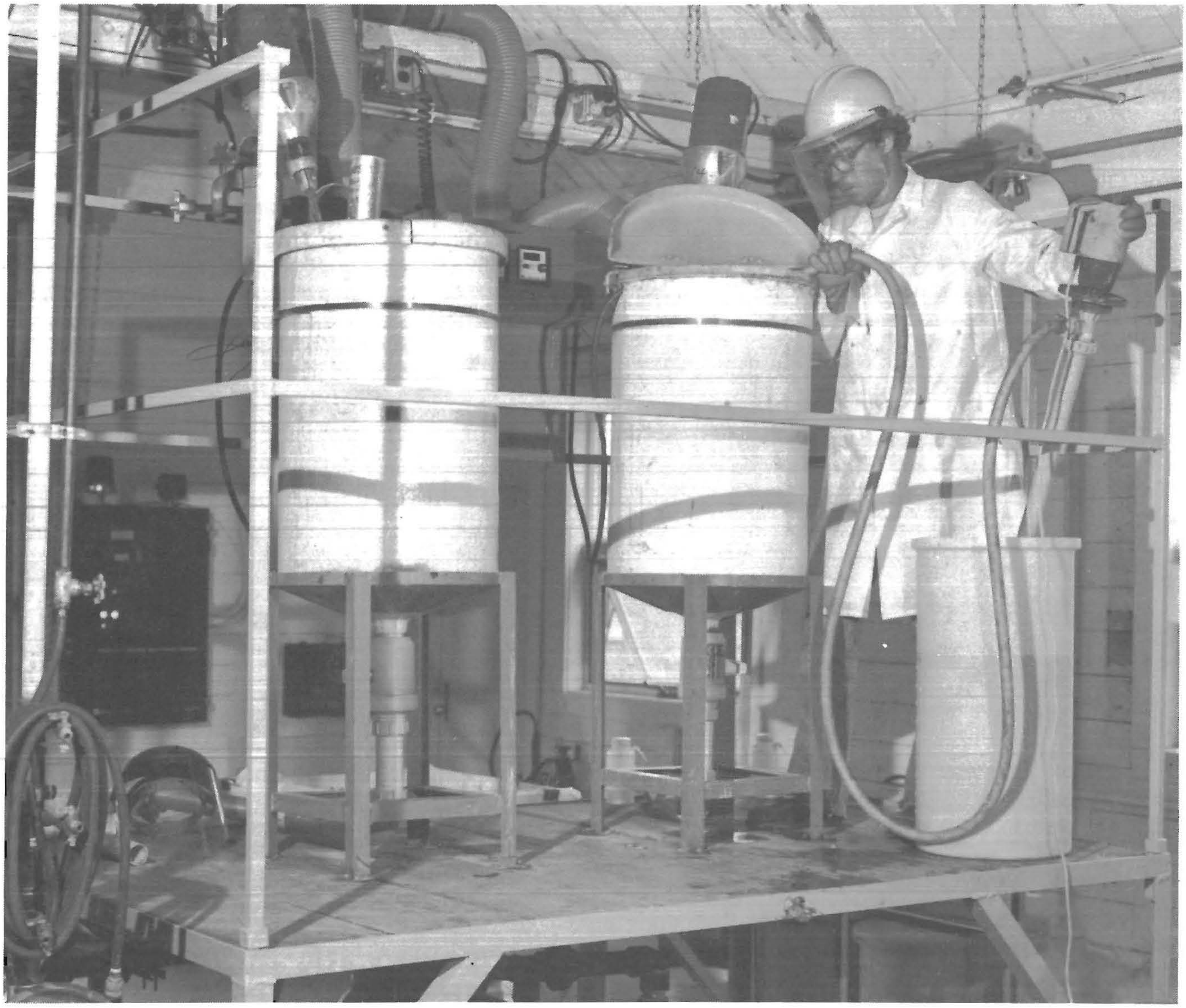

FIGURE 3. - Leach reactors.

pan filters (fig. 4), and a 160-L glass-lined steel tank used to collect the filtrate. The reactors were polypropylene reinforced with a fiberglass casing and with an opening at the conical bottom, to connect the reactors and pan filters with a 7.6-cm valve and pipe. The reactors, each sitting on a stand, were placed on a 1-m-high wooden platform. The two pan filters were arranged side by side next to the platform so that the discharge from the reactor could feed the pan filters by gravitation.

Both the steel tank and vacuum pump were installed under the platform and connected to the pan filters with polyvinyl chloride (PVC) pipes. Each reactor was equipped with a mechanical stirrer and a thermostatically controlled immersion heater (2-kW) in a ~56-cm-long alumina casing. The steel tank, reactors, and filters were all acid resistant. Nylon filter cloths sewed to fit the pan (61 cm wide by 61 cm long by 20 cm deep) and filter papers (S&S No. 595) of size ~1 m^2 were used to line the filter pans. A heavy-duty drum pump, also acid resistant, was employed to transfer liquid to the reactors.

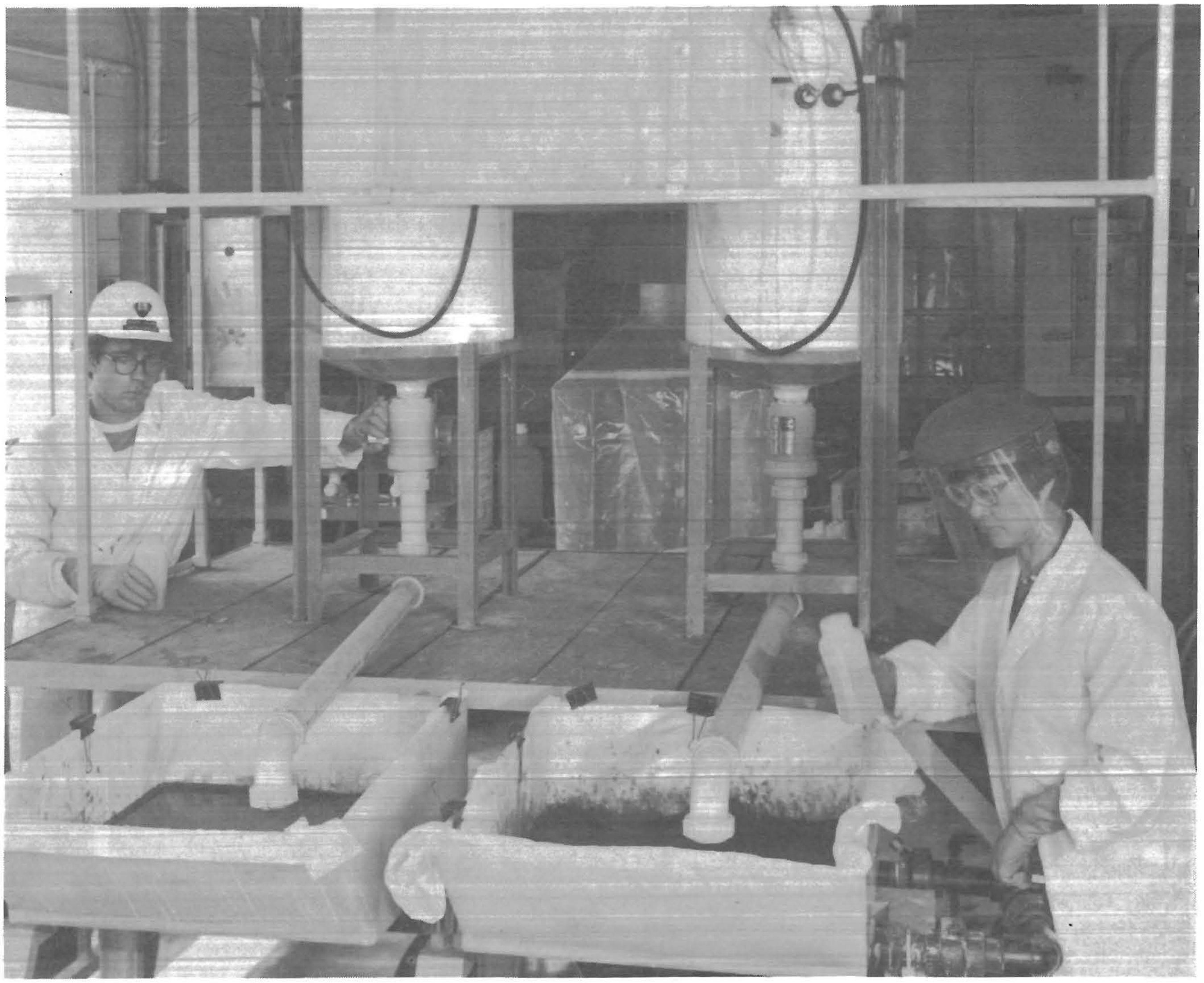

FIGURE 4. - Pan filters.

SLUDGE LEACHING

Sludge was leached in a two-step batch process, as outlined in figure 5. In a typical leach, in the first step, one reactor was filled with distilled water, 10 kg $(NH_4)_2CO_3$ was added, the stirrer was turned on, and then 25 kg wet sludge, shredded to 1/2-in lumps, was added. Finally, 3.75 L NH_4HSO_3 solution and an additional 30 L H_2O were added to increase the volume of the mixture to about 85 L to cover the immersion heater to a safe level. The thermostatic controller was set at 55° C, and the mixture was allowed to digest for 1 h at temperature prior to filtering; 0.4 kg (0.5 pct of bulk) filter aids was added to the mixture and coated the filter paper with a thin layer, which ensured rapid filtering. The cake was thoroughly washed with distilled H_2O to remove any $(NH_4)_2SO_4$. The filtering process usually lasted about 1 h, including washing.

The filtrate, about 90 L in volume, containing $(NH_4)_2SO_4$ and excess $(NH_4)_2CO_3$, was recycled until the concentration of SO_4^{--} was too high to be effective.

The filter cake, containing mainly $PbCO_3$, was divided into two equal parts, and each was placed in a reactor and blended with 10 L H_2O to make a uniform slurry. The necessary amount of waste

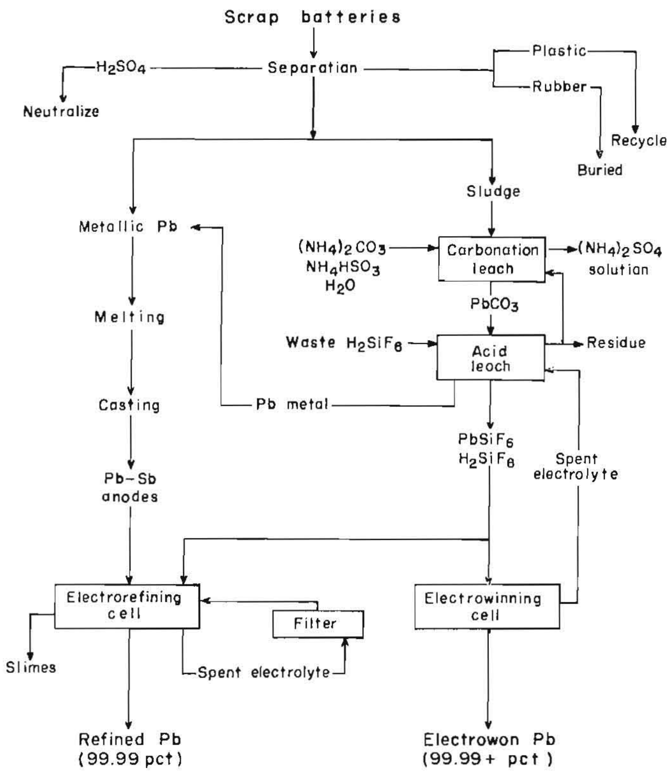

FIGURE 5. - Flow diagram for electrolytic recycling of scrap batteries.

H_2SiF_6 and/or spent electrolyte was added to each reactor to convert the $PbCO_3$ into $PbSiF_6$. Carbon dioxide foam formed immediately as the waste acid was added and was controlled by sprinkling 1 L defoaming agent into each reactor. The slurry was allowed to react with H_2SiF_6 at 45° C for 15 to 30 min before filtering. Again, 0.4 kg filter aids were used to coat the filter paper prior to filtering. The resulting leachates, normally containing 100 g/L lead as $PbSiF_6$ and 90 g/L free H_2SiF_6, with minor amounts of P, Sb, As, Sn and Cu, were suitable for use as electrolyte for electrowinning.

The first 10 leaching experiments were made using lead powder (200 mesh) to reduce PbO_2 during the second-stage acid leach. Later, it was found that NH_4HSO_3, when added to the first-stage carbonation leach, would successfully reduce PbO_2. Because of this change in procedure, a series of bench-scale tests was made to optimize parameters.

ELECTROLYTE

Electrolyte for electrorefining, in volumes of 25 L, was prepared initially from industrial-grade PbO (litharge) powder, technical-grade H_2SiF_6, and additives. Later, waste H_2SiF_6 and PbO were used for most of the electrorefining runs.

Animal glue and calcium lignin sulfonate (1) were the additives used as leveling agents and grain refiners for both electrorefining and electrowinning experiments. Aloes extract (0.5 g/L) was also used in several experiments to compare its performance to that of glue. The starting electrolyte contained 50 to 70 g/L Pb, 90 to 110 g/L free H_2SiF_6, 4.0 g/L calcium lignin sulfonate, and 0.05 g/L glue.

Electrorefining in the 20-L cell was conducted prior to sludge leaching; thus the sludge leachate was not available for electrorefining.

Electrolytes for electrowinning were obtained from leaching sludge. Spent electrolyte, usually low in lead and high in H_2SiF_6, was recycled repeatedly. Phosphorus levels in the electrowinning electrolyte were maintained at 1 to 2 g/L using 85 pct H_3PO_4.

ELECTROREFINING UNIT

The unit used for electrorefining is shown in figure 6. The molded polyethylene cell, 36 cm long by 25 cm wide by 25 cm deep, was used to electrorefine four 2.5-cm-thick impure anodes with three cathodes. The electrodes rested on two copper bus bars and were spaced with 3 cm between the surface of each anode and cathode. The cell was heated by a thermostatically controlled circulating water bath to maintain the electrolyte temperature between 30° and 40° C.

A constant current of about 20 A kept the current density at 170 to 180 A/m^2. The voltage varied from 0.3 to 1.0 V with

FIGURE 6. - Electrorefining unit. *A*, Anode wash tank; *B*, electrolyte storage tanks; *C*, auxiliary cell for monitoring polarization voltage; *D*, constant-temperature water bath; *E*, 20-L multielectrode cell.

variations in electrolyte temperature and as the slime blanket increased in thickness.

Electrolyte was circulated between electrodes by adding it to a trough along one side of the cell and drawing it out from the bottom of the cell at the other side. Electrolyte flowed into the cell through the evenly cut notches made on the trough wall to ensure equal distribution in the cell.

ELECTROWINNING UNIT

The electrowinning unit (fig. 7) consisted of a 20-L cell on a stand next to a 200-L cylindrical tank for storing electrolyte. The tank was equipped with a stirrer, an alumina-sheathed immersion

FIGURE 7. - Electrowinning unit. *A*, 20-L multielectrode cell; *B*, electrodes after a 5-day test; *C*, 200-L electrolyte tank.

heater (2-kW), and an acid-resistant pump. During electrolysis, electrolyte was pumped continuously into the cell bottom through a 2.5-cm PVC pipe from the tank and was allowed to overflow back into the tank through a 5-cm-diam opening on the upper side of the cell. The cell held three cathodes and four PbO_2-Ti anodes.

The parameters used for both electrorefining and electrowinning were similar to those used in the bench-scale studies (1).

The control system included a 40-V, 50-A dc power supply, a chart recorder, an ampere-hour meter, and a digital thermostatic controller for the immersion heater.

RESULTS AND DISCUSSION

METAL RECOVERY

Anode and Slime Blanket

The lead metal obtained from scrap batteries contained 2 to 2.5 pct antimony. Anodes cast from this metal usually produced firm and adherent slime blankets. Electrorefining was an ideal method for eliminating Sb, As, Cu, and Sn from the lead (3). The results of electrorefining in the 20-L cell for 4 to 7 days using anodes cast under various conditions indicate that the firmness of the slime blankets was closely related to the anode grain size. As shown in figure 8A, a large-grain structure resulted when anodes were cast in a heated (300° C) graphite mold, which was cooled slowly. The resulting slime blanket was coarse and loosely attached, which caused it to fall into the cell solution at the least disturbance. Figure 8C shows the fine-grain structure of an anode cast into an unheated steel mold (20° C). The lead melt solidified into numerous layers because of the rapid cooling. The resulting slime blankets were very firm but detached from the anode as their thickness increased with time. A firm and adherent slime blanket was obtained on anodes cast into a steel mold heated to 250° C, which was air-cooled to give a grain structure of approximately 1.30-cm diam (fig. 8B). The quality of the slime blanket was further improved by melting the lead metal at 480° C (1) and holding the melt at temperature for 2 h before pouring.

As in bench-scale electrorefining studies, too much phosphorus in the electrolyte caused poor anode dissolution and the formation of extra-thick slime blankets, which in turn increased the cell voltage and energy consumption. Figure 9 shows that the half-cell voltage increased from 0.36 to 0.59 V at a phosphorus content of 0.35 g/L, and from 0.34 to 1.4 V at a phosphorus content of 0.5 g/L at the end of 4.5 days of electrorefining in the 20-L cell.

Table 3 shows that the amount of slimes generated doubled as the phosphorus content in the electrolyte increased from ~0.5 to ~1.0 g/L, the percentage of antimony in the slimes decreased, while lead content increased regardless of the percentage of antimony present in the anodes. Therefore, it was necessary to eliminate phosphorus as much as possible from the electrolyte before using it for lead electrorefining.

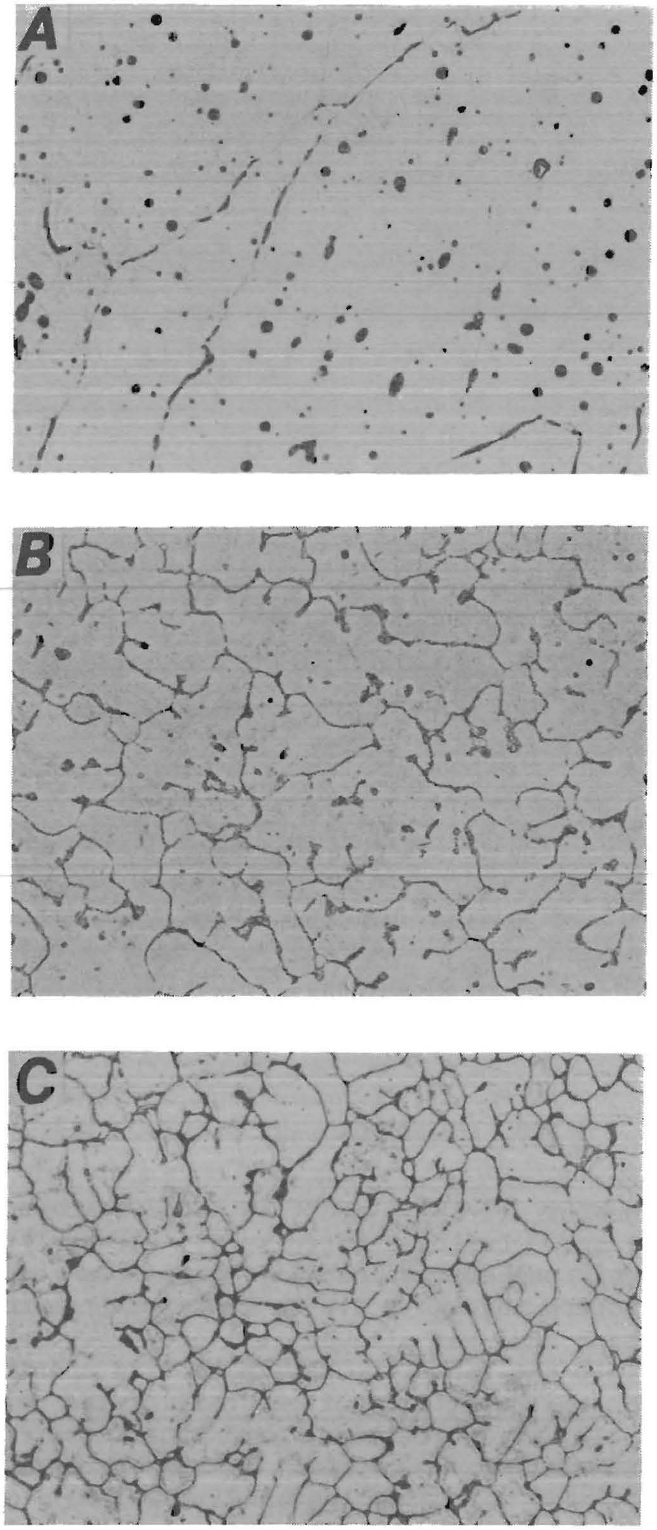

FIGURE 8. - Pb-Sb anodes at 100 X. *A*, Heated graphite mold, 300°C; *B*, heated steel mold, 250°C; *C*, unheated steel mold, 20° C.

TABLE 3. - Effect of phosphorus in electrolyte on formation of anode slimes

Run	Phosphorus in electrolyte, g/L	Slime to Pb deposit,[1] wt pct	Major elements in slime, pct		Sb in cast anode, pct
			Sb	Pb	
1...	0.29	3.03	73.3	11.1	2.0
2...	.49	3.65	61.6	13.6	2.4
3...	.67	4.65	56.9	13.7	2.4
4[2]..	.93	7.50	54.2	25.4	3.0
5[2]..	1.34	8.38	46.7	28.4	3.75

[1]Weight percent of anode slimes to Pb deposit on cathode.
[2]Bench-scale results.

Electrolyte made from PbO and technical-grade H_2SiF_6 contained about 0.35 g/L phosphorus, which was suitable for electrorefining. When phosphorus-containing waste H_2SiF_6 (table 2) was used to dissolve PbO, it was critical to use the stoichiometric amount of acid, so that most of the phosphate compounds were eliminated as a precipitate in the less acidic solution (1). The $PbSiF_6$ solution then obtained was rich in lead and low in H_2SiF_6 and was adjusted to the proper concentration of free acid by adding technical-grade H_2SiF_6.

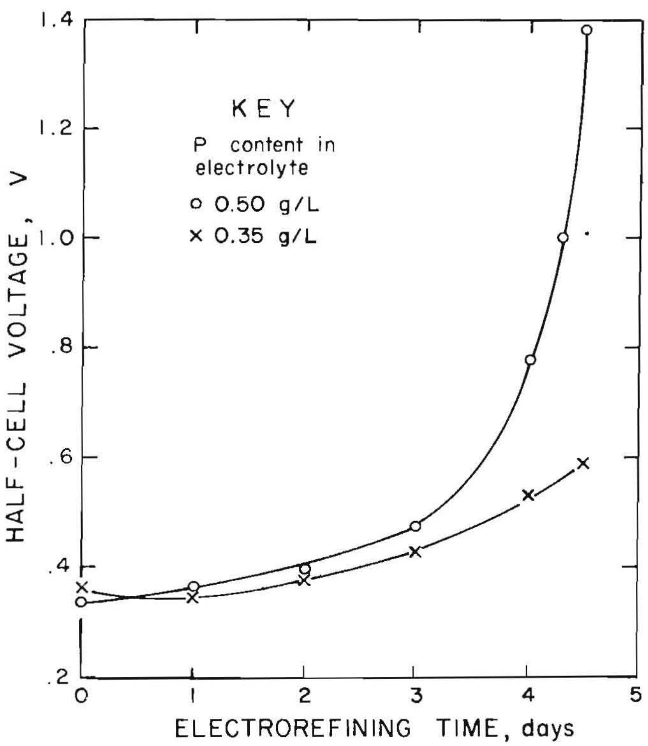

FIGURE 9. - Effect of phosphorus content in electrolyte on cell voltage with time.

The precipitate formed when PbO reacted with waste H_2SiF_6 contained mainly $Pb_5(Cl,F)(PO_4)_3$ and $PbSO_4$. The lead in the lead phosphate compound was recovered by leaching with concentrated H_2SiF_6, and the remaining $PbSO_4$ was then mixed with the battery sludge to recover the lead by the carbonation leaching process.

At the end of each experiment, the electrolyte had less lead and more free H_2SiF_6 because the increase in slime blanket thickness reduced the rate of anode dissolution. Used electrolyte, even contaminated with anode slimes, was filtered and adjusted to the proper concentration of lead, free H_2SiF_6, and additives and was used successfully in subsequent electrorefining experiments.

The lead concentration varying from 50 to 80 g/L had no significant effect on the process. As the free H_2SiF_6 level increased from 75 to 115 g/L, energy consumption decreased from 0.13 to 0.09 kW•h/kg of lead refined, while the current efficiency increased from 97.5 to 99.0 pct. Electrolyte containing high free H_2SiF_6 (~120 g/L) exhibited lower cell voltage, hence lower energy consumption, even when the phosphorus content was 0.6 g/L; however, the resulting cathode deposits, assaying 99.77 pct lead, were brittle and rough.

The antimony-rich slimes can be sold to smelters for producing Pb-Sb alloy in a blast furnace.

TABLE 4. - Partial analyses of final electrolyte and lead cathode deposits for selected runs

Run	Run time, days	Electrolyte, g/L			Analyses of refined Pb, pct					
		Pb	Free H_2SiF_6	P	Pb	Sb	As	Cu	Sn	P
18.......	6	80.4	99.4	0.29	[1]98.9	1.09	<0.005	<0.001	<0.005	<0.001
19.......	4	71.3	88.1	.29	[1]99.97	.028	<.001	.001	<.001	<.001
20.......	4	71.3	95.3	.29	99.99	.007	<.001	.0005	.0015	<.001
21.......	5	70.6	75.6	.49	99.95	.05	<.001	.001	<.001	.001
22.......	4	62.6	110.7	.35	99.99	.007	<.001	.002	<.001	.001
23.......	4	58.3	105.8	.67	99.98	.004	<.001	.001	<.001	.006
24.......	7	69.0	118.9	.57	99.83	.16	<.001	.01	<.001	<.001

[1]Electrolyte was contaminated by slimes at the end of run.

TABLE 5. - Results of electrorefining

Run	Run time, days	Temp, °C	Average voltage, V		Energy consumed, kW·h/kg		Current efficiency, pct	Remarks
			Cell	Total	Cell	Total		
18....	6	37	0.38	0.85	0.10	0.22	97.5	P = 0.29 g/L.
19....	4	37	.36	.77	.095	.206	97.85	P = 0.29 g/L.
20....	4	37	.42	.84	.11	.22	97.75	Low H_2SiF_6, P = 0.29 g/L.
21....	5	37	.50	.83	.13	.22	97.5	Low H_2SiF_6, P = 0.49 g/L.
22....	4	37	.31	.70	.08	.19	98.3	High H_2SiF_6, P = 0.35 g/L.
23....	4	40	.32	.745	.084	.195	98.9	High H_2SiF_6, P = 0.67 g/L.
24....	7	40	.40	.82	.150	.21	98.5	High H_2SiF_6, P = 0.57 g/L.

Cathodes

Electrorefined lead deposits assaying 99.99 pct Pb (table 4) were obtained in the 4-day runs, at a current density of 170 A/m^2, and a temperature of 35° to 40° C, using electrolyte containing 60 to 80 g/L Pb, 90 to ~115 g/L free H_2SiF_6, and less than 0.35 g/L P, along with 4 g/L calcium lignin sulfonate, and 0.04 g/L glue as additives.

The purity of the lead deposits was reduced to less than 99.9 pct when the phosphorus content was greater than 0.5 g/L or in runs longer than 4 days, especially when the electrolyte was contaminated by antimony from the slimes. Then the lead deposits contained 0.03 to 1.1 pct Sb, depending on the degree of slime contamination. Longer electrorefining time also resulted in higher energy consumption and lower current efficiency (table 5).

SLUDGE RECOVERY

Leaching

Fourteen sludge leaching experiments were completed. Lead metal was recovered from the $PbSiF_6$ solution by electrowinning. Each leaching operation produced about 200 L of leachate, containing sufficient amounts of lead and free H_2SiF_6 to support a 3- to 7-day continuous electrowinning test in the 20-L cell.

The wet sludge from scrap batteries consisted of 40 pct $PbSO_4$, 28 pct PbO_2, 2 pct metallic Pb, and 15.6 pct H_2O as received. Initially, sludge was leached with $(NH_4)_2CO_3$ solution to convert $PbSO_4$ into $PbCO_3$, which is soluble in H_2SiF_6. After solid-liquid separation, the residue containing $PbCO_3$ and the unreacted PbO_2 was leached with H_2SiF_6 and lead powder (200 mesh). The lead powder was added to reduce the PbO_2 to acid soluble PbO, as in reaction A.

$$PbO_2 + Pb \rightarrow 2PbO. \qquad (A)$$

Later the procedure was modified to use NH_4HSO_3 in place of the lead powder. The NH_4HSO_3 was added during the first leach along with the $(NH_4)_2CO_3$, and the PbO_2 was converted to $PbSO_4$ and then to $PbCO_3$. Additional $(NH_4)_2CO_3$ was added to handle the $PbSO_4$ from the PbO_2 and NH_4HSO_3 reaction. The residue from the first leach now consisted mainly of $PbCO_3$, which was solubilized by H_2SiF_6 in the second leach. The two-step leaching procedure can be described by the following reactions:

Step 1:

$$PbSO_4 + (NH_4)_2CO_3 \rightarrow PbCO_3\downarrow + (NH_4)_2SO_4. \qquad (B)$$

$$PbO_2 + NH_4HSO_3 + (NH_4)_2CO_3 \rightarrow PbCO_3\downarrow + (NH_4)_2SO_4 + NH_4OH \qquad (C)$$

Step 2:

$$PbCO_3 + H_2SiF_6 \rightarrow PbSiF_6 + CO_2. \qquad (D)$$

The cost of using NH_4HSO_3 for PbO_2 reduction was approximately one-third that of using lead powder.

The best leaching parameters for maximum lead recovery from bench-scale tests were found to be (1) a mole ratio, in the sludge, of 1:2 $Pb:(NH_4)_2CO_3$ and 1:1 $PbO_2:NH_4HSO_3$, (2) a digestion temperature and time of 55° C for 60 min for carbonation and of 45° C for 30 min for the acid leach, and (3) 250 to 400 g sludge per liter of water.

The first large-scale acid leach was conducted with waste H_2SiF_6 (A-1) only. In subsequent leach tests, recycled spent electrolyte was used with the waste H_2SiF_6 as makeup. Waste A-2 was used for runs 2 through 12; A-3 was used beginning with run A-13. If required, phosphoric acid was added. In the beginning, because the spent electrolyte contained organic additives which formed very stable CO_2 foam when used to acid leach $PbCO_3$, it was necessary to add the waste H_2SiF_6 first to reduce the problem of foaming. Later, foaming was controlled by spraying with defoaming agent (DB-110A, Dow-Corning).

Both the waste H_2SiF_6 and the spent electrolyte contained some phosphate compounds. After the acid leach, the final sludge residue contained an insoluble lead phosphate compound $Pb_5(Cl,F)(PO_4)_3$ (pyromorphite) and $PbSO_4$, and was very difficult to filter. The residue also contained minor amounts of Sb, As, and Sn and comprised about 25 wt pct of the wet

TABLE 6. - Analyses of final sludge residue after H_2SiF_6 leach

Run	Wt of sludge, kg	Wt of residue, kg	Free H_2SiF_6[1] g/L	Composition of residue, pct: Pb	P	Sb	As	Sn	Cu	SO_4	Si	Ca
1......	33.3	4.35	125.2	58.0	1.40	0.26	0.08	<0.10	<0.01	[2]8.67	NA	NA
2......	33.3	5.3	86.4	44.9	NA	.32	<.03	<.05	.03	[2]10.02	NA	NA
6......	33.3	8.05	83.5	41.5	1.91	.25	.32	<.10	<.01	.80	11.0	NA
10.....	22.2	5.18	78.2	29.7	.51	.40	.09	.24	NA	.60	NA	NA
11.....	20	4.37	111.0	25.6	.29	.29	.05	<.1	<.01	NA	NA	0.36
12.....	25	4.39	102.0	27.9	.61	.25	.10	.19	NA	NA	13.7	NA
14.....	25	5.37	[3]50.6 [4]82.6	38.2	2.33	.31	.12	.17	NA	[2]4.13	NA	NA

NA Not analyzed.

[1]Concentration of free H_2SiF_6 in leachates.

[2]The high values of SO_4 in residues 1, 2, and 14 were due to poor washing of the $PbCO_3$ filter cake.

[3]1st-batch acid leachate.

[4]2d-batch acid leachate.

sludge. (See table 6.) Adding 0.5 pct (bulk weight of the slurry) of filter aid to the slurry prior to filtering and coating the filter paper in the pan with a 0.3-cm-thick layer of filter aid decreased the filtering time from 6 h or more to about 1 h.

The percentage of the lead recovered was determined from the amount of lead in the $PbSiF_6$ leachate and in the final sludge residue. Similar to the results of bench-scale leaching, the lead recovery from large-scale leaching ranged from 88 to 95 pct.

The analyses of the final leachates are shown in table 7. Since $PbSiF_6$ is very soluble in H_2SiF_6, the concentration of lead ranged from 80 to 140 g/L and the free H_2SiF_6 ranged from 50 to 125 g/L in the sludge leachates; all ranges were proportional to the amount of the input. The concentration of phosphorus depended not only on the amount of input but more so on the concentration of free acid in the leachates. The amount of phosphorus recovered from the waste acid and spent electrolyte after sludge leaching decreased from ~90 to 40 pct as the concentration of the free H_2SiF_6 decreased from over 100 to 70 g/L. To obtain $PbSiF_6$ electrolyte with high lead and low free H_2SiF_6 concentration and also to recover phosphorus efficiently, a two-stage acid leach procedure was employed for leaching runs 7, 11, and 14. As the reaction of the first acid leach was completed, the agitation was stopped, allowing the sludge residue to settle for about 30 min. Then the $PbSiF_6$ solution was siphoned out for filtering. More spent electrolyte, which was high in free H_2SiF_6, was added to dissolve additional amounts of lead phosphate compounds from the residue. As indicated in table 7, the second batch of leachates contained higher concentrations of phosphorus and free H_2SiF_6 than the first batches.

TABLE 7. - Analyses of leachates

Run	Volume, L	Composition of leachates, g/L							Pb recovery, pct
		Pb	Free H_2SiF_6	P	Sb	As	Sn	Cu	
1	200	95.8	125.2	2.3	0.40	0.072	0.026	0.004	88.5
2	180	129.5	86.4	.76	.44	.080	.030	<.001	91
3	208	117.9	92.9	1.01	.47	.072	.034	.001	90.5
4	159	150.4	100.8	1.51	.65	.089	.040	.008	88.0
5	228.5	125.1	83.7	.87	.70	.07	.03	.002	91.3
6	228	122.2	83.5	.79	.72	.05	.023	.001	89.3
7	[1]208	112.7	91.7	1.86	.81	.044	.026	.002	92.0
	[2]45	64.0	107.0	1.86	.81	.048	.026	.002	
8	220	106.7	94.3	1.01	.68	.030	.030	<.001	91.5
9	186	104	75.4	.77	.50	.035	ND	.001	89.2
10	207	113.5	78.2	1.04	.68	.038	.042	<.001	91.6
11	[1]220	82.9	109.2	1.04	.69	.044	.032	.003	95.0
	[2]40	71.3	113.3	1.13	.69	.044	.032	.006	
12	231.5	89.7	102.2	.80	.57	.046	.041	.004	94.5
13	201	108.6	96.0	.80	.58	.037	.046	.004	ND
14	[1]96	138.8	50.6	.28	.58	.023	.011	.005	91.8
	[2]88	106.3	82.6	.63	.65	.040	.299	.004	

ND Not detected. [1]1st-batch acid leach. [2]2d-batch acid leach.

Lead sulfate was found in the residue when (1) fresh waste H_2SiF_6 containing H_2SO_4 was used to acid-leach the $PbCO_3$ sludge, (2) the conversion of $PbSO_4$ to $PbCO_3$ was not complete, or (3) the $PbCO_3$ sludge filter cake was not thoroughly washed to remove all of the $(NH_4)_2SO_4$ residue.

Lead phosphate compound was formed and remained in the sludge residue when using recycled spent electrolyte containing PO_4^{3-} to acid-leach the $PbCO_3$ sludge at lower H_2SiF_6 levels. Lead and phosphorus in the sludge residues can be recovered by releaching with $(NH_4)_2CO_3$ and then with more concentrated H_2SiF_6.

Ammonium sulfate solution is the byproduct of the first step leach. The dilute $(NH_4)_2SO_4$ solution from run 11 was recycled to leach the next batch of battery sludge with additional $(NH_4)_2CO_3$. The recycling of $(NH_4)_2SO_4$ solution continued until run 14, as listed in table 8. The $(NH_4)_2SO_4$ solutions increased in concentration from 43.5 g/L SO_4^{2-} for the first leach to 224 g/L SO_4^{2-} for the third. The lead and arsenic content in the solutions also increased from 3 to 56 ppm and 4 to 19 ppm, respectively.

TABLE 8. - Analyses of $(NH_4)_2SO_4$ solutions

Run	Volume, L	Analysis of $(NH_4)SO_4$ leachates, g/L				
		NH_4	SO_4	CO_3	Pb	As
5[1]..	170	14.6	34.8	NA	0.006	0.004
8[1]..	170	13.8	33.7	NA	.003	.004
10[1].	87	15.4	38.7	NA	.003	.004
11[2].	100	22.6	43.5	NA	.013	.007
12[2].	99	35.5	81.7	14.3	.012	.011
13..	92	53.3	114.0	2.0	.020	.019
14[3].	93	84.5	224.0	61.0	.056	.012

NA Not analyzed.

[1]In runs 5-10 only $PbSO_4$ in the sludge was converted to $(NH_4)_2SO_4$ because Pb powder was used to reduce PbO_2.

[2]In runs 11-12 both $PbSO_4$ and PbO_2 were converted to $(NH_4)_2SO_4$ because HN_4HSO_3 was used to reduce PbO_2.

[3]In run 14, 14.7 kg of $(NH_4)_2CO_3$ was added to the recycled $(NH_4)_2SO_4$ solution as compared to only 7.5 kg added previously.

Electrowinning

Seventeen electrowinning experiments were performed in the 20-L cell, the operating data are given in table 9.

The lead metal deposits recovered from all the sludge leachates were assayed and found to contain 99.995 to 99.999 pct Pb with trace amounts of Sb, As, Cu, Sn, and P (table 10). Among the impurities, copper was the only element in the electrolyte that codeposited with lead on the cathodes, as indicated by the <0.001 g/L Cu in all depleted electrolytes.

The cathode deposits, during electrowinning tests, usually were smooth for the first 3 days, then became rough or granular as the electrolyte decreased in lead content below 25 g/L and increased in free H_2SiF_6 content above ~125 g/L. The current density was 170 A/m^2, and the electrolyte temperature was 30° C. The morphology of the lead cathode deposits was also adversely affected by increasing the current density to 300 A/m^2.

A 4-day bench-scale test was made to see if it would be possible to maintain a fairly constant lead concentration in the electrolyte with time. The test was conducted in a 1-L cell at room temperature (20° to 25° C) and 200 A/m^2 current density. The lead concentration in the electrolyte was maintained at 140 to 150 g/L during the 4-day run by periodically adding a very concentrated stock solution. The composition of the stock solution and the cell electrolyte during the run are given in table 11.

TABLE 9. - Operating data for lead electrowinning

Run[1]	Composition of electrolyte, g/L							C.D.,[2] A/m^3	Temp, °C	Run time, h	C.E.,[3] pct	Energy consumed, kW·h/kg	PbO_2 to Pb deposit,[4] wt pct
	Pb	Free H_2SiF_6	P	As	Cu	Sb	Sn						
1B..	69.2	91.4	1.8	0.045	0.003	0.287	0.026	170	30	93	95.4	0.69	ND
1A..	30.7	117.8	1.8	NA	NA	NA	NA						
2B..	109.8	106.1	2.37	.067	<.001	.370	NA	170	30	168	95.6	.677	ND
2A..	40.8	152	2.8	NA	NA	NA	NA						
3B..	96.1	99.4	1.76	.055	.001	.500	.034	170	30	172	95.6	.706	1.56
3A..	23.2	148.6	1.65	NA	NA	NA	NA						
4B..	100.1	77.2	1.26	.061	.003	.450	.030	170	30	140	96.5	.74	1.63
4A..	32.7	126.8	.81	.07	<.001	.43	.03						
5B..	110	75	2.16	.063	.002	.72	.03	170	30	172	96.5	[5].78	.85
5A..	23.3	134	2.16	.063	<.001	.72	.03						
6B..	108.3	86.7	2.58	.041	<.001	.667	.017	170	30	121.7	97.06	.73	.83
6A..	53.0	121.7	1.86	.041	<.001	.667	.018						
7B..	54.4	118.8	2.17	.041	<.001	.667	.018	170	30	48	97.3	.73	.63
7A..	33.7	130.8	NA	.044	<.001	.714	.017						
8B..	105.7	90.0	1.30	.037	.002	.682	.032	220	29	76	97.8	.74	.83
8A..	61.3	117.8	1.51	.036	<.001	.636	.032	250					
9B..	61.3	117.8	1.51	.036	<.001	.636	.032	300	36	23.5	98.05	.82	.65
9A..	43.9	130.8	1.54	.036	<.001	.682	.032						
10B.	103.2	93.8	1.41	.037	<.001	.640	.033	300	36.5	72	98.6	0.735	0.93
10A.	51.2	129.4	1.39	.035	<.001	.640	.033						
11B.	114.8	95.5	1.53	.061	.003	.600	.036	277	36	73	98.3	.74	.90
11A.	65.06	152.2	1.61	.061	.001	.680	.036						
12B.	99.5	83.4	.76	.037	.001	.480	.057	300	45	72	98.3	.757	2.0
12A.	44.8	119.5	.84	.036	<.001	.520	.078						
13B.	106.9	91.9	1.22	.051	<.001	.708	.050	300	35.8	48	[6]93.0	.81	1.21
13A.	52.4	128.2	1.19	.050	<.001	.708	.050						
14B.	87.8	101.0	1.32	.050	.003	.621	.032	200	25	30.5	96.6	.723	ND
14A.	36.7	136.6	1.40	.048	<.001	.708	.050		40				
15B.	50.1	135.1	1.66	.038	<.001	.706	.031	172	40	28	96	.7013	.78
15A.	38.1	145.1	1.67	NA	NA	NA	NA						
17B.	103.3	98.6	1.37	.038	.004	.676	.038	187	30	72	97	.708	.96
17A.	68.8	119.3	1.33	NA	NA	NA	NA						

NA Not analyzed. ND Not determined.

[1]B = before electrowinning; A = after electrowinning.

[2]C.D. = current density.

[3]C.E. = current efficiency.

[4]Weight pct of PbO_2 formed on anodes to lead deposits on cathodes.

[5]Aloes were used in place of glue as additive.

[6]The cell was shorted near the end of test.

TABLE 10. - Electrowon lead cathodes

Run[1]	Analyses, pct						Run time, h	Cathode wt, kg	Remarks
	Pb	As	Cu	Sb	Sn	P			
1......	99.995	0.0009	0.0024	<0.0001	0.0001	0.001	93	8.076	Very good.
2......	99.997	.0009	.0007	.0008	<.0001	<.001	168	15.093	Rough.
3......	99.997	.0002	.001	.0004	<.0001	<.001	172	15.304	Do.
4......	99.997	.0006	.0015	.0001	<.0001	<.001	140	14.354	Smooth.
5......	99.998	.0001	.0004	.0001	<.0001	<.001	172	18.229	Do.
6......	99.998	<.0001	.0005	.0002	.0001	<.001	121.7	11.270	Excellent.
7......	99.996	<.0001	.0005	.0003	.0001	<.001	48	4.528	Rough.
8......	99.998	<.0001	.0005	.0004	.0001	<.001	76	9.741	Good.
9......	99.9978	<.0001	.0005	.0005	.0001	<.001	23.5	3.694	Very rough.
10.....	99.999	.0001	.0003	.0004	.0001	<.001	72	11.164	Rough.
11.....	99.997	<.0001	.0020	.0006	<.0001	<.001	73	10.478	Good.
12.....	99.997	<.0001	.0010	.0005	.0001	<.001	72	11.252	Very rough.
14.....	99.997	.0010	.003	.0003	.0004	.001	30.5	3.252	Do.
15.....	99.996	.0005	.0015	.0005	.0002	<.001	28	2.670	Rough.
17.....	99.996	.0004	.0032	.0005	.0003	<.001	72	7.015	Smooth.

[1]In runs 13 and 16, the cell was shorted near the end of test.

TABLE 11. - Composition of electrolyte with time

Electrolyte (E)	Composition, g/L		
	Pb	Free H_2SiF_6	P
Stock solution....	193.6	64.6	0.35
E_0--initial.......	149.6	80.4	1.50
E_1--1 day.........	149.2	89.0	1.07
E_2--2 days........	146.3	92.9	1.28
E_3--3 days........	141.5	100.3	1.03
E_4--4 days........	144.2	109.2	1.27

The starting electrolyte contained 3 g/L calcium lignin sulfonate and 0.05 g/L glue. Small amounts of glue and H_3PO_4 were added daily. The resulting cathode deposit was excellent in appearance. The current efficiency was 98.5 pct, and the total energy consumption was 0.735 kW•h/kg of electrowon Pb, which was very reasonable for this low cell temperature (20° to 25° C).

In another 20-L test, the use of 0.5 g/L aloes in place of 0.05 g/L glue as additive improved the morphology of the deposits but also increased the cell voltage and energy consumption.

The cathode current efficiencies increased slightly with increasing current density and flow rate of the electrolyte and ranged from 95 to 98.6 pct, similar to the results of bench-scale tests.

Energy consumption in the 20-L cell using 4.5-cm electrode spacing was 0.7 to 0.8 kW•h/kg of electrowon lead, slightly higher than the 0.66 to 0.7 kW•h/kg for the bench-scale tests using a 3.5-cm spacing.

In an attempt to decrease energy consumption, several electrowinning tests were conducted with the electrode spacing reduced from 4.5 to 3 cm. The reduced spacing resulted in uneven lead deposits on the three cathodes and increased the risk of shorting; the effect on energy consumption was insignificant.

As shown in figure 10, two types of PbO_2-Ti anodes were used in the electrowinning tests. The anodes with the smaller holes (0.9 cm in diam) spaced 1 cm apart were very stable and still in perfect condition after repeated use in eight consecutive tests. The anodes with the larger holes (1.3 cm in diam) spaced 1.3 cm apart tended to develop cracks in the PbO_2 coating after repeated use.

A thin layer of PbO_2 was formed on the anodes during each run. The newly formed

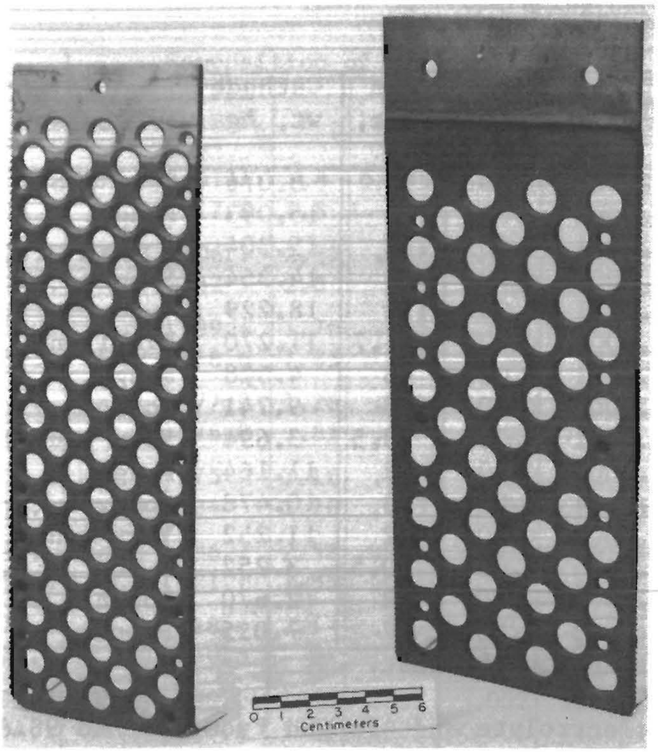

FIGURE 10. - Two types of PbO_2-Ti anodes.

PbO_2 layer was firmly attached to the anodes, did not pollute the cell solution, and was easy to clean after each test. The amount of PbO_2 formed was limited to less than 1 pct of the total weight of the cathode deposits, as long as the phosphorus level in the electrolyte was maintained at greater than 1.2 g/L (table 10). The PbO_2 collected from the anodes was leached with the battery sludge to recover lead as $PbSiF_6$ in the leachates.

The chemical analysis of the PbO_2 layer (bulk) and the Auger electron spectroscopy analysis of the surface of the PbO_2 formed on the anodes during electrowinning are given in table 12.

The bulk PbO_2 layer contained 2.78 pct P, compared with 10.6 pct P on the PbO_2 surface. The mechanism by which phosphorus inhibits excessive PbO_2 formation during lead electrowinning has not been determined.

LEAD MONITORING

The results of lead monitoring during anode casting, sludge leaching (with and without Pb powder), and electrowinning are listed in table 13.

Filters from the personal monitors were pinned to the lapels of the employees, as close to their breathing zones as possible. The reactor monitors were suspended 1 m above and directly over the melting pot, leaching tank, and electrolysis cell. For lead melting, the lead fume was drawn to a baghouse by a cone-shaped duct placed 2/3 m above the pot. The room monitors were approximately 5 to 7 m from the work area. Airborne lead was considerably less when NH_4HSO_3 was used to reduce PbO_2 instead of minus 200-mesh lead powder.

Following 10 sludge leaching operations, the blood lead tests of employees 1 and 2 were normal at 17 and 15 μg/100 mL, respectively.

TABLE 12. - Analyses of PbO_2 layer formed on anodes

PbO_2 sample[1]	Method of analysis	Unit	PbO_2 layer					
			Pb	O	P	As	F	Sb
W/P...........	Chemical...........	wt pct....	72.5	17.2	2.78	0.32	0.10	0.07
W/P...........	Auger..............	at. pct...	29	43	26.5	.05	1.0	NA
		wt pct....	78.9	9	10.6	.5	.25	NA
W/O P.........	Auger..............	at. pct...	60	35	0	4.0	1.0	NA
		wt pct....	93.4	4.2	0	2.25	.14	NA

NA Not analyzed.
[1]W/P = PbO_2 formed on anodes in electrolyte with phosphorus of 2.0 g/L. W/O P = PbO_2 formed in electrolyte without phosphorus.

TABLE 13. - Results of monitoring for airborne lead

Monitor	Pb, µg/m³ of air[1]				
	Anode casting	Sludge leaching			Electrowinning
		Carbonation	PbO_2 reduction		
			With Pb powder	With NH_4HSO_3	
Employee 1........	<5	10.8	[2]328	6.7	NM
Employee 2........	5	6.1	30	8.3	NM
Reactor..........	<5	6.3	11	7.5	<2
Room.............	<5	1.9	1.3	1.7	<1

NM Not monitored.
[1]The proposed industry standard is 50 µg/m³.
[2]Employee wore a dust mask when handling the 200-mesh Pb powder.

ECONOMIC EVALUATION

Based on the data from bench-scale tests, a preliminary economic evaluation (4) of the process was performed by the Process Evaluation Staff of the Bureau of Mines.

The evaluation was based on a plant designed to process 10,000 batteries per day and recover about 100 tpd of lead. This scale is equivalent to the capacity of a large secondary smelter. The plant is divided into five sections as shown by the flowsheet in figure 11: feed preparation, anode casting, leaching, electrolysis, and ammonia recovery. The evaluation was based on the flowsheet, except that lead powder was used in sludge leaching to reduce PbO_2 during the acid leach, which was more costly than using NH_4HSO_3.

The capital cost was a "study estimate" used by Weaver and Bauman (6). Since the treatment of slag and anode slimes was not complete, the accuracy of the cost estimate may not be within the assumed ±30 pct. Capital cost was $21 million, and the operating cost per kilogram of lead recovered was 35.2 cents (16.0 cents per lb), excluding the cost of scrap batteries.

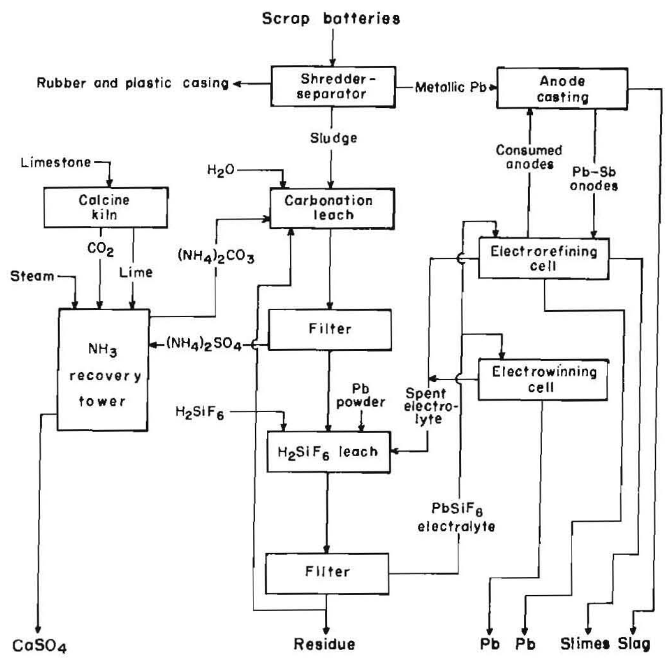

FIGURE 11. - Proposed plant design and process to recover 100 tpd of lead.

CONCLUSIONS

High-purity lead was recovered from scrap batteries by electrorefining lead metal and by leaching-electrowinning lead from sludge.

This recycling process minimizes environmental and health impacts, as shown by the results of lead-in-air and lead-in-blood monitoring. The working environment may be further improved when the leaching process is automated and operated in a closed system to avoid the escape of NH_3 gas and recover CO_2 for recycling as $(NH_4)_2CO_3$.

In the leaching process, using NH_4HSO_3 to reduce PbO_2 in place of the 200-mesh lead powder was more cost effective and resulted in lower emissions.

Similar to the bench-scale results, the current efficiencies were 97 to 99 pct for both electrorefining and electrowinning under a wide range of parameters. The total lead recovery for this process was approximately 92 pct.

Maximum energy consumption, based on the cell voltage, was 90 and 800 kW•h per metric ton of lead electrorefined and electrowon, respectively. Care must be taken to reduce the electrical transmission loss from the power supply to the cell, which could be as high as 110 kW•h per metric ton of lead deposit in this electrolysis system.

The byproduct of the sludge leaching is ammonium sulfate solution, which can be used as fertilizer or recycled to recover NH_4OH.

The spent electrolyte was repeatedly recycled to leach more sludge without any impurity buildup.

Because of the discovery that small amounts of phosphorus in the electrolyte will prevent PbO_2 formation at anodes, lead electrowinning could become a viable commercial process.

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