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# **Electrolytic Method for Recovery of Lead From Scrap Batteries**

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## CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Acknowledgments.....	3
Materials, equipment, and procedures.....	4
Battery scrap.....	4
Electrodes.....	4
Electrolyte.....	4
Cells.....	6
Operating the electrolytic cell.....	7
Results and discussion.....	8
Electrorefining.....	8
Battery scrap.....	8
Operating parameters.....	8
Electrolyte composition.....	8
Additive concentration.....	9
Current density, electrolyte temperature, and electrode spacing.....	10
Cycle time.....	10
Slime blanket.....	10
Phosphorus content.....	11
Characterization of slimes.....	12
Energy consumption.....	13
Electrowinning.....	14
Battery sludge.....	14
Sludge leaching.....	14
Operating parameters.....	15
Anodes.....	16
Cathode quality.....	17
Energy consumption.....	18
Conclusions.....	18
References.....	19

## ILLUSTRATIONS

1. Depiction of combination electrorefining and electrowinning method for recovering and recycling lead from scrap batteries.....	3
2. Anodes used for electrorefining and electrowinning.....	5
3. Battery sludge leaching and electrowinning flow diagram.....	7
4. Effect of phosphorus concentration on PbO <sub>2</sub> formation.....	16

## TABLES

1. Average composition of battery waste material.....	4
2. Typical analysis of waste H <sub>2</sub> SiF <sub>6</sub> .....	6
3. Conditions for electrorefining anodes made from the metallic lead recovered from scrap batteries.....	8
4. Description of bone gelatin used as leveling agent.....	9

## TABLES--Continued

	<u>Page</u>
5. Variation in typical composition of anode slimes after electrorefining in electrolyte prepared from reagent-grade and waste $H_2SiF_6$ .....	11
6. Change in composition of waste acid electrolyte with time.....	11
7. Composition of electrorefined lead.....	12
8. Solubility of the slimes in 10-pct solutions using various reagents, and chemical analysis of the solutions used for the solubility determinations.....	12
9. Theoretical composition of anode slimes produced in waste acid electrolyte.....	13
10. Change in composition of recycled electrolyte.....	17
11. Chemical analysis of electrowon lead.....	17

# ELECTROLYTIC METHOD FOR RECOVERY OF LEAD FROM SCRAP BATTERIES

by

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## ABSTRACT

Bench-scale research at the Bureau of Mines has resulted in the successful development of a combination electrorefining-electrowinning method for recycling all the lead in scrap batteries. The method reduces energy consumption and eliminates toxic emissions, in contrast to present pyrometallurgical smelting, and the lead produced is pure enough for use in maintenance-free batteries.

Anodes cast from molten lead scrap were electrorefined in 1- and 2-liter plastic cells using an electrolyte composition of 70 g/l Pb and 90 g/l free  $H_2SiF_6$  (fluosilicic acid). Both reagent-grade and waste  $H_2SiF_6$  were used. Cathode starting sheets were made from refined lead. Aloes, and later bone gelatin, and calcium lignin sulfonate addition agents were employed.

The sludge remaining after separation of the lead metal was treated in a two-step leaching operation to solubilize the lead for recovery by electrowinning. Conditions for electrowinning were essentially the same as for electrorefining, except that insoluble  $PbO_2$ -Ti (lead dioxide-coated titanium) anodes were used.

The best results for both electrorefining and electrowinning were obtained with a current density of 170 amp/m<sup>2</sup> and a cell temperature of 25° to 35° C. Cathode purity ranged from about 99.9 to 99.99+ pct Pb. Maximum energy consumption after 3 days, for electrorefining and electrowinning, was 90 and 700 kwhr per metric ton of refined lead, respectively.

## INTRODUCTION

One objective of the Bureau of Mines is the secondary recovery of metals, minerals, and other values from waste products and the development of uses for them. In line with this objective, research was initiated to develop an environmentally acceptable alternative to the pyrometallurgical processes

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currently used by the secondary lead industry. These processes produce 45 pct of this country's needs. The majority of the metal supplied to secondary lead smelters is in the form of scrap lead-acid batteries. The lead metal and the sludge are separated from the case and the electrolyte and are smelted at high temperatures in a reverberatory or blast furnace (8).<sup>3</sup> Emissions of lead and sulfur oxide fumes during pyrometallurgical smelting are very difficult to control, making it virtually impossible for the industry to meet the emission standards recently promulgated by the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA) (2, 12). Officials from industry and EPA estimate that strict enforcement of the new standards will result in the closing of more than 90 pct of the secondary lead smelters in the United States (9).

The smelters have an additional burden to produce a product that is purer than ever before for use in the new maintenance-free (MF) batteries (11).

Work at the Bureau of Mines Rolla Research Center has resulted in the development of a nonpolluting and energy-efficient method for recycling all the lead in scrap batteries (fig. 1). The lead metal, separated by screening, is melted and cast into anodes for electrorefining using a modified Betts process. Electrorefining is based on the principle that impurities in the anode will be trapped and held in a slime blanket on the surface of the anode as it dissolves. Antimony and bismuth, either singularly or in combination, are the two principal elements that promote slime blanket adherence. Previous work has shown (7) that as little as 1 pct Sb is sufficient to form an adherent slime blanket on lead anodes. Thus, anodes made from scrap battery grid metal containing several percent antimony should be particularly suited to electrorefining.

The problem heretofore has been how to recover the lead from the battery sludge, which consists of roughly 60 pct  $\text{PbSO}_4$ , 21 pct Pb, and 19 pct  $\text{PbO}_2$ . In the method developed at Rolla, the sludge is treated in a two-step leaching operation to produce  $(\text{NH}_4)_2\text{SO}_4$  (ammonium sulfate) for fertilizer and  $\text{PbSiF}_6$  (lead fluosilicate) solution, from which the lead is recovered by electrowinning.

Excessive  $\text{PbO}_2$  formation at the anode is the main reason lead is not being recovered by electrowinning in a commercial process at the present time. A major breakthrough was made in this research with the discovery that  $\text{PbO}_2$  formation is prevented by the presence of small amounts of phosphorus in the electrolyte.

Bench-scale work has been successfully completed, and anodes made from scrap battery lead metal are presently being electrorefined in a 20-liter multielectrode cell in a process research unit (PRU) that was constructed to investigate the electrorefining of Missouri low-antimony lead bullion (7). At completion of the electrorefining tests, the PRU will be used to investigate electrowinning. The information obtained in these larger scale tests will be

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<sup>3</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

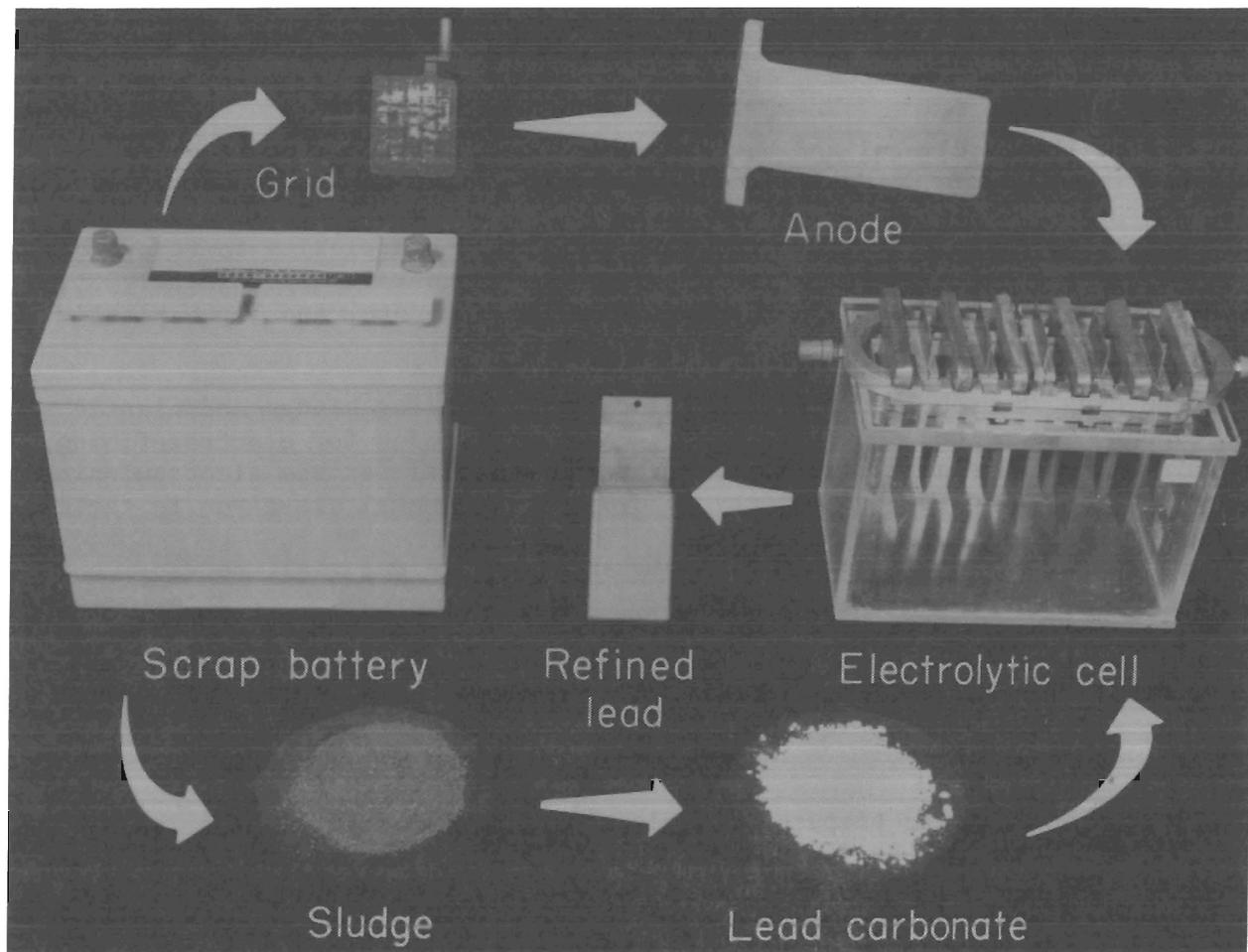


FIGURE 1. - Depiction of combination electrorefining (top path) and electrowinning (bottom path) method for recovering and recycling lead from scrap batteries.

used to further study the electrorefining-electrowinning method for recovering lead from scrap batteries and to complete an economic evaluation.

#### ACKNOWLEDGMENTS

Thanks are due to Cominco, Ltd., Trail, British Columbia, Canada; RSR Corp., Dallas, Tex.; and Peter Cooper Corp., Oak Creek, Wis., for furnishing materials used in this investigation.

The helpful suggestions on lead electrorefining by Cliff Krauss, Development Superintendent, Plant Control, and Bob Kerby, Research Metallurgist, both with Cominco, Ltd., 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. The material was typical of that charged to their reverberatory furnaces. After washing to remove adhering sludge, screening through a 28-mesh screen, and handpicking to remove the plastic and rubber, a 40-pound sample was found to contain approximately 86 pct Pb (mostly grid metal), 9 pct sulfate-oxide sludge, and 5 pct plastic and rubber.

The plus 28-mesh lead fraction, along with adhering sludge and plastic and rubber, was melted and subsequently cast into anodes for electrorefining. The minus 28-mesh sludge fraction was the raw material for the electrowinning operation. Analyses of the battery sludge and lead metal are given in table 1.

TABLE 1. - Average composition of battery waste material, percent

Material	Pb	Ag	As	Bi	Ca	Cu	Fe	Mg	Ni	Sb	Sn	SO <sub>4</sub>
Sludge.....	68.9	0.01	0.04	0.02	0.04	<0.01	0.12	<0.01	0.01	0.45	<0.01	15.1
Lead metal....	85.4	.01	1.6	.03	.07	.03	.04	.03	.01	4.5	.17	9.6

Electrodes

Impure anodes were prepared for electrorefining by melting the lead-antimony metal at 425° to 450° C and pouring into a carbon mold. A ZnCl<sub>2</sub>-NaCl flux was used as a cover on the molten bath to prevent oxidation and subsequent loss of antimony to the dross, as the melt was skimmed prior to casting the anodes. Each anode weighed about 700 to 800 grams, was 1.0 cm thick by 4 cm wide by 12 cm high, and had a 1.5- by 10-cm integrally cast bus bar, making a T-shape (fig. 2) (7). The total working area was approximately 56 cm<sup>2</sup>.

Patented insoluble PbO<sub>2</sub>-Ti (lead dioxide-coated titanium) anodes developed at the Rolla Research Center (10) were used for electrowinning. The PbO<sub>2</sub>-Ti anodes were approximately the same width and height as the lead anodes, but they were only about 0.5 cm thick. Also, while the impure lead anodes were solid, the PbO<sub>2</sub>-Ti anodes had evenly spaced, approximately 1-cm-diam. holes throughout the surface to aid adherence of the PbO<sub>2</sub> coating and electrolyte circulation (fig. 2).

Cathodes, which measured 5 cm wide by 15.5 cm long, were cut from 0.1-cm-thick corroding grade lead sheet.

Electrolyte

Initially, electrolyte used for electrorefining was prepared by adding commercial-grade PbO (litharge) powder to a solution of reagent-grade (RG) H<sub>2</sub>SiF<sub>6</sub> (fluosilicic acid) and deionized water at 40° C to get the desired concentration. The RG acid contained approximately 30 pct H<sub>2</sub>SiF<sub>6</sub> and had a specific gravity of 1.27. A white precipitate, which formed during mixing of the

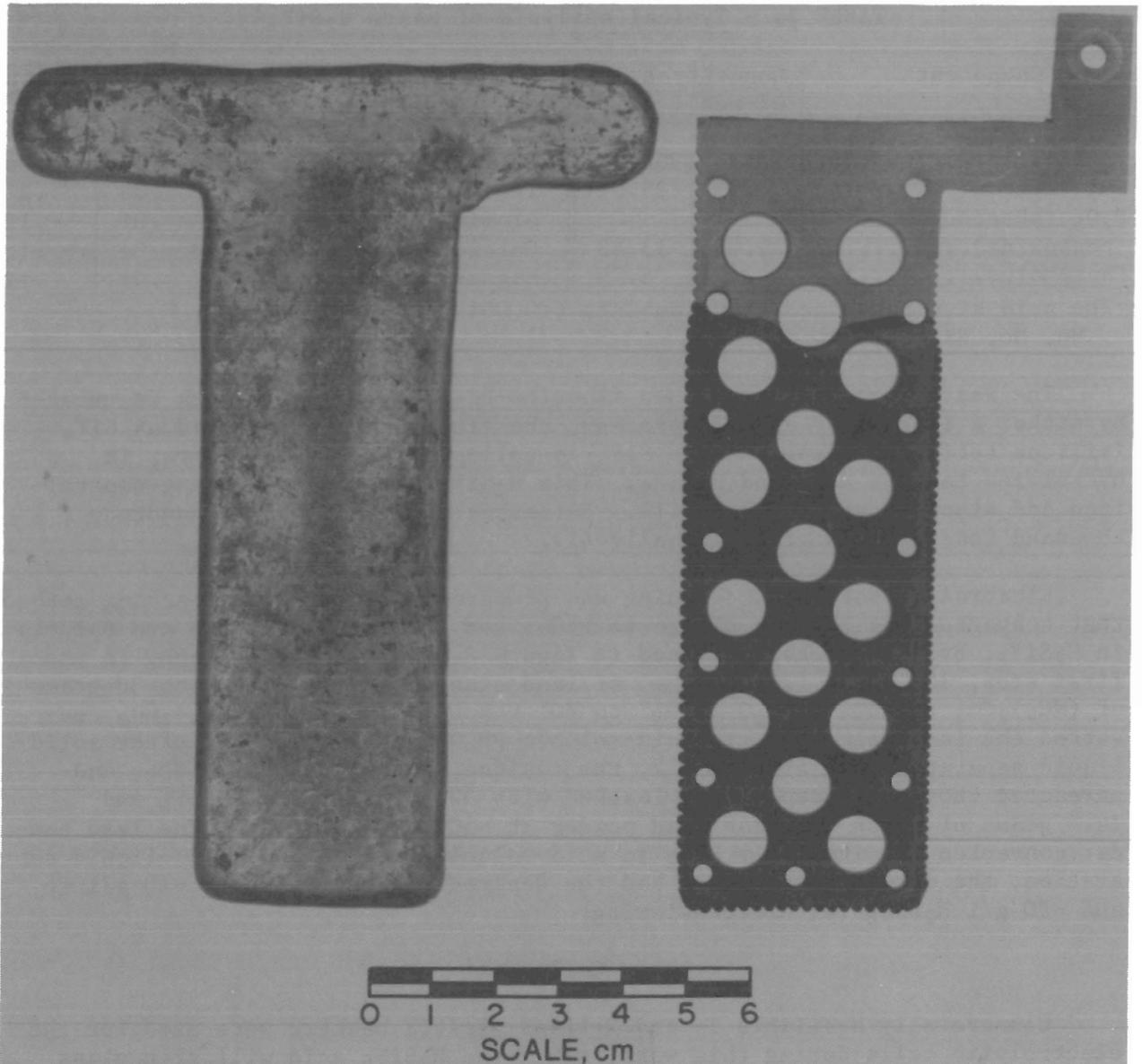


FIGURE 2. - Anodes used for electrorefining (left) and electrowinning (right).

PbO and acid, was removed from the electrolyte by filtration prior to electrorefining.

Later, waste  $\text{H}_2\text{SiF}_6$  (table 2) with a specific gravity of 1.232 was used in place of the RG acid to prepare electrolyte for both electrorefining and electrowinning. The acid had been generated during the production of phosphate fertilizer.

TABLE 2. - Typical analysis of waste  $\text{H}_2\text{SiF}_6$ <sup>1</sup>

Component	Concentration		Component	Concentration	
	wt-pct	g/l		wt-pct	g/l
$\text{H}_2\text{SiF}_6$ (fluosilicic acid).....	24.8	305.5	$\text{SO}_4$ (sulfate).....	0.26	3.20
$\text{NO}_3$ (nitrate).....	2.03	25.01	Sodium.....	.07	.86
$\text{P}_2\text{O}_5$ (phosphorus pentoxide).....	1.09	13.43	Iron.....	.03	.37
Phosphorus.....	.47	5.79	Aluminum.....	.01	.12
			Calcium.....	.01	.12
			Magnesium.....	.01	.12

<sup>1</sup>The acid also contained trace amounts (<0.001 pct) of B, Cr, Cu, K, Mn, Mo, Ni, Pb, Ti, and V.

The waste acid is formed when fluorine-bearing phosphate rock is treated by either a thermal or an acid process, the fluorine being evolved as  $\text{SiF}_4$  (silicon tetrafluoride). As the  $\text{SiF}_4$  is collected in wet scrubbers, it hydrolyzes to give  $\text{SiO}_2$  and  $\text{H}_2\text{SiF}_6$ . This  $\text{H}_2\text{SiF}_6$  is presently being neutralized and disposed of in a landfill. Estimates are that several hundred-thousand tons are discarded annually (1).

Electrolyte for electrowinning was prepared by a two-step leaching method that converted the battery sludge to  $\text{PbCO}_3$  and  $\text{PbO}$ , both of which are soluble in  $\text{H}_2\text{SiF}_6$ , by the process outlined in figure 3. In a typical leach, in the first step, 100 grams (dry weight) of lead sludge were reacted with 30 grams of  $(\text{NH}_4)_2\text{CO}_3$  and 600 ml  $\text{H}_2\text{O}$  at 55° to 60° C for 1 hour. The  $(\text{NH}_4)_2\text{CO}_3$  converted the insoluble  $\text{PbSO}_4$  to acid-soluble  $\text{PbCO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ . After solid-liquid separation, in step 2, the residue, containing Pb,  $\text{PbCO}_3$ , and unreacted  $\text{PbO}_2$  from step 1, was leached with 500 ml of waste  $\text{H}_2\text{SiF}_6$  and 14.5 grams of minus 200-mesh lead powder at ~50° C for 1 hour. The lead powder converted the insoluble  $\text{PbO}_2$  to acid-soluble  $\text{PbO}$ . After solid-liquid separation, the resulting solution had the desired concentration of ~70 g/l Pb and ~90 g/l  $\text{H}_2\text{SiF}_6$  for electrowinning.

#### Cells

Commercially available 1- and 2-liter plastic beakers were used for the electrolytic cells during this work, since the  $\text{H}_2\text{SiF}_6$  acid will etch glass over a long period of time. A 0.3-cm-thick Teflon<sup>4</sup> top was used to hold and space the electrodes and to retard solution evaporation. The top was of sufficient diameter to cover the cell, with a 0.3-cm slot for inserting the cathode into the center of the cell. Precisely 3 cm on each side of the center slot and parallel to it, two ~1.0-cm by 5-cm openings were cut for inserting the lead anodes. An oval-shaped copper bus bar was placed on top of the cover to support the two anodes and maintain the desired 3-cm electrode spacing. The copper bus bar also served as the electrical connection. Later, the multi-electrode plastic cell depicted in figure 1 was used, as the scale of the work was increased.

<sup>4</sup>Reference to specific equipment (or trade names or manufacturers) does not imply endorsement by the Bureau of Mines.

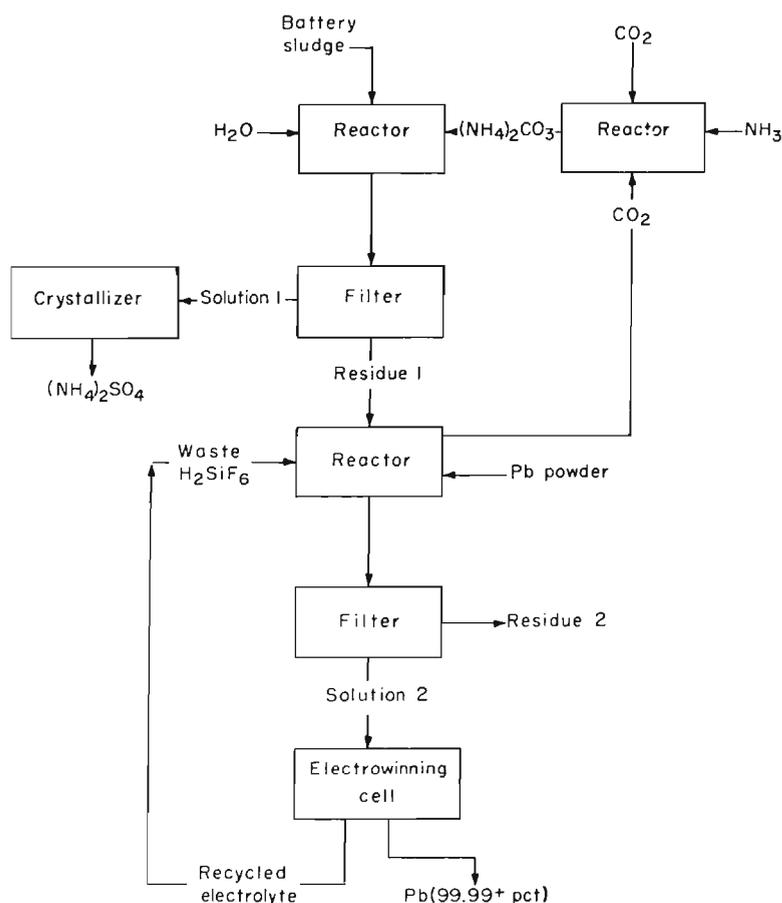


FIGURE 3. - Battery sludge leaching and electro-winning flow diagram.

### Operating the Electrolytic Cell

The clean dry cell was filled with electrolyte of the desired concentration and placed inside a water reservoir on top of a magnetic stirrer. The stirrer was activated to spin a Teflon-covered magnet to stir the solution. Initially, aloes and calcium lignin sulfonate were added to the electrolyte as leveling agent and grain refiner, respectively. Aloes is a natural plant extract imported from South Africa, and lignin is a byproduct of pulp and paper manufacture. Later, bone gelatin and hesperidin were substituted for aloes as the leveling agent. Water from a constant-temperature, recirculating water bath was pumped in and out of the reservoir, and the temperature of the electrolyte was allowed to stabilize at the desired setting.

The cathodes and anodes were lightly cleaned with a plastic scouring pad and wiped with a disposable wipe dampened with acetone. After cleaning, the cathode was inserted into the slot in the Teflon top and slid into the center. The anodes were attached to the copper bus bar and placed through the slots on both sides of the cathode. Leads from the power supply were attached to the cathode and the copper bus bar, the electrodes were placed into the cell, and the power supply was turned to the desired current setting. A Luggin capillary assembly containing PbSiF<sub>6</sub>-H<sub>2</sub>SiF<sub>6</sub> electrolyte and a reference electrode made from a rod of refined lead, as described by Kerby and Jackson (3), was used to monitor cathode polarization during electrolysis. The probe tip of the Luggin capillary was inserted through a hole in the Teflon top and immersed in the solution close to the cathode surface.

All electrolyses were performed galvanostatically using a 40-volt, 50-amp dc power supply. A chart recorder and an ampere-hour meter were used to monitor important operating parameters during the experiments.

## RESULTS AND DISCUSSION

Electrorefining

## Battery Scrap

During melting of the plus 28-mesh fraction of the smelter scrap containing lead from the battery lugs and grid metal (mostly grid metal), and plastic and rubber from the battery case material and plate separators, a great deal of smoke and fume was evolved. Obviously, the plastic and rubber will have to be separated from the lead prior to melting in order to avoid a potential pollution problem.

Several methods to do this are being investigated, but the one that seems to hold the most promise is to wash the lead and plastic and rubber with an ammonium carbonate solution in a revolving drum that contains a rotating screen, so that attrition scrubbing removes the adhering sludge. The washing is followed by flotation to separate the plastic and rubber from the lead. The wash water can then be used in the sludge leaching operation.

## Operating Parameters

Anodes prepared from melted lead battery scrap were electrorefined in both RG and waste  $\text{H}_2\text{SiF}_6$ . The conditions used (table 3) are approximately the same as those found best for electrorefining primary lead, as reported previously (7).

TABLE 3. - Conditions for electrorefining anodes made from the metallic lead recovered from scrap batteries

<u>Parameter</u>	<u>Value selected</u>
Electrolyte composition, g/l:	
Lead.....	70
$\text{H}_2\text{SiF}_6$ .....	90
Additive concentration, g/l:	
Bone gelatin.....	0.02-0.04
Calcium lignin sulfonate.....	4.0
Current density.....amp/m <sup>2</sup> ..	170
Electrolyte temperature.....° C..	35
Electrode spacing.....cm..	3
Cycle time.....days..	1,3

Electrolyte Composition

The starting electrolyte composition of 70 g/l Pb as  $\text{PbSiF}_6$  and 90 g/l free  $\text{H}_2\text{SiF}_6$  is the same as that of a typical electrolyte used at Cominco's lead refinery at Trail, British Columbia.

During electrorefining, the concentration of lead and acid in the electrolyte remains relatively constant because lead from the anodes goes into solution at approximately the same rate as lead is deposited at the cathode. Also,  $\text{H}_2\text{SiF}_6$  is very stable, and losses during electrolyses are negligible.

The white precipitate formed during mixing of PbO and H<sub>2</sub>SiF<sub>6</sub> was identified by X-ray analysis as PbFCl and PbSO<sub>4</sub>. The amount of this precipitate was dependent on the amount of chloride and/or sulfate impurities in the PbO and H<sub>2</sub>SiF<sub>6</sub>, but, in general, the weight of the precipitate was approximately 2 pct of the lead added.

#### Additive Concentration

Based on data in a landmark paper by Krauss (4), cathode polarization measurements were monitored with a Luggin capillary and controlled between 60 and 100 mv to give a smooth cathode deposit. Krauss's work has shown that polarization values greater than 100 mv result in a deposit with "wire growth," and at values less than 60 mv, the deposit has a rough nodular structure. Accordingly, it was determined that 0.6 g/l aloes and 4.0 g/l calcium lignin sulfonate were the optimum concentrations of addition agents to control cathode polarization within the desired range and give a level cathode deposit.

Later, a low-molecular-weight bone gelatin was used as a replacement for the aloes, a rather costly imported product. This gelatin was a white free-falling powder with an amino acid profile basically the same as that of other bone gelatins. A further description of the gelatin is given in table 4.

TABLE 4. - Description of bone gelatin used as leveling agent

<u>Physical and chemical properties and components</u>	<u>Results</u>
Isoelectric point.....	4.5-5.0
pH of 10 pct solution at 25° C.....	5.0-5.5
Moisture content.....pct..	7-9
Ash.....pct..	1 <sup>2</sup>
NaCl.....pct..	1 <sup>1</sup>
Nitrogen.....pct..	215
Heavy metals.....ppm..	<50
<u>Arsenic.....ppm..</u>	<0.8

<sup>1</sup>Maximum.

<sup>2</sup>Minimum.

The amount of bone gelatin added to the electrolyte was varied from 0.01 to 0.04 g/l, and the amount of lignin was varied from 2 to 4 g/l with 0.02 to 0.04 g/l bone gelatin. The resulting cathodes were all good with near 100-pct current efficiencies. However, a few nodules did form on the cathodes when the amount of lignin was less than 4.0 g/l. The best combination of addition agents for 1- and 3-day electrorefining tests was found to be 0.02 to 0.04 g/l bone gelatin and 4.0 g/l calcium lignin sulfonate. The bone gelatin was less expensive per pound and more readily available than aloes; it also had the advantage that cell voltage and cathode polarization were more stable and easier to control during electrorefining.

Following the work of Kerby and Jackson (3), hesperidin, a product made from orange peels, was also tried as a replacement for aloes. Initial results, using 0.5 g/l hesperidin with 4.0 g/l lignin sulfonate, were encouraging, and it appears that hesperidin can replace aloes as a leveling agent.

Hesperidin, like bone gelatin, has the advantage of uninterrupted source of supply. Also, because the material tested had a high nonpathogenic bacteria count and was unsuitable for use as a human food supplement, the normal market for hesperidin, it should be available at a very low price.

#### Current Density, Electrolyte Temperature, and Electrode Spacing

Each of these operating parameters was varied over a wide range of conditions, the same ones reported previously (7), and the values given in table 3 were found to be the best to give consistently good cathode deposits at near 100-pct current efficiency.

#### Cycle Time

Two of the main factors limiting cycle time are the slime blanket thickness and loss of adherence. During electrorefining, as the slime blanket increases in thickness on the anode surface, the potential drop across the slime blanket increases. It becomes increasingly favorable for elements with half cell potentials close to that of lead to dissolve with lead and, ultimately, to deposit with lead on the cathode. Also, after an extended time, the slime blanket may cease to be adherent and fall, resulting in short-circuiting and contamination of the cathode metal. Thus, there is a limiting electrolysis cycle time that is largely determined by the desired purity of the cathode lead.

In these experiments, lead of 99.9+ pct purity was still being produced after 3 days of electrorefining in RG acid electrolyte. Copper, antimony, arsenic, and other potential impurities (table 1) were easily retained in the slime blanket. Tin, with a half cell potential within 10 mv of leads, was the only element of major concern. During 3 days of electrorefining, the amount of tin in the electrolyte did increase from almost 0 g/l to ~0.06 g/l, but the amount of tin in the refined lead was only 0.013 pct.

Although the tin concentration in the cathode lead was within acceptable levels after 3 days of electrorefining, it is probable that longer electrolysis cycle times would result in unacceptable deposits. Fortunately, tin is one of the easiest elements to remove from lead. During melting of the cathodes, tin will report to the dross on top of the molten lead and will be removed as the dross is skimmed prior to casting the lead in the desired form for market.

#### Slime Blanket

The slime blankets formed on anodes electrorefined in electrolyte prepared from both RG and waste  $H_2SiF_6$  were firm and adherent, yet easily removed with a spatula or dull knife blade. The use of waste acid had no effect on current efficiencies or cathode morphology. All current efficiencies were near 100 pct, and cathode deposits were all excellent in appearance. However, the composition of the slimes produced in waste acid electrolyte was markedly different from that of the slimes produced in RG acid electrolyte. As shown in table 5, test 2, the slimes formed when using waste acid weighed more and contained more lead and less antimony.

TABLE 5. - Variation in typical composition of anode slimes after electrorefining in electrolyte prepared from reagent-grade and waste H<sub>2</sub>SiF<sub>6</sub>

Test	H <sub>2</sub> SiF <sub>6</sub>	Cycle time, days	Weight of slimes, g	Composition, wt-pct						
				Pb	Sb	Ag	As	Cu	P	Sn
1.....	Reagent grade.	3	15.5	10.6	75.0	0.06	4.6	1.2	ND	0.78
2.....	Waste..	3	35.5	41.1	40.8	.04	2.6	.75	1.7	.56
3.....	..do...	4.3	37.2	17.6	66.5	.08	4.7	.97	.5	.78

ND Not detected.

During electrorefining in electrolyte prepared from RG acid (test 1), the cell voltage increased from 0.27 to ~0.3 volt as the slime blanket increased in thickness during the 3-day cycle. When waste acid was used (test 2), the voltage went as high as 0.9 volt with an average value of ~0.6 volt. The weight of the slime more than doubled when waste acid was substituted for RG acid. When the same solution as used for test 2 was used for an additional 4.3-day cycle (test 3), after adjusting the concentration of lead and additives, the voltage stabilized and averaged only 0.33 volt.

#### Phosphorus Content

X-ray analyses of the slimes from waste acid electrolyte indicated that they contained several phosphate salts such as Pb<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>, PbO·Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, etc. Apparently, the reaction of phosphorus with lead is responsible for the extra-thick slime blanket, which, in turn, increases the cell voltage when electrorefining in electrolyte prepared from waste acid. Obviously, the reason for the lower cell voltage recorded in test 3 was that much of the phosphorus was removed from the electrolyte in the previous test (table 6).

TABLE 6. - Change in composition of waste acid electrolyte with time

Cycle time, days	Composition of electrolyte, g/l							
	Pb	Ag	As	Cu	P	Sb	Sn	Free H <sub>2</sub> SiF <sub>6</sub>
Test 2:								
0.....	80.6	<0.001	0.024	<0.001	1.9	0.012	0.007	94.8
1.....	76.9	<.001	.006	<.001	1.2	.013	.034	92.9
2.....	67.5	<.001	.017	<.001	.96	.272	.059	92.4
3.....	55.5	<.001	.025	<.001	.92	.209	.078	94.3
Test 3: <sup>1</sup>								
0.....	73.3	<.002	.03	<.001	.76	.21	.09	93.3
1.....	72.3	<.002	<.025	<.002	.47	.03	.10	90.9
2.....	71.7	<.002	<.025	<.002	.41	.03	.10	83.9
3.....	66.3	<.002	<.025	<.003	.68	.04	.18	89.4
4.3.....	63.0	<.002	<.025	.009	.61	.03	.12	88.5

<sup>1</sup>The electrolyte used for this test was made from the electrolyte used in test 2 after 3 days of electrorefining by adding concentrated PbSiF<sub>6</sub> solution to raise the lead content. The concentration of the additives was also adjusted to the desired level.

Not only did the presence of phosphorus in the electrolyte result in an increase in cell voltage, but the levels of antimony and tin were also higher with high phosphorus levels, resulting in less pure cathodes (table 7). Both the antimony and tin content in the electrolyte decreased to a lower constant value as the phosphorus content decreased to ~0.6 pct in test 3. Accordingly, the refined lead from test 3 contained 99.98 pct Pb, purer than that from test 2.

TABLE 7. - Composition of electrorefined lead

Test	Cycle time, days	Composition, wt-pct						
		Pb	Ag	As	Cu	P	Sb	Sn
2	3	99.59	<0.0001	0.006	0.0004	0.003	0.403	0.0014
3	4.3	99.98	<.003	<.0001	<.002	.002	.002	.005

There appear to be at least two ways that the phosphorus content of the electrolyte prepared from waste acid can be controlled. One is to make a preliminary run, during which the phosphorus reports to the slime blanket and is removed from the electrolyte. The second method is to remove the phosphorus prior to electrorefining. Preliminary test results indicate that phosphorus in electrolyte prepared from waste acid can be lowered to a harmless level before electrolysis by adding controlled amounts of PbO to precipitate the phosphorus as an insoluble lead-phosphate compound.

#### Characterization of Slimes<sup>5</sup>

X-ray, petrographic, and chemical methods were used to characterize the slimes generated during electrorefining of lead anodes in electrolyte prepared from both RG and waste  $H_2SiF_6$ .

The solubility of the slimes (table 5) was determined in hot, 10-pct solutions of  $HNO_3$ ,  $HCl$ ,  $H_2SO_4$ , and  $KOH$ . The solubilities and chemical analyses of these solutions were calculated using the total sample weight used for the solubility determinations (table 8). Qualitative analysis indicated the presence of minor amounts of fluorides and organics.

TABLE 8. - Solubility of the slimes in 10-pct solutions using various reagents, and chemical analysis of the solutions used for the solubility determinations

Reagent	Solubility, pct	Composition, wt-pct				
		Pb	Sb	As	Cu	Sn
$HNO_3$ .....	43.5	30.0	10.7	1.3	0.74	<0.1
$HCl$ .....	54.6	22.4	16.5	.3	.46	.2
$H_2SO_4$ .....	14.9	<.1	7.4	.4	<.01	.1
$KOH$ .....	43.9	6.5	20.0	.4	<.01	.2

<sup>5</sup>The substantial contribution of Bill Jones, Supervisory Chemist, Rolla Research Center, to this section of the report is gratefully acknowledged.

The composition of the anode slimes was theorized from solubility data (5), solubility studies, microscopic examination of the slimes and insoluble residues from the solubility studies, and chemical analysis of the solutions resulting from solubility studies. The theoretical composition of the anode slimes produced in waste acid electrolyte are presented in table 9. The theoretical composition of anode slimes produced in RG acid electrolyte were determined to be the same as given in table 9 except for the absence of compounds containing phosphorus.

TABLE 9. - Theoretical composition of anode slimes produced in waste acid electrolyte

<u>Element</u>	<u>Composition</u>
Lead.....	Lead phosphates, lead dioxide, lead fluoride, and metallic lead.
Antimony....	Antimony oxide and metallic antimony.
Arsenic.....	Alloy of arsenic and arsenic fluoride.
Copper.....	Metallic copper.
Tin.....	Tin phosphate or tin fluoride.

In addition to having a very complex structure, the slimes were composed of extremely fine particles, in the range below 1  $\mu\text{m}$ . Physical separation would be very difficult, if not impossible. However, both a hydrometallurgical and pyrometallurgical method have shown promise for recovering the valuable constituents from the slimes. Further work is being done to determine the most desirable treatment method from both an economical and environmental standpoint.

#### Energy Consumption

In any electrometallurgy process, the total energy requirement is composed of the thermodynamic energy requirement ( $\Delta G = -nFE$ ), the cathodic and anodic overpotentials, and the ohmic potential drop in the electrolyte and the cell hardware. In electrowinning, the thermodynamic energy requirement is a large part of the total energy requirement; however, in electrorefining, where both electrode reactions are nearly identical, the free-energy change ( $\Delta G$ ) is nearly zero, and the energy required for electrorefining is quite low. Because of this low thermodynamic energy requirement, the ohmic potential losses in the cell hardware are a significant part of the total energy requirement; therefore, particular attention must be paid to electrical connections, size of bus bars, power leads, etc.

As expected, energy consumption for electrorefining anodes made from scrap battery lead increased linearly with increasing current density and electrode spacing and decreased linearly with increasing cell temperature. The presence of phosphorus in waste acid electrolyte resulted in thicker slime blankets and an increase in energy consumption.

The primary reason for selecting the values of the parameters listed in table 3 was that they gave good, smooth cathode deposits. Minimal energy

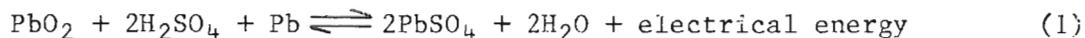
consumption was a secondary consideration. Using these parameters, after 3 days of electrorefining anodes made from scrap battery lead, in both RG and waste  $\text{H}_2\text{SiF}_6$  electrolyte, energy consumption was 0.07 and 0.09 kw/hr/kg of refined lead, respectively. Of course, longer cycle times would result in proportionate increases in energy usage because of the increasing potential drop across the slime blanket as it increased in thickness.

### Electrowinning

Unlike electrorefining, in which soluble impure anodes are used, electro-winning requires insoluble inert anodes.

### Battery Sludge

In addition to lead metal (~4.5 kg, mostly in the form of grids), the balance of the lead in batteries is in the form of a Pb and  $\text{PbO}_2$  paste, or active material that is applied to the grids. This active material, which has a very fine particle size to promote quick reaction rates, is the part of the battery that reacts with the  $\text{H}_2\text{SO}_4$  electrolyte to store and release energy according to the following equation:



The forward reaction is the energy release, or discharge reaction, and the reverse reaction is the energy storage, or charge reaction. Any unreacted active materials, plus the discharge-charge reaction products, plus corroded or reacted grid metal, are what is referred to here as sludge. The composition and amount of this sludge largely depend on the number of discharge-charge cycles and the length of time the battery has been out of service.

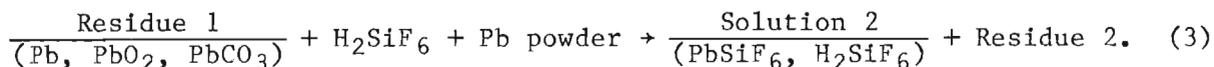
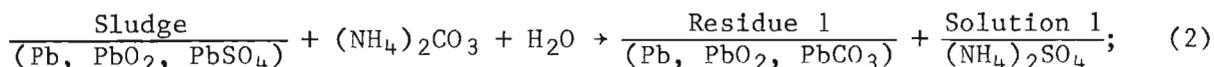
The specific gravity of the electrolyte in a new SLI (starting, lighting, and ignition) battery is 1.275, and the specific gravity of the electrolyte in a fully discharged battery (minimum useful voltage output) is 1.125. These values correspond to a sulfate ion concentration of ~470 and 200 g/l, respectively. Since the average SLI battery contains about 4 liters of electrolyte, 11.25 moles of acid are consumed during full discharge of the battery.

The average battery paste contains 11.5 moles of lead and 10.1 moles of  $\text{PbO}_2$  (6). If 11.25 moles of acid react during full discharge, and assuming equal reaction with Pb and  $\text{PbO}_2$ , the average battery sludge would contain approximately 5.88 moles (1.22 kg) of Pb, 4.48 moles (1.07 kg) of  $\text{PbO}_2$ , and 11.25 moles (3.41 kg) of  $\text{PbSO}_4$ . The total weight of sludge per battery would be ~5.7 kg, of which 19 pct would be  $\text{PbO}_2$ , 21 pct Pb, and 60 pct  $\text{PbSO}_4$ . If the battery sits for any appreciable time after discharge, further reaction of the lead components would occur and the percentage of sulfate would increase while the percentage of Pb and  $\text{PbO}_2$  decreased.

### Sludge Leaching

After extensive experiments, the two-step leaching procedure outlined in figure 3 was developed to solubilize the lead in the sludge for recovery by

electrowinning. Equations 2 (step 1) and 3 (step 2) indicate the reactions occurring during the leaching operation:



In step 1, the conversion of  $\text{PbSO}_4$  to  $\text{PbCO}_3$  was nearly quantitative when a 100-pct excess of the stoichiometric amount of  $(\text{NH}_4)_2\text{CO}_3$  was reacted with the sludge at  $55^\circ$  to  $60^\circ$  C for 1 hour. Further work will be necessary to determine the optimum conditions for crystallization of the  $(\text{NH}_4)_2\text{SO}_4$  from solution 1 and its suitability for use as fertilizer. In addition to  $(\text{NH}_4)_2\text{SO}_4$ , solution 1 contained approximately 10 ppm each of arsenic and lead.

Overall recovery of lead by sludge leaching typically ran 92 to 93 pct. Repeated attempts to improve these results were unsuccessful. Examination of residue 2 revealed that it was mainly  $\text{PbSO}_4$ . This at first seemed to indicate that the conversion of  $\text{PbSO}_4$  to  $\text{PbCO}_3$  in step 1 was incomplete. However, the problem was traced to the waste acid, which was found to contain sulfate ions (table 2). During leaching of residue 1, in step 2, the sulfate ions in the waste acid converted some of the lead in the solution to insoluble  $\text{PbSO}_4$ . Residue 2 is now being recycled to step 1 to convert this additional  $\text{PbSO}_4$  to  $\text{PbCO}_3$ .

When 100 grams of sludge were treated by the method outlined in figure 3,<sup>6</sup> solution 2 contained the approximate concentration of lead and free acid (70 g/l Pb, 90 g/l  $\text{H}_2\text{SiF}_6$ ) desired for electrowinning.

#### Operating Parameters

Using electrolyte prepared by leaching battery sludge, as described, and two graphite anodes and a lead cathode, a series of experiments was initiated to determine the best operating parameters for electrowinning.

With the exception of the electrolyte temperature of  $35^\circ$  C, the parameters used for electrorefining (table 3) were also used for electrowinning. Ambient temperature was found to be suitable for electrowinning, and excellent cathode deposits were obtained at 98-pct current efficiency during 1- and 3-day tests with variations in electrolyte temperature from  $25^\circ$  to  $35^\circ$  C. Sufficient heat was generated during electrolysis to maintain the temperature within this range so that no external source of heat was necessary.

Although the current density used for these tests was the same as for electrorefining ( $170 \text{ amp/m}^2$ ), indications are that much higher current densities might be used, and this possibility will be investigated in future work.

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<sup>6</sup>Reagent amounts are given in the discussion of the two-step leaching method in the "Electrolyte" section.

The starting electrolyte concentration of 70 g/l Pb, 90 g/l  $\text{H}_2\text{SiF}_6$  was the same as that used for electrorefining. During electrorefining, dissolution of the impure lead anode helped maintain the lead concentration constant. However, during electrowinning with inert anodes, the concentration of lead in the electrolyte continually decreased. As the lead content of the solution was reduced to <20 g/l, granular and finally spongy lead was deposited, but the cathode still analyzed 99.99+ pct Pb.

#### Anodes

The graphite anodes used during the initial tests deteriorated rapidly during electrowinning, and they were replaced with patented  $\text{PbO}_2$ -Ti anodes developed at the Rolla Research Center (10). The  $\text{PbO}_2$ -Ti anodes were found to be particularly suited to electrowinning, and, unlike the graphite anodes, they did not deteriorate during electrolysis. A pair of these  $\text{PbO}_2$ -Ti anodes were used for more than 42 days accumulative electrowinning time, and they still appeared to be like new.

The potential for recovering lead by electrowinning has always been great, but the method has never been used commercially because no one has been able to solve the problem of excessive  $\text{PbO}_2$  formation at the anodes. The problem was solved during the course of this investigation by the discovery that small amounts of phosphorus in the electrolyte will prevent  $\text{PbO}_2$  formation.

Using electrolyte prepared with RG acid containing no phosphorus, the amount of insoluble  $\text{PbO}_2$  deposited on the anodes equaled the amount of lead

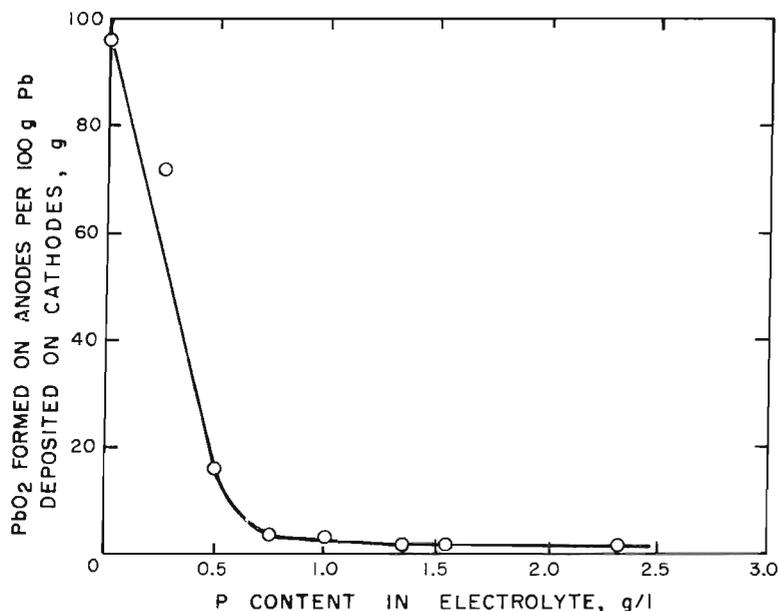


FIGURE 4. Effect of phosphorus concentration on  $\text{PbO}_2$  formation.

deposited at the cathode. Using the same solution with 1.5 g/l phosphorus added as  $\text{H}_3\text{PO}_4$ , approximately 1 gram of  $\text{PbO}_2$  was deposited at the anodes and 100 grams of lead was deposited at the cathode during a 1-day test. Figure 4 illustrates the remarkable effect of phosphorus in the electrolyte on  $\text{PbO}_2$  formation at the anodes.

In addition to  $\text{H}_3\text{PO}_4$ , a number of other inorganic acids, as well as organic acids, salts, and oxides containing phosphorus, were tested, and all were found to inhibit  $\text{PbO}_2$  formation at the anodes. However, the fact that the waste acid

already contains phosphorus (table 2) makes it particularly suited to preparing electrolyte for electrowinning.

#### Cathode Quality

Excellent cathode deposits were produced in all electrowinning tests, first with 0.6 g/l aloes and 4.0 g/l calcium lignin sulfonate as addition agents, and later with 0.02 to 0.04 g/l bone gelatin substituted for the aloes. Current efficiencies, on the average, were 96 pct. The lead produced in 3 day tests was purer than that produced during electrorefining and averaged 99.99+ pct.

As electrolyte was recycled after electrowinning to leach more sludge, the Luggin capillary was used to monitor cathode polarization and bring the concentration of addition agents up to the proper level to control the polarization voltage within the desired range of 60 to 100 mv.

The data in table 10 indicate how the electrolyte changed in composition during electrowinning and recycling. During electrowinning, the lead concentration decreased and the acid concentration increased from the nominal values as lead was removed from the electrolyte at the cathode. Also, the concentration of Cu, Sb, and Sn increased during recycle of electrolyte. However, copper was the main impurity to codeposit with the lead (table 11).

TABLE 10. - Change in composition of recycled electrolyte

Test <sup>1</sup>	Number of times electrolyte was recycled	Composition of electrolyte, g/l						
		Pb	As	Cu	P	Sb	Sn	Free H <sub>2</sub> SiF <sub>6</sub>
4B	0	68.37	0.07	0.005	2.59	0.38	0.03	86.6
4A	0	10.15	.07	<.001	2.54	.37	.03	135.5
5B	1	81.22	.07	.008	2.65	.59	.06	88.32
5A	1	33.15	.06	<.001	2.67	.57	.04	116.64
6B	3	84.8	.06	.007	2.77	.79	.07	88.6
6A	3	35.8	.06	.002	2.74	.81	.09	138.7

<sup>1</sup>B suffix indicates before electrowinning. A suffix indicates after electrowinning.

TABLE 11. - Chemical analysis of electrowon lead

Test	Number of times electrolyte was recycled	Composition, pct					
		Pb	As	Cu	P	Sb	Sn
4	0	99.99+	<0.001	0.003	0.001	<0.001	<0.001
5	1	99.99+	<.001	.007	.001	<.001	<.001
6	3	99.99+	<.001	.007	.004	<.001	<.001

In addition to copper, the cathode from test 6 also showed an increase in phosphorus concentration. The amount of phosphorus in the electrolyte should be easily controlled as phosphorus is removed in the as yet unexplained

reaction at the anode that inhibits  $\text{PbO}_2$  formation. Auger electron spectroscopy analysis indicates that phosphorus is present on the  $\text{PbO}_2$ -Ti anode surface after electrowinning.

### Energy Consumption

The thermodynamic energy requirement for electrowinning, unlike that for electrorefining, is a large part of the total energy requirement.

The cathodic and anodic reactions occurring during electrowinning are given in equations 4 and 5, respectively, and the overall reaction is given in equation 6:



If the reasonable assumption is made that both  $\text{PbSiF}_6$  and  $\text{H}_2\text{SiF}_6$  are highly ionized, since  $\text{PbSiF}_6$  is soluble in the solution and  $\text{H}_2\text{SiF}_6$  is a strong acid, the standard potential for the cathode reaction is essentially the reduction potential for lead; i.e.,  $\text{Pb}^{++} + 2\text{e}^- \rightarrow \text{Pb}$ ,  $\epsilon^\circ = -0.126 \text{ v}$ .

The standard overall cell potential ( $\epsilon_{\dagger}^\circ$ ), and thus the thermodynamic energy contribution, is a large part of the total energy requirement for electrowinning. Given the same electrolyte, current density, electrode spacing, and electrolyte temperature, the total energy requirement for electrowinning for a 3-day cycle averaged approximately 8 to 10 times more than for electrorefining, or  $\sim 0.7 \text{ kWhr/kg}$  versus  $0.07$  to  $0.09 \text{ kWhr/kg}$  refined lead. Unlike electrorefining, in which a growing slime blanket caused a constantly increasing potential, the overall cell potential for electrowinning was relatively constant with time at  $\sim 2.5$  volts.

### CONCLUSIONS

The bench-scale work described in this report for recovering the lead from scrap batteries by a combination electrorefining-electrowinning procedure shows a great deal of promise.

Lead of sufficient purity for the manufacture of maintenance-free batteries was produced with minimal pollution and relatively low energy consumption. A particular advantage was the ability to use waste  $\text{H}_2\text{SiF}_6$  as the electrolyte.

Because of the discovery that small amounts of phosphorus in the electrolyte will prevent  $\text{PbO}_2$  formation at anodes, lead electrowinning could become a viable commercial process.

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