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Hydrometallurgical Process for Producing Lead and Elemental Sulfur From Galena Concentrates

By Agnes Y. Lee, Ann M. Wethington, and Ernest R. Cole, Jr.

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	kW·h/kg	kilowatt hour per kilogram
A/m^2	ampere per square meter	L	liter
¢	cent	m	meter
°C	degree Celsius	m^2	square meter
cm^2	square centimeter	min	minute
g	gram	mV	millivolt
g/L	gram per liter	pct	percent
h	hour	tr oz/mt	troy ounce per metric ton
kg	kilogram	V	volt
kW	kilowatt	W	watt
kW·h	kilowatt hour	wt pct	weight percent

HYDROMETALLURGICAL PROCESS FOR PRODUCING LEAD AND ELEMENTAL SULFUR FROM GALENA CONCENTRATES

By Agnes Y. Lee,[1] Ann M. Wethington,[2] and Ernest R. Cole, Jr.[3]

ABSTRACT

The Bureau of Mines has developed an effective hydrometallurgical method to recover high-purity Pb metal and elemental S from galena concentrates. This low-temperature process eliminates S gases and Pb emissions, in contrast to the current high-temperature smelting technology.

The method consists of (1) oxidative leaching with H_2O_2, PbO_2, and waste fluosilicic acid at 95° C to produce a solution of $PbSiF_6$ and a residue containing elemental S, (2) electrowinning the $PbSiF_6$ solution at 35° C to produce 99.99 pct Pb metal and H_2SiF_6, and (3) solvent extraction to recover S, leaving a residue containing Cu, Ag, and other metal values.

Spent electrolyte was recycled repeatedly, with impurity buildup controlled by controlling the leach parameters.

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INTRODUCTION

A major cost factor in the sintering and smelting process for producing Pb is the control needed to meet existing environmental standards for Pb emissions. Another issue is the current concern over acid rain, which will in all probability result in even more stringent controls on emission of S gases.

Researchers at the Bureau of Mines have developed an effective low-temperature leaching-electrowinning method $(\underline{1})^4$ to produce Pb metal and elemental S from galena concentrates. The method reduces Pb emissions and totally eliminates the formation of S gases. The elemental S produced is more economical to store and ship than the sulfuric acid (H_2SO_4) generated by the high-temperature smelting process.

This hydrometallurgical method consists of leaching galena concentrates in waste fluosilicic acid (H_2SiF_6) with hydrogen peroxide (H_2O_2) and lead dioxide (PbO_2) as oxidants:

$$2PbS + 3H_2SiF_6 + H_2O_2 + PbO_2$$

$$\rightarrow 3PbSiF_6 + 4H_2O + 2S°. \qquad (A)$$
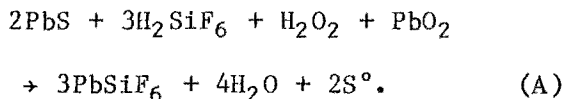
After solid-liquid separation to obtain the Pb fluosilicate solution and the residue containing elemental S, electrowinning of the aqueous $PbSiF_6$ solution at 35° C produces Pb metal and H_2SiF_6 ($\underline{2}$-$\underline{6}$):

$$PbSiF_6 + 2H^+ + 2e^- \rightarrow Pb + H_2SiF_6. \qquad (B)$$
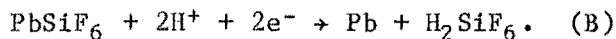
The H_2SiF_6 is then recycled to leach more PbS. Sulfur is recovered from the leach residue by solvent extraction.

Several galena leaching processes have been investigated, including processes using ferric chloride ($\underline{7}$), ferric sulfate ($\underline{8}$), nitric acid ($\underline{9}$), and ammonium acetate solutions ($\underline{10}$). The leached $PbCl_2$

and $PbSO_4$ salts have a very limited solubility in aqueous solution, making aqueous electrolysis difficult ($\underline{11}$). Lead metal was recoverable from $PbCl_2$ by molten-salt electrolysis ($\underline{7}$) operated at 450° C. It is known that electrowinning of Pb in HNO_3 and H_2SiF_6 solutions yields Pb metal at the cathodes and at the same time PbO_2 at the anodes ($\underline{8}$-$\underline{9}$).

Recent investigations on Pb recovery from battery sludge ($\underline{2}$-$\underline{6}$, $\underline{12}$) have shown that small amounts of a phosphate or an arsenic compound in the H_2SiF_6 electrolyte will prevent the formation of PbO_2 on anodes, making Pb electrowinning a viable process.

Figure 1 is the flow diagram of the oxidative leaching-electrowinning process. The parameters for each unit process were investigated in bench-scale experiments and tested on a larger scale. The unit process included oxidative leaching, lead electrowinning, activated carbon treatment of spent electrolyte, and S removal by solvent extraction.
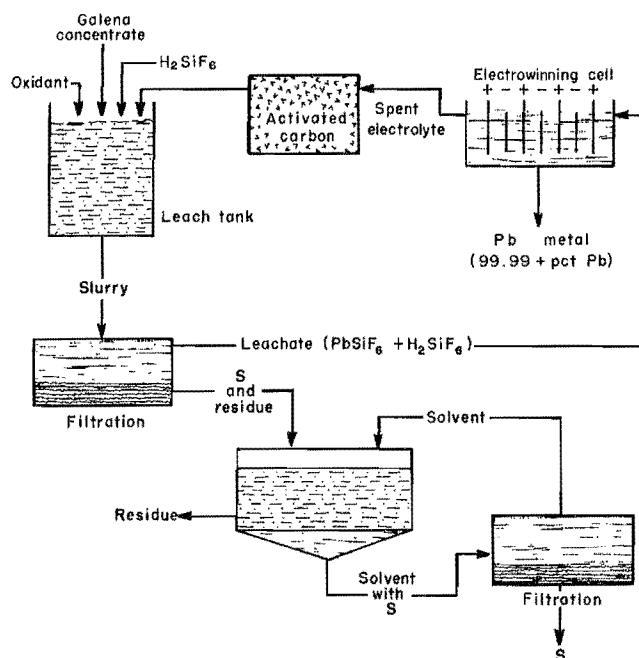

FIGURE 1.—Flow diagram for producing Pb from galena concentrates by leaching and electrowinning.

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^{4}Underlined numbers in parentheses refer to items in the list of references at the end of this report.

MATERIALS, EQUIPMENT, AND PROCEDURES

OXIDATIVE LEACHING

Galena concentrates, obtained several times from a Missouri Pb smelter, were analyzed and found to contain 74.4 to 78.3 pct Pb depending on the acquisition date. The results of chemical and screen analysis of typical samples are given in tables 1 and 2, respectively. Sample 1 was used in bench-scale tests and sample 2 in large-scale tests.

An ore mineralization study showed that the galena was present largely as free particles, and only small amounts were found in association with chalcopyrite, quartz, pyrite, dolomite, and sphalerite.

Initially, technical-grade H_2SiF_6 was used to leach the PbS concentrates.

Later, waste H_2SiF_6 and recycled spent electrolyte ($H_2SiF_6 + PbSiF_6$) were employed. The waste H_2SiF_6 was a byproduct of phosphate fertilizer manufacturing (2). The oxidants used were hydrogen peroxide (35 pct H_2O_2) solution and PbO_2 powder (86.1 pct Pb), both technical grade.

A redox meter with a Pt electrode and an Ag-AgCl reference electrode were used to measure the redox potential of the oxidative leaching reaction.

The amounts of galena concentrates and H_2SiF_6 acid used in each leach experiment were calculated so that the resulting leachate would contain about 90 g/L Pb and 90 g/L free H_2SiF_6.

The leach procedure, for bench-scale tests, was to mix 100 mL H_2SiF_6 (200 g/L) solution with 2 mL H_2O_2 and 0.5 g PbO_2 in a 250-mL tall form beaker, followed by the addition of 20 g PbS concentrate. As the mixture was heated to the desired temperature, H_2O_2 was slowly added to initiate the leach reaction. Subsequently, PbO_2 powder was added to maintain the redox potential. When the redox potential of the leach mixture dropped below 480 mV, more PbO_2 was added to raise it to at least 480 mV, but not higher than 550 mV. The leach reaction was complete when the redox potential remained above 480 mV. The mixture was then filtered to separate the residue from the leachate.

Leach parameters, such as temperature, time, concentration of acid, and amounts of oxidants used, were investigated in

TABLE 1. – Analyses of galena concentrates, weight percent

Element	Sample 1	Sample 2
Pb.....................	78.30	74.40
S......................	14.10	13.70
Zn.....................	2.38	1.10
Fe.....................	.92	1.25
Mg.....................	.41	.28
Cu.....................	.35	.47
Ca.....................	.10	.49
Al.....................	.09	NA
Co.....................	.05	.06
Ni.....................	.03	.04
Sb.....................	<.03	<.03
Ag.....................	NA	<.01

NA Not analyzed.

TABLE 2. – Screen analysis of galena concentrates

	Screen size, mesh					
	+100	-100, +150	-150, +200	-200, +270	-270, +400	-400
Pct retained......	1.08	0.14	8.49	15.93	3.65	70.11
Assay, pct:						
Pb..............	78.6	79.30	80.00	80.40	81.00	74.20
Zn..............	1.60	1.90	2.10	3.30	3.00	2.80
Fe..............	.50	.60	.30	.40	.50	1.20
Cu..............	.23	.18	.15	.16	.15	.40
Ni..............	.03	.02	.03	.03	.03	.07
Co..............	.02	.02	.02	.03	.03	.06

bench-scale experiments using 20- to 200-g samples of PbS.

Large-scale leaching, using 10 kg PbS and 75 L H_2SiF_6 solution, was conducted in a 100-L reactor described previously (4).

LEAD ELECTROWINNING

Electrolyte was prepared from the PbS leachates, which contained 80 to 100 g/L Pb as $PbSiF_6$ and 90 to 100 g/L free H_2SiF_6. Prior to electrolysis, glue and calcium lignin sulfonate (lignosite) were added as leveling agent and grain refiner, respectively, and H_3PO_4 was added to prevent excess PbO_2 formation on the anodes (2-4).

Lead electrowinning experiments were conducted in a 1-L cell (2) for 8 h using two PbO_2-coated titanium anodes (13) and one pure Pb sheet cathode. The electrolyte temperature was 35° C, and the current density was varied from 180 to 250 A/m^2.

Large-scale electrowinning tests were performed in a 20-L cell for 5-day runs; 200 L of electrolyte was stored in a tank and circulated through the cell as described in RI 8857 (5). The cell had four PbO_2-Ti anodes (10 by 26 by 0.4 cm) and three Pb cathodes (12 by 28 by 0.16 cm).

RECYCLING OF ELECTROLYTE

Lignosite and glue were removed from spent electrolyte by mixing the electrolyte with activated C (minus 325 mesh) in a beaker at ambient temperature for 30 min and then filtering to obtain the clear H_2SiF_6 solution and C residue. The amount of C used was 12.5 g/L of spent

electrolyte for bench-scale tests, or 1.25 kg/100 L for large-scale treatment in the 100-L reactor.

SULFUR EXTRACTION

The typical galena leach residue contained about 40 to 50 pct elemental S. Solvent extraction was investigated for recovering S from the residue.

The apparatus used for recovering S by solvent extraction consisted of a 2-L glass filter reactor heated with an electric mantle (fig. 2). The reactor head was equipped with three necks to accomodate a thermocouple, a glass stirrer, and a Graham condenser to recover solvent vapor. The bottom of the reactor was sealed with a fritted glass disc to retain particles larger than 10 µm, and a stopcock opening was used for solvent drainage. The solvent was removed from the residue by vacuum filtering. A flask was used to collect the hot S-carrying solvent. Two cold traps were used in the vacuum line to collect solvent fumes during the hot filtration.

The S extraction procedure was to slurry 100 g of dried residue with 800 mL of mixed solvents of tetrachloroethylene and kerosene in the glass reactor, heat to 110° to 118° C, and hold for 5 min before filtering. This arrangement facilitated rapid removal of the hot S-carrying solvent and prevented solidification of the S during filtering. After cooling to ambient temperature to allow the S to crystallize out of solution, S was filtered from the solvent, which was recycled for S extraction. The recovered S was dried at 90° C to remove any residual solvent.

RESULTS AND DISCUSSION

LEACHING REACTIONS

The chemical equations (9) for PbS leaching in acid solution with and without oxidants [O] follow:

$$PbS + 2H^+ + [O] \rightarrow Pb^{2+} + S° + H_2O; \quad (C)$$

$$PbS + 8H^+ + 8[O] \rightarrow PbSO_4 + 4H_2O; \quad (D)$$

$$PbS + 2H^+ \rightarrow Pb^{2+} + H_2S. \quad (E)$$
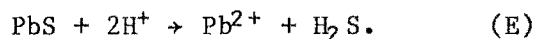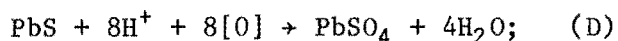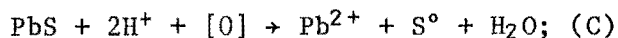
Reaction C shows that oxidative leaching of PbS will yield Pb salt and elemental S. Reaction D suggests $PbSO_4$ may form if the redox potential of the solution is too high. Reaction E indicates H_2S will form when leaching in acid solution if the redox potential is too low.

FIGURE 2.—Sulfur extraction apparatus.

The leach procedure was developed based on the above information. To avoid the generation of H_2S, one-fourth of the required oxidant was added to the H_2SiF_6 solution prior to the addition of PbS. During leaching, the redox potential in the leach mixture was controlled between 480 and 500 mV to prevent oxidizing the S into $PbSO_4$ as in reaction D. The reaction is exothermic, and it is necessary to add H_2O_2 slowly through a burette to avoid overheating the leach solution. After adding the H_2O_2, PbO_2 was added slowly to control the redox potential above 480 mV until the reaction was complete.

The reactions occurring during the oxidative leaching of PbS concentrates with H_2SiF_6 solution follow:

$$PbS + H_2O_2 + H_2SiF_6$$

$$\rightarrow PbSiF_6 + 2H_2O + S^\circ; \qquad (F)$$

$$PbS + PbO_2 + H_2SiF_6$$

$$\rightarrow PbSiF_6 + PbO + H_2O + S^\circ. \qquad (G)$$
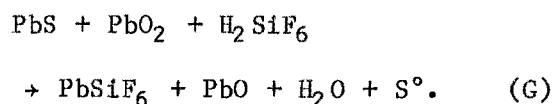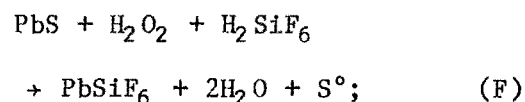
The PbO reacts with additional H_2SiF_6:

$$PbO + H_2SiF_6 \rightarrow PbSiF_6 + H_2O. \qquad (H)$$
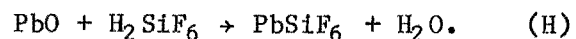
At the end of leaching, the mixture was filtered to separate the leachate from the residue. The residue consisted of elemental S and metal values. The leachate was sent to electrowinning to recover pure Pb metal.

LEACHING PARAMETERS--BENCH-SCALE TESTS

Oxidants

Lead extraction was 98 pct on the minus 400-mesh PbS samples and 96 pct on the as-received concentrates if H_2O_2 and PbO_2 were used as oxidants. Other oxidants, such as air, oxygen, ozone, HNO_3, and MnO_2, used alone or in combinations with H_2O_2, resulted in less than 80-pct Pb extraction during screening tests.

The effect of using different combinations of H_2O_2 and PbO_2 on PbS leaching was insignificant, as shown in table 3. Leaching experiments showed that H_2O_2 was a more efficient oxidizer to initiate the leach reaction; also, it was less expensive than PbO_2 ($0.51/kg versus $1.54/kg, as listed in the Chemical Marketing Reporter, April 28, 1986). Thus, it is beneficial to use H_2O_2 to leach PbS and only use PbO_2 at the end of the leach to avoid oxidizing PbS into $PbSO_4$.

Temperature

Leaching temperatures had a great influence on reaction rate and Pb extraction, as shown in table 4. When leaching below 80° C, the reaction rate was thought to be too slow for any practical application. Lead extraction was 96 pct when leaching at 95° C for 35 min using H_2O_2 and PbO_2 as oxidants. The leaching rate increased greatly, and the required leaching time was reduced from 90 to 35 min as the temperature increased from 90° to 95° C.

Time

Table 5 shows that Pb extraction was increased from 92 to 96 pct as leaching time increased from 30 to 60 min at 95° C.

Initial leaching was rapid as shown in figure 3, but as the elemental S formed

TABLE 3. - Effect of various amounts of oxidation agents on lead extraction

Test	H_2O_2 (35-pct), mL	PbO_2, g	Pb extraction, pct
1	0	16.0	92.0
2	2.5	17.0	95.0
3	5.0	9.8	95.0
4	7.5	8.1	96.8
5	10.0	5.7	95.1
6	19.0	0	96.0

TABLE 4. - Effect of time and temperature on lead extraction

Leach temp, °C	Leach time, min	Pb extraction, pct
50	335	62.3
70	240	91.5
80	90	76.0
90	75	90.1
90	90	97.5
95	35	96.0
95	75	96.5

TABLE 5. - Effect of leach time on lead extraction[1] at 95° C

	Leach time		
	30 min	60 min	90 min
Pb extraction..............pct..	92.3	95.6	96.4
Analysis of leachate, g/L:			
Pb...............................	163.500	176.700	180.300
Free H_2SiF_6...................	62.900	55.400	52.300
Zn...............................	.540	.619	.683
Fe...............................	.369	.415	.091
Cu...............................	.050	.091	.109
Ni...............................	.012	.014	.007
Co...............................	.006	.007	.007

[1]200 g PbS in 1 L H_2SiF_6 solution (200 g/L H_2SiF_6).
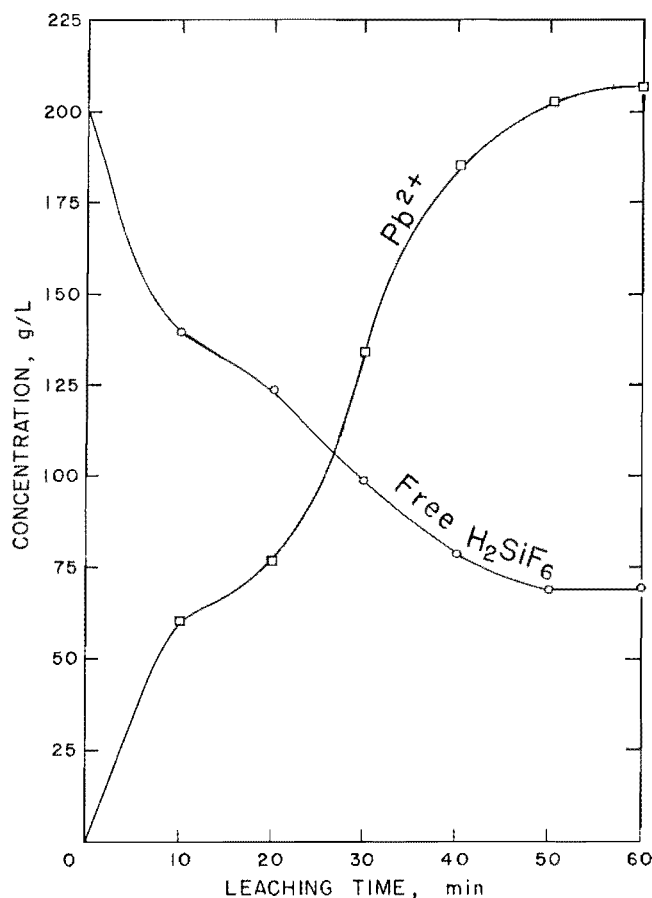
FIGURE 3.—Dissolution of Pb in H₂SiF₆ solution during oxidative leaching at 95° C.
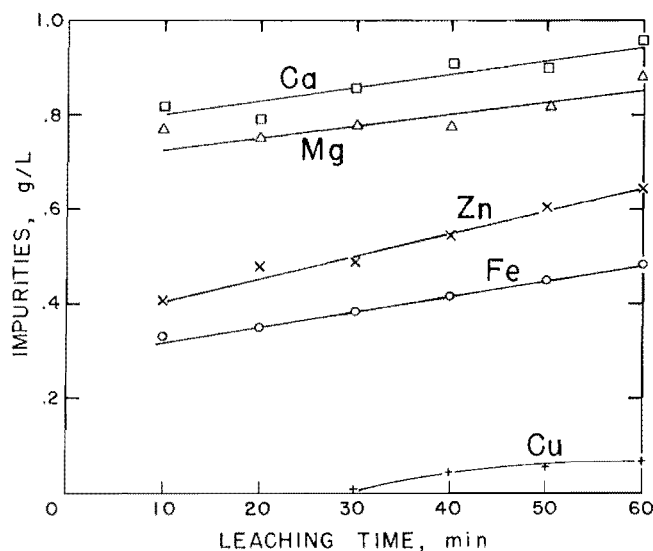
FIGURE 4.—Dissolution of impurities with leaching time.

and coated the PbS particles, further reaction was probably diffusion controlled and the leach rate was reduced. However, the effect of the S coating was not critical, because of the fine particle size of the PbS.

The dissolution of impurities (at 90° C) increased with leaching time as shown in figure 4.

Fluosilicic Acid

The amounts of PbS, PbO_2, and $H_2 SiF_6$ used in a leach test determined the concentration of $PbSiF_6$ and free $H_2 SiF_6$ in the pregnant leachate. Increasing the concentration of free $H_2 SiF_6$ above 56 g/L had no significant effect on Pb extraction, as shown in table 6; extraction of impurities decreased with decreasing concentration of free $H_2 SiF_6$.

Lead extractions of 96, 91, and 96 pct were achieved using $H_2 SiF_6$ solutions made from technical-grade, waste, and recycled acid, respectively, under similar conditions. Waste $H_2 SiF_6$ contained HCl (1.7 g/L) and $H_2 SO_4$ (0.64 g/L) as impurities, which formed some insoluble Pb salts during leaching, resulting in lower Pb extraction. Recycled electrolyte, in which impurities were removed during prior leaching, was as reactive as technical-grade $H_2 SiF_6$.

LARGE-SCALE LEACHING TESTS

Results of large-scale leaching experiments are given in table 7. Lead recoveries of 93.6, 91.1, and 95.6 pct were achieved when leaching with technical, waste, and recycled $H_2 SiF_6$, respectively. The results are in good agreement with the bench-scale tests, except longer times were required. The consumption of oxidants in the large-scale leach was about 30 pct less than in the bench-scale tests. Hydrogen peroxide seemed to react more efficiently in a large reactor, probably because it was introduced into the bottom of the reactor through a capillary tube.

TABLE 6. - Effect of H_2SiF_6 concentration[1] at 95° C for 90 min

| | H_2SiF_6 (from technical-grade acid) | | | |
	175 g/L	200 g/L	250 g/L	300 g/L
Pb extraction.............................pct..	89.0	97.5	95.4	95.7
Analysis of leachate, g/L:				
Pb...	180	179	184	177
Free H_2SiF_6...................................	32	56	94	133
Zn...	.57	.75	.82	1.00
Fe...	.53	.61	.61	.67
Cu...	.12	.13	.13	.18
Ni...	.015	.018	.017	.022

[1]20 g PbS in 100 mL H_2SiF_6 solution.

TABLE 7. - Large-scale leaching tests[1]

	Test 1	Test 2	Test 3
Test parameters:			
H_2SiF_6.................L..	40	50	75
H_2O.....................L..	44	26	14
PbS....................kg..	12	12	7.5
H_2O_2 (35-pct).........L..	4.5	4.13	4.1
PbO_2.................kg..	3.5	3.83	0.39
Temp...................°C..	95-98	95-98	95-98
Time...................h..	2.5	2.5	2.0
Results:			
Lead extraction.....pct..	93.6	91.1	95.6
Partial analysis:			
Leachate:			
Volume...............L..	83.3	75.14	95.6
Pb.................g/L..	137.2	147.3	83.7
Free H_2SiF_6........g/L..	98.4	103.4	93.4
Zn.................g/L..	0.36	0.36	0.50
Fe.................g/L..	0.34	0.34	0.71
Cu.................g/L..	0.09	0.02	0.04
Residue:			
Weight.............kg..	3.11	3.79	1.74
Pb.................pct..	25.6	28.4	23.3
S° (elemental)....pct..	43.7	31.5	49.0
S^T (total).......pct..	54.0	37.3	59.3
Zn.................pct..	4.03	2.43	3.2
Fe.................pct..	4.00	3.39	4.4
Cu.................pct..	2.18	1.70	2.5
Ni.................pct..	0.34	0.29	0.31
Co.................pct..	0.22	0.19	0.22
Ag.................pct..	<0.01	0.01	0.01

[1]Test 1: Technical H_2SiF_6 containing 396 g/L H_2SiF_6.
Test 2: Waste H_2SiF_6 containing 305 g/L H_2SiF_6.
Test 3: Recycled H_2SiF_6 containing 160 g/L H_2SiF_6.

ELECTROWINNING

Bench Scale (1-L Cell)

Lead cathode deposits of 99.9- to 99.99-pct purity were obtained from electrowinning the electrolyte prepared from

the leach solution at 35° C and 200 A/m² for 8 h. The purity of electrowon Pb depended on the amount of Cu^{2+} ions in the electrolyte, as shown in table 8.

Table 9 gives the results of 10 consecive recyclings of electrolyte in bench-scale leach-electrowinning experiments.

TABLE 8. - Analysis of electrolyte and the resulting lead deposits

| | H_2SiF_6 leach | | | |
	Technical grade	Waste	Recycled 1	Recycled 3
Leach time................min..	40	90	60	60
As-leached electrolyte:[1]				
Analysis, g/L:				
Pb............................	104	86	124	116
Free H_2SiF_6.................	93	92	106	63
Zn............................	0.35	0.49	0.63	0.68
Fe............................	0.20	0.42	0.68	0.75
Cu............................	0.004	0.152	0.038	0.016
Pb deposit, pct:				
Pb............................	99.99	99.96	99.99	99.99
Cu............................	0.0007	0.02	0.003	0.0025
Fe............................	0.0002	0.0025	<0.001	0.0002
Zn............................	<0.0001	<0.001	<0.001	<0.0001

[1]Additives, in g/L, 3 lignosite, 0.06 glue, and 0.8 P as H_3PO_4 were added to the leach solution prior to electrowinning.

TABLE 9. - Results of 10 consecutive recyclings of electrolyte
in bench-scale leach-electrowinning experiments

| Recycle No. | Leaching time, min[1] | Analyses of leachates, g/L | | | | | Electrowinning | |
		Pb	Free H_2SiF_6	Zn	Fe	Cu	CE, pct	EC, kW·h/kg
0[2]............	90	86	92	0.49	0.43	0.152	90	0.68
1.............	55	94	92	.54	.58	.016	89	.68
2.............	60	93	92	.70	.75	.010	87.4	.72
3.............	60	88	87	.68	.75	.016	87.4	.71
4.............	58	83	82	.70	.86	.004	86.3	.72
5.............	41	77	93	.75	.87	.008	86.7	.72
6.............	40	77	97	.77	.89	.007	86.1	.71
7.............	41	73	92	.72	.90	.009	84.8	.72
8.............	39	71	85	.70	.84	.007	87.1	.71
9.............	39	71	84	.69	.85	.008	85.8	.72
10............	47	80	82	.72	.92	.011	84.7	.73

CE Current efficiency. EC Energy consumption.
[1]Time used for adding H_2O_2 and PbO_2 to the PbS-H_2SiF_6 leach mixture.
[2]Bench-scale leaches using 100 g, or less, of PbS and 1.4 to 1.2 L of spent electrolyte, and electrowinning in 1-L cell at 1.5 A for 8 h.

iments. The success of these repeated leaching-electrowinning tests demonstrated the feasibility of the process. Average current efficiency and energy consumption were 86 pct and 0.72 kW·h/kg, respectively.

The effects of the electrolyte concentration and current density on Pb electrowinning were studied in an artificial electrolyte made from technical H_2SiF_6 and PbO to avoid any complication. Concentrations of 60 to 160 g/L Pb and 40 to 140 g/L free H_2SiF_6 had little effect on current efficiency and energy consumption, which ranged from 93 to 97 pct and 0.62 to 0.64 kW·h/kg, respectively. Table 10 gives the effect of current density; the current efficiency, energy consumption, and Pb production rate all increased with current density increasing from 150 to 300 A/m².

Large Scale (20-L Cell)

The 200-L electrolyte used for the 20-L cell test was prepared from solutions from large-scale leaching experiments. The solution contained higher amounts of Cu^{2+} (0.04 to 0.09 g/L) than the bench-scale leachates because a longer leaching time was required. The resulting electrowon Pb contained 99.96 Pb, 0.04 Cu, and <0.001 Zn and Fe. Table 11 gives the analysis of electrolyte (before and after use), the parameters used, and the results of electrowinning.

IMPURITIES

The major impurities in the PbS leach liquors are ions of Ca, Mg, Fe, Zn, Al, and Cu with trace amounts of Co and Ni. Results of tests showed Al, Ca, Mg, and

TABLE 10. – Effect of current density on lead electrowinning (at 35° C in 1-L cell for 8 h)

Current density, A/m²	Current efficiency, pct	Energy consumption, kW·h/kg	Wt of Pb deposit, g	Cell voltage, V
150	92	0.653	32.1	2.32
175	93	.647	38.0	2.33
200	94	.665	43.5	2.42
250	96	.674	55.2	2.50
300	97	.690	66.8	2.59

TABLE 11. – Twenty-liter-cell electrowinning tests

	H_2SiF_6 test 1		Recycle test 1	
	Initial	Final	Initial	Final
Electrolyte, g/L:				
Pb...............................	108.6	54.1	103.6	90.2
Free H_2SiF_6.....................	98.4	138.2	90.2	126.8
Zn...............................	0.46	0.47	0.50	0.51
Fe...............................	0.45	0.46	0.71	0.71
Cu...............................	0.085	0.014	0.043	0.007
Electrowinning:				
Current density.........A/m²..	250		180	
Time......................h..	120		147	
Weight of Pb deposits.....kg..	11.222		9.886	
Cell voltage...............V..	2.7		2.66	
Current efficiency.......pct..	96.3		95.1	
Energy consumption...kW·h/kg..	0.725		0.724	

Zn had no adverse effect on Pb electro-winning, except for Zn when its concentration was greater than 10 g/L. Copper ions tend to codeposit with the Pb on the cathode, especially at current densities greater than 200 A/m^2. The presence of ferric ions in the electrolyte reduces the current efficiency as plotted in figure 5. For example, as the concentration of ferric ions increases from 0 to 1 and then to 2 g/L, the current efficiency decreases from 95 to about 87 and then to less than 80 pct. The effect of trace amounts of Ni and Co was not studied.

Table 9 gives the results of 10 consecutive bench-scale leach, electrowinning experiments using recycled electrolyte with C treatment indicated that the buildup of major impurities could be controlled by controlling the leach parameters, e.g., by reducing the leaching time and lowering the free H_2SiF_6 concentration. As shown in figure 6, the
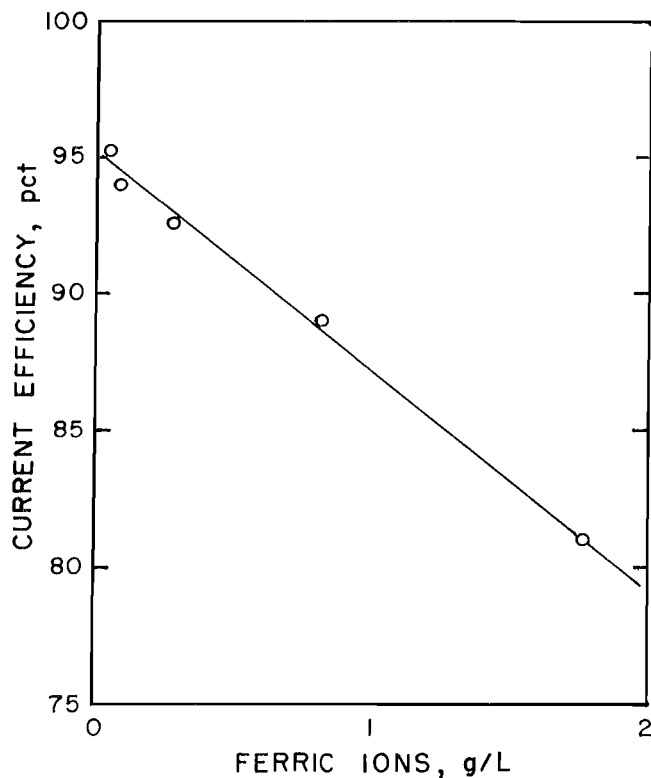
concentration of major impurities reached an equilibrium value after the fourth recycling of, in g/L, 2.67 Ca, 1.35 Mg, 0.88 Fe, 0.72 Zn, 0.38 Al, 0.008 Cu. Current efficiency and energy consumption for the 4th to 10th recycling were all close to 86 pct and 0.72 kW·h/kg, respectively, as compared to 95 pct and 0.64 kW·h/kg for single-cycle electrolyte.

SULFUR

Elemental S was separated from the leach residues by treating with a mixture of tetrachloroethylene (TCE) and kerosene at 115° C. There was 99-pct removal of the elemental S and over 90-pct recovery. Approximately 9 pct of the S did not crystallize out of solution upon cooling of the solvent. The average solvent recovery was about 92 pct after each

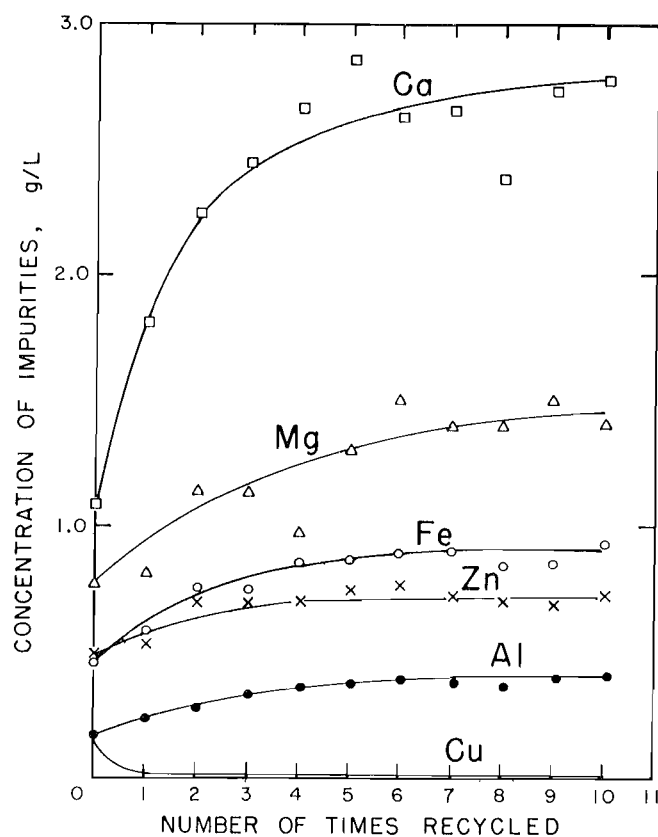FIGURE 5.—Effect of ferric ions on current efficiency.

FIGURE 6.—Impurity buildup with number of times recycled.

extraction, with most solvent loss occurring during filtration. The solvent was subsequently lost in the drying of elemental S. Fresh mixed solvent was added to the used to make up the required volume before recycling. The major impurity in the solvent was Pb at 0.005 g/L after the 10th recycling.

Less than 50 pct of the S was recovered from fresh solvent, but S recoveries averaged over 90 pct by the second recycling. One percent S° was left in the residue after treating the residue with solvent that was saturated with S° at ambient temperature. Table 12 details the effects of different ratios of TCE and kerosene on S extraction and indicates that the 1:1 ratio gives the highest recovery of S.

Wet residue, as received from the H_2SiF_6 leach, was heated in a 1:1 ratio TCE-kerosene. A heavy froth developed during heating, and an azeotropic mixture formed at 99.2° C. This temperature was too low for effective S extraction, and attempts to raise it only resulted in loss of solvent. Pure wet S under the same conditions did not produce the froth, and 113° C was easily obtained. The reason for the different reactions was not determined, but it was decided to use dried residue in all tests.

RESIDUE

As shown in table 13, removing the elemental S upgraded the H_2SiF_6 leach

TABLE 12. – Effect of various mixtures of kerosene and tetrachloroethylene (TCE) on sulfur recovery

Solvent	Temp,[1] °C	S recovery, pct	S in residue, pct
100 pct kerosene........	118	86.0	5.6
60 kerosene–40 TCE......	118	93.9	6.1
50 kerosene–50 TCE[2].....	113	95.0	1.1
40 kerosene–60 TCE......	116	94.3	4.4
100 pct TCE.............	118	90.4	5.4

[1]At the end of 5-min hold time, which started when the mixture reached 113° C.

[2]Solvent mixture used after 10 cycles; all other solvents were saturated with S° but recycled only 2 or 3 times.

TABLE 13. – Comparison of galena concentrates and residues

	PbS concentrates	H_2SiF_6 residue	S° removed residue	Releached residue
Weight....................g..	1,000	232	132	46.3
Partial analysis, pct:				
Pb.........................	74.4	25.6	50.1	5.4
S° (elemental)............	ND	43.7	1.1	NA
SO_4.....................	ND	6.1	13.2	NA
S (total).................	13.7	54.0	20.3	NA
Fe........................	1.30	4.0	6.1	15.9
Zn........................	1.10	4.0	5.2	12.2
Cu........................	.47	2.2	3.5	7.6
Ni........................	.09	.34	.50	1.26
Co........................	.07	.22	.37	.90
Ag........................	<.001	<.01	[1].035	[2].08

NA Not analyzed.   ND Not detected.   [1]11.3 tr oz/mt.   [2]25.7 tr oz/mt.

residue to 11 tr oz/mt Ag and 50 pct Pb, PbS, and PbSO$_4$ compounds.

The S-free residue was subjected to a three-step releach consisting of (1) oxidative leach with H$_2$SiF$_6$ to form PbSiF$_6$ and S°, (2) carbonation leach to convert PbSO$_4$ into PbCO$_3$ (2), and (3) H$_2$SiF$_6$ leach to dissolve PbCO$_3$. As a result of releaching, the residue was upgraded to

contain 26 tr oz/mt Ag and, in pct, 12.2 Zn, 7.6 Cu, 1.26 Ni, and 0.9 Co, while Pb was reduced from 50 to 5.4 pct.

This final residue became a marketable raw material. The analyses of each residue were given in table 13 to compare with the 1,000-g-PbS-concentrates analysis.

CONCLUSIONS

A process has been developed to produce Pb and elemental S of 99.99-pct purity from galena concentrates by hydrometallurgical and electrometallurgical methods. This process eliminates S gases and Pb emissions. The elemental S produced is easier to transport and store than is the H$_2$SO$_4$ generated by the pyrometallurgical method.

The unit processes investigated and optimized by bench-scale testing included oxidative leaching of PbS with H$_2$SiF$_6$, electrowinning the leach solution to produce high-purity Pb metal, carbon

treatment of spent electrolyte for recycling, and S removal from the leach residue by solvent extraction. The first three processes were also tested in larger scale experiments to demonstrate that they were technically feasible.

Pressure leaching of PbS concentrates in H$_2$SiF$_6$ acid under oxygen pressure is being investigated to reduce the need for H$_2$O$_2$ and PbO$_2$ as oxidants. Methods to remove ferric ions from electrolyte are being studied to reduce the energy consumption for electrowinning.

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