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# Pressure Leaching of Galena Concentrates To Recover Lead Metal and Elemental Sulfur

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

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BUREAU OF MINES



UNITED STATES DEPARTMENT OF THE INTERIOR

U.S. Bureau of Mines  
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**UNITED STATES DEPARTMENT OF THE INTERIOR  
Manuel Lujan, Jr., Secretary**

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### UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/m <sup>2</sup>	ampere per square meter	mV	millivolt
°C	degree Celsius	min	minute
g	gram	pct	percent
g/L	gram per liter	psi	pound (force) per square inch
h	hour	psig	pound (force) per square inch, gauge
L	liter	tr oz/mt	troy ounce per metric ton
mL	milliliter	wt pct	weight percent
mL/g	milliliter per gram		

# PRESSURE LEACHING OF GALENA CONCENTRATES TO RECOVER LEAD METAL AND ELEMENTAL SULFUR

By Agnes Y. Lee,<sup>1</sup> Ann M. Wethington,<sup>2</sup> and Ernest R. Cole, Jr.<sup>3</sup>

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## ABSTRACT

As part of the U.S. Bureau of Mines program to improve base metal leach systems, pressure leaching of galena (PbS) concentrates in fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) solution was investigated. Lead extraction was 93 pct when PbS was pressure leached in  $\text{H}_2\text{SiF}_6$  at 95° C with 200-psig  $\text{O}_2$  pressure for 40 min, using ferric nitrate [ $\text{Fe}(\text{NO}_3)_3$ ] as a catalyst. The effects of several catalysts,  $\text{O}_2$  pressure, time, and acid concentration on leaching were determined. The purified leach solution was electrowon to recover high-purity Pb metal. The  $\text{H}_2\text{SiF}_6$  used in leaching and electrowinning can be recycled continuously. A flow diagram was proposed based on this investigation.

Elemental sulfur ( $\text{S}^0$ ) was recovered from the leach residue by solvent extraction. A method was also developed for treating the final residue to segregate the important byproduct elements such as Ag, Cu, and Zn and enable their recovery by standard commercial processes.

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## INTRODUCTION

Hydrometallurgy offers the potential for reduced environmental hazards compared with the present pyrometallurgical smelting process. An effective oxidative leaching-electrowinning method to recover high-purity Pb metal and S<sup>0</sup> from PbS concentrates without S-bearing gases and Pb emissions has been developed (1).<sup>4</sup> This method consisted of leaching PbS concentrates in waste H<sub>2</sub>SiF<sub>6</sub> with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and lead dioxide (PbO<sub>2</sub>) as oxidants. After solid-liquid separation to obtain the lead fluosilicate (PbSiF<sub>6</sub>) solution and the residue containing S<sup>0</sup>, electro-winning of the aqueous PbSiF<sub>6</sub> solution at 35° C produced Pb metal and H<sub>2</sub>SiF<sub>6</sub> (2-5). The H<sub>2</sub>SiF<sub>6</sub> is then recycled to leach more PbS. Sulfur is recovered from the leach residue by solvent extraction.

A preliminary process evaluation of the above mentioned leaching-electrowinning method indicated that H<sub>2</sub>O<sub>2</sub> is an expensive oxidant for producing Pb. Therefore, a

method for O<sub>2</sub> pressure leaching of PbS was developed to solubilize Pb into H<sub>2</sub>SiF<sub>6</sub> solution, then Pb metal was recovered from the leachate by electro-winning.

The leaching parameters investigated were pressure, catalysts, temperature, acid concentration, and time. Since pressure leaching solubilized more impurities into the leachate, two methods for removing Fe, Ni, Co, Cu, and other impurities from the leachate were studied and compared. High-purity Pb metal was electro-won from the purified leachates with 95 pct current efficiency.

Elemental sulfur, a commercially valuable product, was recovered from the leach residue by solvent extraction. A method was developed for treating the final residue to segregate the other important byproduct elements such as Ag, Cu, and Zn and enable their recovery by standard commercial processes.

## MATERIALS, EQUIPMENT, AND PROCEDURES

### PRESSURE LEACHING

PbS concentrates used for leaching experiments were obtained from a Missouri Pb smelter. The concentrates were dried, mixed, and sampled by screen and chemical analysis (1) and were found to contain, in percent, 74.4 Pb, 13.7 S, 1.25 Fe, 1.1 Zn, and 0.47 Cu with trace amounts of Ni, Co, and Ag. Seventy percent of the PbS concentrates passed through a 400-mesh screen.

The leaching reagents were H<sub>2</sub>SiF<sub>6</sub>, O<sub>2</sub> pressure, and distilled water. Technical grade HNO<sub>3</sub>, PbO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and Zn(NO<sub>3</sub>)<sub>2</sub> were used as oxidants and catalysts for the pressure leaching. Three types of H<sub>2</sub>SiF<sub>6</sub> solutions—technical grade acid, waste acid from a phosphate fertilizer company (2), and recycled spent electrolyte—were used in the leaching experiments. The analysis of the three solutions is given in table 1. The recycled electrolyte also contained, in grams per liter, 1.1 Ca, 0.78 Mg, 0.015 Ni, and 0.006 Co.

Table 1.—Partial analysis of H<sub>2</sub>SiF<sub>6</sub> solution used for leaching experiments, grams per liter

H <sub>2</sub> SiF <sub>6</sub> solutions	H <sub>2</sub> SiF <sub>6</sub>	Pb	Fe
Technical ..	396	0.002	0.005
Waste . . . .	305	.020	.036
Recycled ..	157	23.8	.480

Pressure leaching experiments were conducted in a standard Parr<sup>5</sup> pressure reactor as shown in figure 1. This

<sup>4</sup>Italic numbers in parentheses refer to items in the list of references at the end of this report.

<sup>5</sup>Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

1-L stainless steel reactor was modified with a Teflon (fluorocarbon polymer) impeller and Teflon stirring shaft to provide vigorous mixing and a Teflon dip tube to allow O<sub>2</sub> to be introduced below the surface of the liquid. The surfaces of the thermowell and reactor head were protected from the acid environment with printed circuit board maskant. A 1-L glass liner in the reactor was used to contain the corrosive leaching slurry.



Figure 1.—Pressure leaching of galena concentrates.

Unless otherwise stated, the following procedure was used for all tests. After the addition of 300 mL of solution containing 160 g/L  $\text{H}_2\text{SiF}_6$  to the 1-L glass liner, 2 g of  $\text{PbO}_2$  and 2 mL of  $\text{HNO}_3$  were added before the addition of 30 g PbS concentrates and the desired catalyst. The  $\text{PbO}_2$  added initially with the  $\text{H}_2\text{SiF}_6$  supplied  $\text{O}_2$  and prevented the formation of hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas (1), and  $\text{HNO}_3$  acted as a strong oxygen carrier (6) to enhance the efficacy of pressurized  $\text{O}_2$ . The mixture was then placed in the autoclave, pressurized to 200 psig with  $\text{O}_2$ , and heated to 80° C. At that temperature, an exothermic reaction caused the leaching temperature to climb rapidly from 95° to 100° C, after which external cooling or heating was used to maintain the temperature about 95° C for 1 h. At the end of the hour, the reaction vessel was removed from the heater and rapidly cooled to room temperature before opening. The reaction mixture was filtered and washed to separate the residue from the leachate. Elemental sulfur was extracted from the residue using a 50:50 mixture of tetrachloroethylene and kerosene at 115° C as described in a previous Bureau report (1).

$\text{H}_2\text{SiF}_6$  and Pb concentrations in the leachates were determined by titration with sodium hydroxide (NaOH) and EDTA (disodium ethylenediaminetetraacetate), respectively. The concentration of the impurities was determined by atomic absorption.

### PURIFICATION OF LEACHATES

Two methods for purifying pressure-leached solutions were investigated. In both methods, reagent grade chemicals and general laboratory equipment was used.

In method 1, Fe in the leachate was removed with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) by precipitation as an insoluble ferric phosphate compound (7) under controlled conditions of

pH and redox potential. The procedure used was as follows: (1) the redox potential was increased to about 350 mV versus an Ag-AgCl (silver chloride) reference electrode by adding  $\text{H}_2\text{O}_2$ , and (2) the required  $\text{H}_3\text{PO}_4$  was added and the pH adjusted to 0.9 with ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). The leachate was heated to 50° C, the pH readjusted to 1.9, and the temperature was maintained between 50° and 60° C for 1 h. Filtration to remove the Fe compound was rapid. The amount of  $\text{H}_3\text{PO}_4$  (85 pct) needed to react with Fe was 1.4 mL/g Fe, roughly 16 pct more than the stoichiometric requirement. Copper was eliminated by cementation with Pb powder.

In method 2, Pb in the leachate was precipitated with a stoichiometric amount of sulfuric acid ( $\text{H}_2\text{SO}_4$ ), leaving all the impurities in the  $\text{H}_2\text{SiF}_6$  solution. Filtering out the lead sulfate ( $\text{PbSO}_4$ ) left the solution to be recycled to leach more PbS. The  $\text{PbSO}_4$  was then reacted with ammonium carbonate [ $(\text{NH}_4)_2\text{CO}_3$ ] solution to form lead carbonate ( $\text{PbCO}_3$ ). Fresh, high-purity  $\text{H}_2\text{SiF}_6$  or recycled electrolyte was used to dissolve the  $\text{PbCO}_3$  to generate  $\text{PbSiF}_6$  electrolyte (2).

### LEAD ELECTROWINNING

Lead electrowinning experiments were performed in  $\text{PbSiF}_6$  electrolyte at 35° C and 200 A/m<sup>2</sup> current density with  $\text{PbO}_2$ -coated Ti anodes (8) and Pb sheet cathodes using an electrowinning method developed in previous work (3-4). Three varieties of electrolytes—the as-leached solution, solution purified with  $\text{H}_3\text{PO}_4$ , and solution purified with  $\text{H}_2\text{SO}_4$ —were electrowon to study the effectiveness of purification methods. The leveling agent and grain refiner added to the electrolyte were 4 g/L calcium lignin sulfonate and 0.05 g/L animal glue.

## RESULTS AND DISCUSSION

### PRESSURE LEACHING

#### Recycled $\text{H}_2\text{SiF}_6$

Pressure leaching of PbS concentrates with recycled spent electrolyte resulted in a much higher Pb extraction than leaching with technical grade  $\text{H}_2\text{SiF}_6$  or waste  $\text{H}_2\text{SiF}_6$  as shown in table 2. Lead extraction was 93 pct for the recycled  $\text{H}_2\text{SiF}_6$  compared with 40 and 69 pct for the technical and waste  $\text{H}_2\text{SiF}_6$ , respectively. Apparently, the impurities contained in the recycled electrolyte acted as catalysts during leaching.

**Table 2.—Results of pressure leaching PbS in different  $\text{H}_2\text{SiF}_6$  solutions**

$\text{H}_2\text{SiF}_6$ (160 g/L) leaching solution	Pb extraction, pct
Technical . . .	40
Waste . . . . .	69
Recycled . . .	93

### Oxygen Pressure

The effect of  $\text{O}_2$  pressure on leaching is given in table 3. The leaching solution was recycled  $\text{H}_2\text{SiF}_6$ . Pressure leaching using 200 psig of  $\text{O}_2$  gave the highest Pb extraction, therefore this pressure was used for the balance of the experimental work.

**Table 3.—Effect of oxygen pressure on lead extraction**

$\text{O}_2$ pressure, psig	Pb extraction, pct
150 . .	87.8
175 . .	90.0
200 . .	93.0
250 . .	91.6

## Temperature

Previous studies (*I*) indicated atmospheric leaching of PbS was an exothermic reaction, and the optimum leaching temperature was found to be 95° C. During pressure leaching, the reaction started at 80° C. The temperature of the leaching slurry rose rapidly to 95° C or more. Since temperatures above 105° C resulted in a breakdown of the acid, often external cooling was required to prevent overheating.

## Catalysts

HNO<sub>3</sub> and several inorganic ions were investigated as possible catalysts. The effect of HNO<sub>3</sub> in a 30-min leach in recycled electrolyte is described in table 4. Leaching was discontinued after 30 min because with longer time it was difficult to distinguish between the effects of the different catalysts. Without using HNO<sub>3</sub> in the leaching solution, Pb extraction was only 28.4 pct in recycled electrolyte. Adding 1 mL of HNO<sub>3</sub> (1.008 g/mL) was not sufficient, while the use of 1.5 to 3.0 mL resulted in 87 to 91 pct extraction. Impurity extraction and insoluble PbSO<sub>4</sub> formation increased proportionally with additional HNO<sub>3</sub>. The optimum amount of HNO<sub>3</sub> was determined to be 1.5 to 2.0 mL for each 30 g of PbS leached to avoid excessive formation of PbSO<sub>4</sub>, which is not soluble in H<sub>2</sub>SiF<sub>6</sub> solution.

Table 4.—Effect of HNO<sub>3</sub> concentration on lead extraction

HNO <sub>3</sub> used, mL	Pb extraction, pct	Residue	
		Weight, g	SO <sub>4</sub> , pct
0 . . . .	28.4	23.72	ND
1 . . . .	55.0	19.64	ND
1.5 . . .	87.4	10.13	3.6
1.75 . .	87.4	9.87	4.7
2 . . . .	88.6	9.58	5.8
2.5 . . .	88.8	9.63	7.5
3 . . . .	91.1	9.18	10.7

ND Not determined.

A catalyst screening study indicated that the addition of Fe(NO<sub>3</sub>)<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, or Ni(NO<sub>3</sub>)<sub>2</sub> to the technical grade H<sub>2</sub>SiF<sub>6</sub> solution also increased Pb extraction. In table 5, Fe and Ni were better than Cu and Zn with Fe being the most efficient catalyst. Both Fe and Ni were the subjects of further study.

Table 6 shows the effect of increasing amounts of Fe and Ni ions in the solution on percent of Pb extraction as well as an analysis of the resulting leach liquors. For these tests, 30 g of PbS concentrates were pressure leached in 300 mL of 160-g/L technical grade acid for 1 h. Table 6 also gives the analysis of the resulting leachates, which contained Fe, Cu, Ni, and Co as impurities.

Table 5.—Effect of catalyst on lead extraction

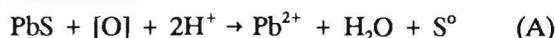
Catalyst added	Pb extraction, pct	Leachate (0.350 L), g/L				
		Pb	Fe	Zn	Cu	Ni
None . . . . .	40	17.6	0.37	0.25	0.10	0.02
1 g Zn(NO <sub>3</sub> ) <sub>2</sub> . . .	45	19.4	.45	2.43	.10	.02
1 g Cu(NO <sub>3</sub> ) <sub>2</sub> . .	61	42.0	.51	.20	.47	.02
1 g Ni(NO <sub>3</sub> ) <sub>2</sub> . . .	79	55.0	.77	.59	.12	.69
1 g Fe(NO <sub>3</sub> ) <sub>3</sub> . . .	92.7	62.7	1.66	.70	.39	.07

Table 6.—Effect of iron and nickel ion concentration on lead extraction

Addition, g	Pb extraction, pct	Leachate (0.345 L), g/L					
		Pb	Free H <sub>2</sub> SiF <sub>6</sub>	Fe	Cu	Ni	Co
Fe(NO <sub>3</sub> ) <sub>3</sub> :							
0.25 . .	89.8	62.6	73.6	0.99	0.26	0.059	0.034
0.50 . .	92.7	65.6	69.2	1.19	.33	.061	.036
1.00 . .	92.7	65.6	69.1	1.34	.35	.064	.035
2.00 . .	93.8	66.2	67.9	1.79	.37	.069	.037
Ni(NO <sub>3</sub> ) <sub>2</sub> :							
0.25 . .	51.6	35.9	107	.30	.002	.017	.038
0.50 . .	65.9	45.9	92.6	.47	.080	.25	.025
1.00 . .	79.0	59.5	86.1	.68	.120	.65	.027
2.00 . .	85.5	59.5	74.3	.77	.177	1.21	.032

It became apparent after these tests that the Fe (0.48-g/L) and (table 1) content of recycled electrolyte contributed to the increased Pb extraction when this electrolyte was used for leaching in the earlier tests. For this reason and because the use of recycled electrolyte would more closely duplicate industry practice, recycled electrolyte was used for the balance of the experiments.

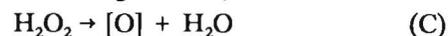
The ideal oxidative leaching of PbS in an acid medium is given by reaction A.



Since PbSO<sub>4</sub> is not soluble in H<sub>2</sub>SiF<sub>6</sub>, any PbSO<sub>4</sub> formed must be filtered out and treated separately, therefore further oxidation of sulfide sulfur to sulfate as in reaction B should be minimized.



Here [O] is written for the equivalent of one atom of oxygen in the oxygen carrier. For example, H<sub>2</sub>O<sub>2</sub> used in the previous atmospheric leaching studies (*I*) is an oxidant that provided [O] continuously through the continued additions of H<sub>2</sub>O<sub>2</sub> to the leaching mixture, as in reaction C.



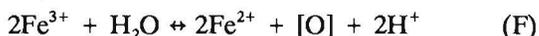
The reaction is not reversible, so H<sub>2</sub>O<sub>2</sub> is an oxidant, but not an oxygen carrier. Bjorling (*6*) suggested that O<sub>2</sub> gas does not attack PbS or any other metal sulfide crystal. This O<sub>2</sub> pressure leaching study indicated that the [O] required to oxidize PbS was provided continuously by

HNO<sub>3</sub> and O<sub>2</sub> according to reactions D and E, since HNO<sub>3</sub> acted as an oxygen carrier.



During pressure leaching, the oxidizing potential was determined by the amount of HNO<sub>3</sub> used and the O<sub>2</sub> pressure applied.

In addition, the ions of Fe and other metals contained in the leaching solution probably acted as catalysts to promote the reactions between HNO<sub>3</sub> and O<sub>2</sub> for producing [O]. Iron ions might also act as an oxygen carrier (6) as in reaction F.



Lead extraction was only 40 pct in the technical H<sub>2</sub>SiF<sub>6</sub> leaching as listed in table 2 using HNO<sub>3</sub>, but not the Fe catalyst, and Pb extraction was only 28 pct in the recycled H<sub>2</sub>SiF<sub>6</sub> leaching as listed in table 4 using Fe<sup>3+</sup> without the use of HNO<sub>3</sub>. These results clearly indicate that the synergistic effect of HNO<sub>3</sub> and Fe<sup>3+</sup> ions was essential to the success of pressure leaching of PbS concentrates.

#### Time

All tests were from 30- to 60-min long with timing started when the designated temperature was attained.

#### Free H<sub>2</sub>SiF<sub>6</sub>

The effect of free H<sub>2</sub>SiF<sub>6</sub> concentration on Pb extraction was studied. Tests were conducted using 30, 40, and 50 g of PbS concentrates in 300 mL of recycled spent electrolyte at 200 psig O<sub>2</sub> at 95° to 100° C for 60 min. In general, metal extraction decreased with free acid concentration as listed in table 7.

Table 7.—Effect of free H<sub>2</sub>SiF<sub>6</sub> concentration on metal extraction

PbS concentrates, g	Extraction, pct				Free H <sub>2</sub> SiF <sub>6</sub> in leachate, g/L
	Pb	Fe	Zn	Cu	
30	93.4	100	69	100	92.4
40	93.4	100	53	91	79.2
50	92.5	77.9	52	79.7	52.1

## PURIFICATION OF LEACHATES AND ELECTROWINNING

Attempts to electrowin the as-leached solutions to recover the Pb were only partly successful. Both current efficiencies and cathode morphologies were marginal, and it was obvious that it would be necessary to reduce the amount of impurities in the solution before electrowinning. Two methods of purification were investigated, and an analysis of the resultant solutions is given in table 8 as well as an analysis of the as-leached PbSiF<sub>6</sub> solution for comparison.

In method 1, a process developed by Dahnke (7) was used to remove the Fe as an insoluble ferric phosphate (FePO<sub>4</sub>) compound. The low (1.9) pH required for this method was a major advantage over the traditional Fe removal process that requires a pH of from 3 to 5 to precipitate the Fe as ferric hydroxide [Fe(OH)<sub>3</sub>], which is very difficult to filter. In contrast, the FePO<sub>4</sub> precipitate is readily filterable.

The pH of the as-leached solution was ~0, and it was necessary to add a large amount of concentrated NH<sub>4</sub>OH (67 mL for 1 L of leachate) to raise the pH to 1.9. NH<sub>4</sub>OH was chosen to increase the pH because NaOH and KOH formed a jell-like sodium fluosilicate (Na<sub>2</sub>SiF<sub>6</sub>) or potassium fluosilicate (K<sub>2</sub>SiF<sub>6</sub>) precipitate.

Unfortunately, method 1 was only partly successful. Iron was reduced by about 1 g/L and much of the Cu was removed by the Pb powder addition after Fe removal, but the solution still contained the majority of the Co, Ni, and Zn as indicated in table 8, and the current efficiency was only 83 pct. Also, about 8 pct of the Pb had been removed. Nickel and cobalt could be removed by cementation on Pb powder at pH 3.5, but most of the Pb was lost at this pH as well.

In method 2, the Pb was precipitated with stoichiometric additions of H<sub>2</sub>SO<sub>4</sub> leaving the impurities in the solution. The PbSO<sub>4</sub> was then carbonated with ammonium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and the resulting PbCO<sub>3</sub> was dissolved in H<sub>2</sub>SiF<sub>6</sub> (1) giving a relatively pure solution (table 8) that upon subsequent electrowinning gave 95 pct current efficiency and 99.999 pct Pb deposit.

There are several advantages to the use of method 2: (1) low H<sub>2</sub>SO<sub>4</sub> consumption, only a stoichiometric amount is needed to precipitate Pb; (2) the ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] generated during the conversion of the PbSO<sub>4</sub>

Table 8.—Analyses of PbSiF<sub>6</sub> solution and current efficiency of lead electrowinning

PbSiF <sub>6</sub> solution	Analysis, g/L							Current efficiency, pct	Cathode deposit, Pb pct
	Pb	Free H <sub>2</sub> SiF <sub>6</sub>	Fe	Zn	Cu	Ni	Co		
As-leached	79.8	91.2	1.25	0.770	0.310	0.065	0.034	70	99.96
Purified:									
H <sub>3</sub> PO <sub>4</sub>	73	90	.29	.620	.004	.060	.030	83	99.99
H <sub>2</sub> SO <sub>4</sub>	96	82	.03	.007	<.001	<.001	<.001	95	99.999

to  $\text{PbCO}_3$  can be used as fertilizer or recycled to recover  $\text{NH}_3$  (1); (3) the solution stripped of Pb can be recycled and the impurities catalyze the pressure leaching; and (4) the necessity to remove calcium lignin sulfonate from the spent electrolyte is eliminated because spent electrolyte is used for dissolving  $\text{PbCO}_3$  not for pressure leaching (1).

### LEACH RESIDUES

A typical residue, ~8.5 g, left from a 90 pct Pb extraction leach was partially analyzed and found to contain, in percent, 23 Pb, 2.1 Fe, 2.0 Zn, 1.1 Cu, 37.1  $\text{S}^\circ$ , and 6.4  $\text{SO}_4$ .

After S removal, the Pb concentration in the  $\text{S}^\circ$  free residue was upgraded to 58 pct, and the amounts of Cu, Fe,  $\text{SO}_4$ , and Zn were increased proportionally. The major Pb compounds in the residue were identified as  $\text{PbSO}_4$ , unreacted PbS, and varying combinations of Pb with  $\text{PO}_4$ , Si, and F. The residue was pressure leached with  $\text{H}_2\text{SiF}_6\text{-O}_2$  to solubilize PbS followed by a carbonation leach to convert  $\text{PbSO}_4$  to  $\text{PbCO}_3$  and an  $\text{H}_2\text{SiF}_6$  leach to dissolve the  $\text{PbCO}_3$  (1). The final residue still contained 5 pct Pb. In addition, it also contained, in percent, 0.9 Co, 8 Cu, 1 Ni, and 12 Zn, as well as ~26 tr oz/mt Ag making it a valuable byproduct.

Various procedures have been tested, including leaching with brines (9-10), acids (11), or alkalis; roasting before leaching (12); and pressure leaching to recover the metal

values from the final residue. The brine leaches,  $\text{FeCl}_3$  or  $\text{NaCl}$ , solubilized only one-half of the Ag and even less of the other metal values. Alkali leaching was only marginally effective. An  $\text{H}_2\text{SO}_4$  leach using residues roasted at  $500^\circ\text{C}$  produced the most promising results. A study of leaching conditions using a  $2^3$  factorial design with two constants and three variables was completed. The constant was a pulp containing 10 wt pct residues in 1.8 M  $\text{H}_2\text{SO}_4$ , with temperature (T), time (t), and pressure (P) as variables. The range of the variables was as follows:

	Low	High
P ..	200 psi	300 psi
T ..	$145^\circ\text{C}$	$165^\circ\text{C}$
t ...	30 min	1 h.

The results, based on the amount of residue remaining after leaching, indicated T was the most significant variable with the interaction of P and t having a possible effect. One other run was completed using conditions far outside the factorial limits. Results from runs at the upper and lower limits of the factorial design test and the extra run are tabulated in table 9. These results indicate Pb and Ag can be almost completely separated from the other metal values in the leach residue. This should facilitate their recovery.

Table 9.—Results of factorial design tests<sup>1</sup>

Distribution, pct	Test 1		Test 2		Test 3	
	Filtrate	Residue	Filtrate	Residue	Filtrate	Residue
Pb .....	ND	100	ND	100	ND	100
Fe .....	99.5	.5	98.8	1.2	14.3	85.8
Zn .....	100	ND	99.4	.6	5.8	95.2
Cu .....	98.3	1.7	97.6	2.4	18.7	81.3
Ag .....	ND	100	ND	100	ND	100
Ni .....	94.8	5.2	94.2	5.8	31.1	69.0
Co .....	98.5	1.5	97.4	2.6	31.2	68.5

ND Not determined.

<sup>1</sup>Leaching conditions:

Test	Pressure, psig	Temp, °C	Time, min
1 ..	300	165	60
2 ..	200	145	30
3 ..	50	100	30

### CONCLUSIONS

A conceptual flow diagram was developed to recover Pb metal and  $\text{S}^\circ$  from PbS concentrates (fig. 2), without the S gases and Pb emissions attendant to the present pyrometallurgical Pb smelting process. The process consists of (1) pressure leaching of PbS concentrates in  $\text{H}_2\text{SiF}_6$  solution with  $\text{O}_2$  pressure as a replacement for the large amounts of  $\text{H}_2\text{O}_2$  required as an oxidant in the atmospheric leaching process (1), (2) purification of leachates,

and (3) electrowinning of Pb metal from the purified  $\text{PbSiF}_6$  solution.

This method produces high-purity (99.999 pct) Pb metal, although extra  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{CO}_3$  are needed to purify the leachate, but  $(\text{NH}_4)_2\text{SO}_4$  is generated as a valuable byproduct that has potential application as a fertilizer.

Other advantages are (1)  $\text{H}_2\text{SiF}_6$  can be recycled continuously in the pressure leaching process without removing

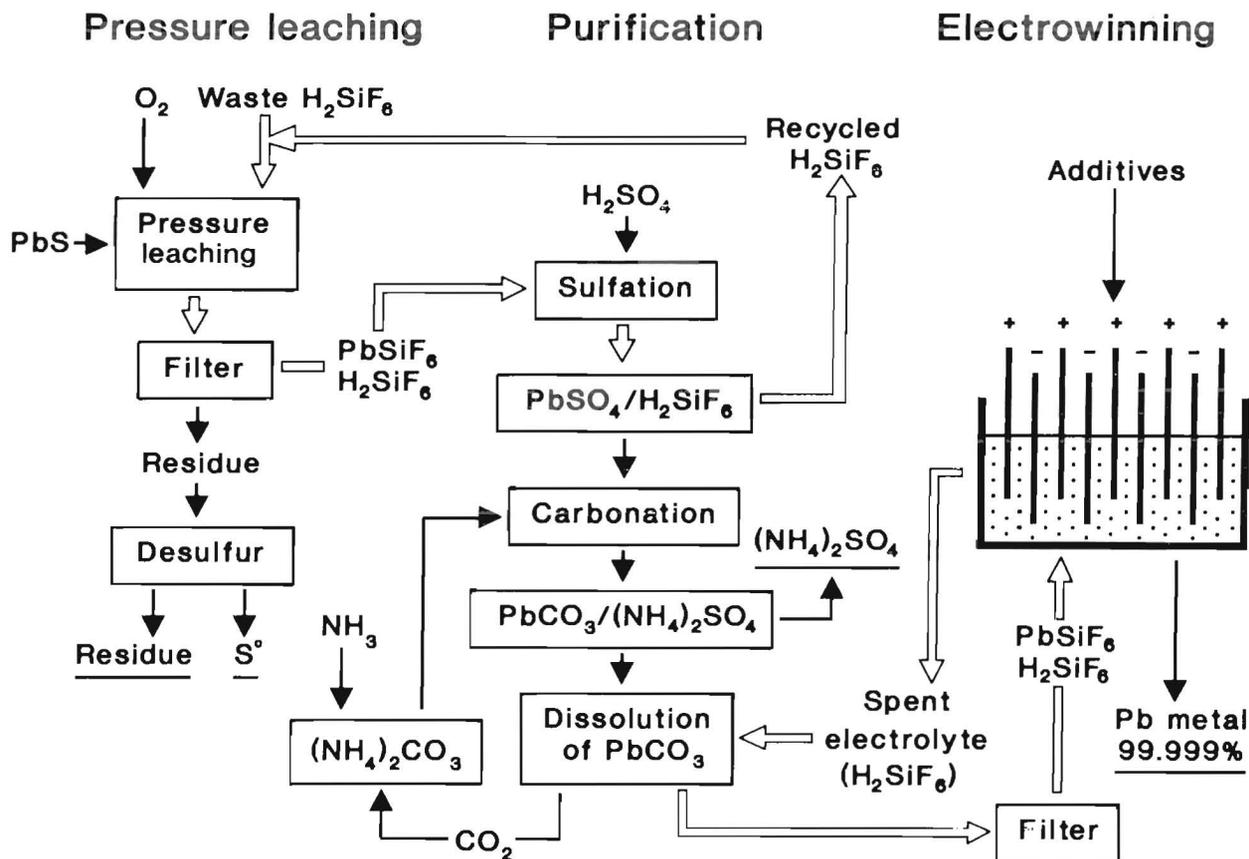


Figure 2.—Flow diagram for pressure leaching, purification, and electrowinning.

catalytic Fe and Ni ions, although at some point a bleed stream will probably be necessary, and (2) spent electrolyte can be used to dissolve  $\text{PbCO}_3$  without activated carbon treatment to remove the organic additives, such as calcium lignin sulfonate and glue, used as leveling agents during electrowinning (5).

More work is necessary to perfect the method for recovery of values from the residue since the economics of the process will probably be dictated by the value of the recovered byproduct metals.

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