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# Recovery of Silver, Gold, and Lead From a Complex Sulfide Ore Using Ferric Chloride, Thiourea, and Brine Leach Solutions

By R. G. Sandberg and J. L. Huiatt



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A·h	ampere hour	m	meter
A/m <sup>2</sup>	ampere per square meter	<u>M</u>	molar
°C	degree Celsius	mL	milliliter
cm	centimeter	mL/min	milliliter per minute
g	gram	min	minute
g/L	gram per liter	oz	troy ounce
h	hour	oz/st	troy ounce per short ton
kg	kilogram	pct	percent
L	liter	ppm	part per million
L/min	liter per minute	V	volt
lb/st	pound per short ton		

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# RECOVERY OF SILVER, GOLD, AND LEAD FROM A COMPLEX SULFIDE ORE USING FERRIC CHLORIDE, THIOUREA, AND BRINE LEACH SOLUTIONS

By R. G. Sandberg<sup>1</sup> and J. L. Huiatt<sup>2</sup>

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## ABSTRACT

The Bureau of Mines investigated a hydrometallurgical procedure to recover gold, silver, and byproduct lead from a complex lead-zinc sulfide ore. A ferric chloride ( $\text{FeCl}_3$ ) preleach, at 40° C in 6 h, extracted about 50 pct of the zinc and formed insoluble silver and lead chlorides. Subsequent acid thiourea leaching, for 1 to 3 h at 40° C, extracted about 85 pct of the gold and silver. Lead chloride was solubilized from the remaining residue with NaCl brine solution at 55° C in 1 h. Lead metal was recovered from the brine solution in an electrolytic cell with an anion permselective membrane at a current efficiency of 95 pct and current density of 100 A/m<sup>2</sup>. Spent  $\text{FeCl}_3$  leach solution was reoxidized in the anode compartment at a current efficiency between 75 and 95 pct.

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## INTRODUCTION

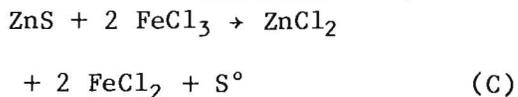
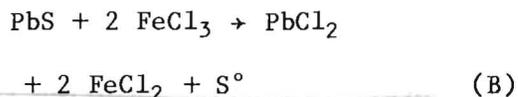
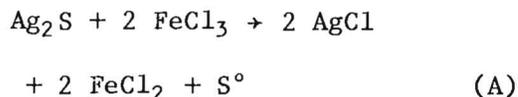
Independent mine operators have difficulty marketing complex gold-silver concentrates and ores (1).<sup>3</sup> Generally, complex sulfide concentrates and ores cannot be handled by existing smelters. Even when handling them is technically possible, smelter charges and transportation costs become limiting factors. Hydrometallurgical methods are seriously being considered to provide a simple, inexpensive, low-pollution process to treat complex gold-silver ores on a small scale because building small smelters is generally not economically feasible.

Recovery of gold and silver has been based on caustic cyanidation since the 1890's. However, not all ores are amenable to cyanidation, particularly those containing sulfides (chalcopyrite, sphalerite, galena, etc.). Gold and silver extraction is usually low and cyanide consumption is high because of base metal complex formation. Several researchers (2-5) reported acidic thiourea to be more reactive and less affected by sulfide minerals in complex ores; but, as with caustic cyanide, gold and silver extraction is usually low with complex sulfide gold-silver ores. A procedure to extract silver from sulfide ores with FeCl<sub>3</sub> was patented by Hey in 1922 (6). Considerable work was completed by Wong (7) to recover lead from a galena concentrate with a combined FeCl<sub>3</sub>-NaCl leach solution. Because both lead and silver were solubilized, silver recovery from high-silver ore would be difficult. Similar methods were used by Scheiner (8-10) to extract silver and other metals from a complex sulfide concentrate. These methods required a Cl<sub>2</sub>-O<sub>2</sub> or FeCl<sub>2</sub>-O<sub>2</sub> leach at elevated pressure and temperature to form insoluble lead and silver chlorides, which were then solubilized in hot brine (PbCl<sub>2</sub>) and strong caustic cyanide solutions (AgCl).

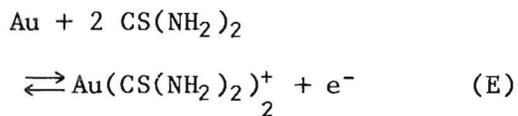
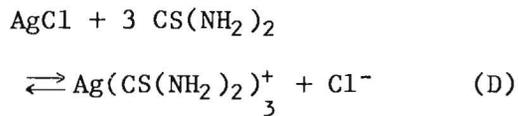
The objective of this Bureau of Mines study was to investigate a hydrometallurgical method to recover silver, gold, and

byproduct lead from a complex sulfide ore using an acid system at atmospheric pressure and moderate temperature. The proposed method consists of--

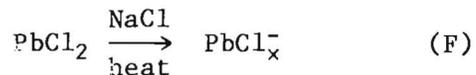
1. Leaching a sulfide ore with an acidic FeCl<sub>3</sub> solution to form insoluble silver and lead chlorides. A portion of the zinc is also extracted:



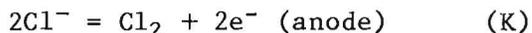
2. Solubilizing the silver and gold with an acidified thiourea leach solution and then recovering the gold and silver with ion-exchange resin, aluminum precipitation, or electrolysis:



3. Solubilizing the PbCl<sub>2</sub> with an acidified NaCl brine leach solution:



4. Recovering lead metal and regenerating the spent FeCl<sub>3</sub> leach solution by electrolysis:



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

## MATERIALS

Material used in this study was obtained from a deposit in central Nevada. The chemical analysis of the ore is listed in table 1.

TABLE 1. - Chemical analysis of ore

	<u>Conc, pct</u>
Ag.....	158
Au.....	1.1
Pb.....	39
Zn.....	18
Fe.....	7.9
As.....	.81
Cd.....	.29
Mn.....	.22
Cu.....	.086
Co.....	.016
<hr/>	
<sup>1</sup> oz/st.	

The sample was dry-ground to minus 10 mesh in a laboratory roll crusher. Charges weighing 1 kg were wet-ground in distilled water at 50 pct solids using a 10-kg ball charge. Total grinding time was 45 min, which resulted in 90 pct of the material passing 200 mesh. The slurry was filtered, and the filter cake was dried at ambient temperature for several days.

Reagent-grade chemicals were used throughout the investigation. Analyses were conducted by atomic adsorption spectroscopy (AAS) or by fire assay. Gold analysis was somewhat erratic, and the results varied when test series were repeated; however, the trends were similar. This variation was probably because the gold was unevenly dispersed throughout the ore.  $\text{FeCl}_2$  concentration was determined by a standard dichromate titration and thiourea by an iodine titration.

## OPERATING PROCEDURE, RESULTS, AND DISCUSSION

## LEACHING

Ferric Chloride

Because Wong (7) extensively investigated extraction of lead from galena concentrates, only minimal effort was expended to investigate the  $\text{FeCl}_3$  leaching phase of the process. However, because Wong's work was with a high-grade galena concentrate (74 pct Pb), some research was conducted to obtain maximum silver chloridization.

$\text{FeCl}_3$  leach solution was prepared by adding reagent-grade  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  to water acidified to pH 0.5 with HCl, and then heating to 40° C in a Pyrex<sup>4</sup> beaker. Samples were mixed with the heated leach solution for a specified time, then filtered in a Buchner funnel containing fiberglass filter paper to separate the leach solution from the residue containing lead-silver chlorides and gold. The

extent of  $\text{AgCl}$  and  $\text{PbCl}_2$  formation was determined by leaching the residue with 20 to 25 g/L NaCN at pH 11 to extract the  $\text{AgCl}$ , and with 250 g/L NaCl to extract the  $\text{PbCl}_2$ . Without a pre- $\text{FeCl}_3$  leach, silver extraction with the NaCN solution was about 20 pct. Results of the  $\text{FeCl}_3$  leach tests are listed in table 2. Silver extraction increased from 61 to 76 pct with increasing  $\text{FeCl}_3$  concentration, and from 76 to 95 pct as the retention time was increased from 3 to 6 h at the highest  $\text{FeCl}_3$  concentration. Zinc extraction increased with increasing  $\text{FeCl}_3$  concentration and was also somewhat dependent on time. Lead extraction was 93 pct with a 2-h leaching time, and increasing  $\text{FeCl}_3$  concentration did not increase lead extraction. Lead extraction was not followed further because of the research by Haver (11), who showed lead extraction from a galena concentrate to be 96 to 99 pct in 1 to 2 h at 50° C. Longer times and higher temperatures resulted in further dissolution of other elements, but did not significantly increase lead extraction.

<sup>4</sup>Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 2. - Ferric chloride leaching<sup>1</sup>

FeCl <sub>3</sub> ·6H <sub>2</sub> O, g/L	Time, h	Metal extraction, pct		
		Ag <sup>2</sup>	Pb <sup>3</sup>	Zn
52.....	2	61	93	0
	3	61	NA	14
102.....	2	76	93	50
105.....	3	76	NA	37
	6	95	NA	59

NA Not analyzed.

<sup>1</sup>50 g ore added to 1 L pH 0.5 HCl solution at 40° C.

<sup>2</sup>AgCl extracted from FeCl<sub>3</sub> leach residue with NaCN.

<sup>3</sup>PbCl<sub>2</sub> solubilized from FeCl<sub>3</sub> leach residue with NaCl.

Additional, larger scale tests were conducted to generate spent leach solution for electrolytic regeneration experiments and to generate residue for thiourea and brine leaching experiments to recover gold, silver, and lead. In these tests, 350 g FeCl<sub>3</sub>·6H<sub>2</sub>O was added to 3,500 mL of deionized water (acidified with 45 mL of concentrated HCl) and heated to 40° C in a 4-L beaker. Dried, minus 200-mesh material (175 g) was mixed with the leach solution for 6 h and filtered. Averaged analyses of the FeCl<sub>3</sub> leach solutions and residues are listed in tables 3 and 4, respectively. The major metals present in the spent leach solution were iron, zinc, and lead. Zinc buildup in the recycled leach solution can possibly be controlled by pH adjustment and sulfide precipitation; however, Wong (7) determined that zinc buildup reached a maximum of 15 g/L after many leaching cycles and did not cause a problem in that process. Further buildup of silver and lead in the leach solution is not anticipated because of their insolubility.

#### Thiourea

Laboratory tests were conducted to study the effect of thiourea concentration, H<sub>2</sub>SO<sub>4</sub> concentration, CuSO<sub>4</sub> addition, temperature, solids content, and retention time on leaching gold and silver. Residue from FeCl<sub>3</sub> leaching, which had an analysis similar to that listed in

TABLE 3. - Typical spent FeCl<sub>3</sub> leach solution analysis

	Conc, g/L
Ag.....	17.4
Au.....	<sup>1</sup> <.01
Fe.....	23
Zn.....	2.4
Pb.....	.9
Co.....	.32
Mn.....	.13
Cd.....	<sup>1</sup> 76
Cu.....	<sup>1</sup> 6
As.....	<sup>1</sup> <5

<sup>1</sup>ppm.

TABLE 4. - Typical FeCl<sub>3</sub> leach residue analysis

	Conc, pct
Ag.....	<sup>1</sup> 49.0
Au.....	1.1
Pb.....	37.5
Zn.....	9.2
Fe.....	6.4
As.....	.67
Cd.....	.15
Mn.....	.12
Cu.....	.077
Co.....	.015

<sup>1</sup>oz/st.

table 4, was used in the thiourea leaching investigation to extract gold and silver. Generally, the test procedure consisted of mixing 10 g of FeCl<sub>3</sub> leach residue in 250 mL of leach solution containing 20 g/L thiourea and 4.6 g/L H<sub>2</sub>SO<sub>4</sub>, leaching for 3 h at 40° C, then filtering through Whatman No. 42 filter paper.

Increasing the initial thiourea concentration from 2 to 30 g/L increased silver extraction from 65 to 87 pct and gold extraction from 55 to 80 pct (fig. 1). Thiourea consumption increased from 5 to 67 lb/st.

H<sub>2</sub>SO<sub>4</sub> had little effect on the silver, but increased H<sub>2</sub>SO<sub>4</sub> concentration decreased gold extraction (fig. 2). Gold extraction increased from 70 to 80 pct as the H<sub>2</sub>SO<sub>4</sub> concentration increased from 0 to 29.3 g/L but decreased to 50 pct at higher H<sub>2</sub>SO<sub>4</sub> concentrations.

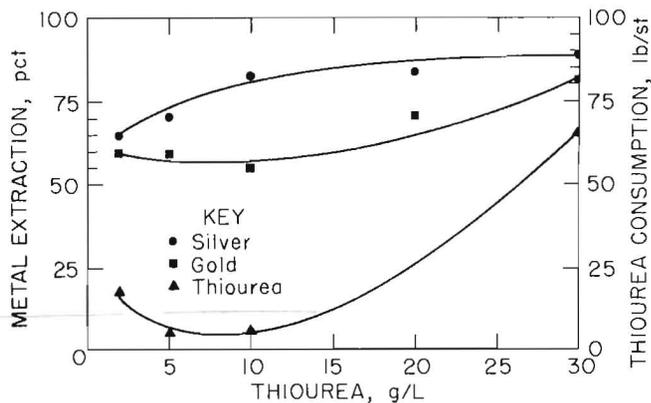


FIGURE 1. - Effect of thiourea concentration on gold and silver extraction.

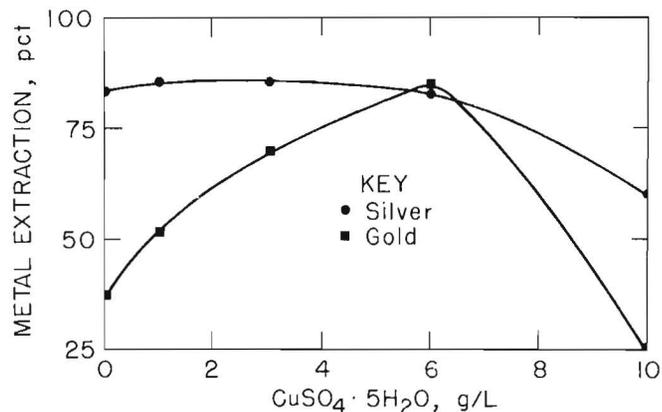


FIGURE 3. - Effect of  $\text{CuSO}_4$  addition on gold and silver extraction.

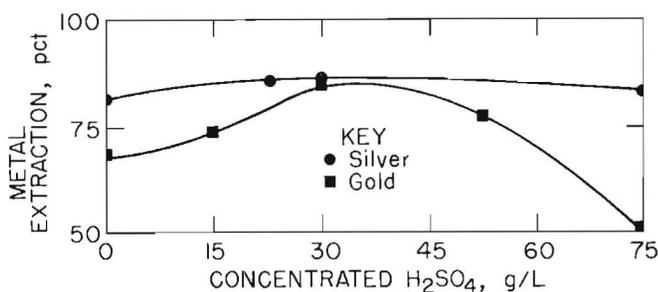


FIGURE 2. - Effect of  $\text{H}_2\text{SO}_4$  concentration on gold and silver extraction.

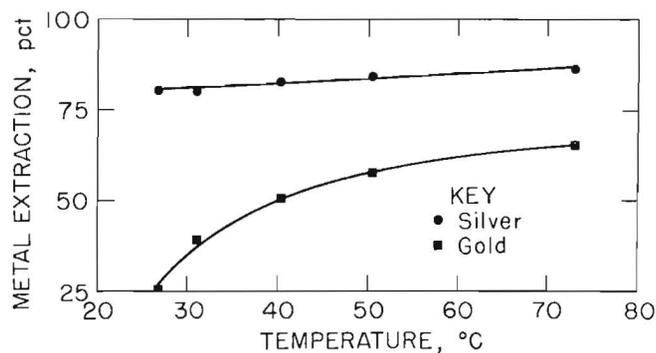


FIGURE 4. - Effect of temperature on gold and silver extraction.

Previous research (12) has shown that the presence of  $\text{Cu}^{2+}$  increases gold extraction by acting as an oxidation catalyst. Figure 3 shows that the addition of 6 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to the thiourea leach solution produced a maximum gold extraction of 85 pct. This was nearly 170 pct greater than the extraction obtained without  $\text{CuSO}_4$  addition. Silver extraction decreased slightly with the addition of this amount of  $\text{CuSO}_4$ .

Increasing temperature increased gold extraction but had minimal effect on silver extraction (fig. 4). Gold extraction increased from 25 to 50 pct as the temperature was increased from ambient to 40° C and to 65 pct at 73° C. Although thiourea consumption data were erratic, the trend clearly showed increased thiourea consumption with increased temperature--particularly above 40° C.

Figure 5 shows the effect of increasing solids content on gold and silver leaching using 20 g/L thiourea. Neither gold nor silver was affected to any great

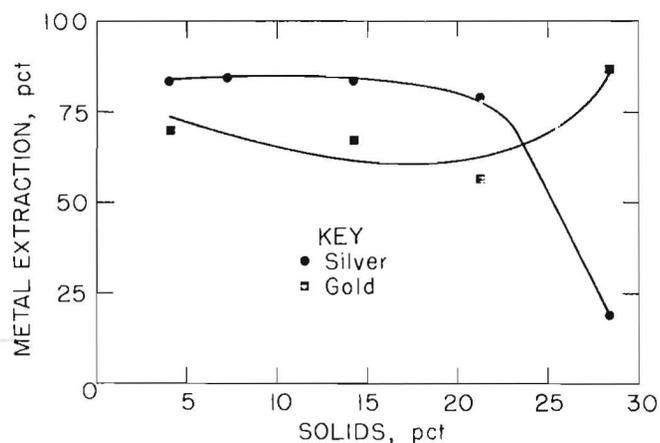


FIGURE 5. - Effect of increased solids on gold and silver extraction.

extent as solids content was increased from 4 to 21 pct; however, above 21 pct solids, silver extraction decreased from between 75 to 80 pct down to 20 pct while gold extraction increased considerably.

All leach solutions, except those obtained from the tests with <7 pct solids, formed a white precipitate after filtration. The precipitate contained about 15 pct Pb, 1.2 oz/st Ag, and sulfur, which may indicate that a lead-silver thiourea complex had formed. Although solutions made with higher solids content are less stable, a higher solids content has considerable advantage. As the solids were increased from 4 to 21 pct, silver in the leach solution increased from about 60 to 368 ppm. Thiourea consumption increased with increased solids, from about 36 lb/st residue, at 7 pct solids, to 46 lb/st residue at 21 pct solids.

The effect of retention time on precious metal extraction is shown in figure 6. Silver extraction was 70 pct complete in 15 min and increased to over 85 pct complete in 3 h. Gold extraction increased linearly from nearly 0 pct in 15 min to about 75 pct in 60 min, then decreased with additional time. Thiourea consumption also increased slightly with increased time.

Tables 5 and 6 list representative analyses of the thiourea leach solution and residue, respectively. The main contaminants in the leach solution were iron, lead, and zinc. The leach residue contained some silver and gold, along with  $PbCl_2$ , and the remaining zinc and iron. A second thiourea leach did not extract significant gold or silver. Silver was reduced from 8 to 5 oz/st with a 20-g/L thiourea leach. Finer grinding may liberate more gold and silver.

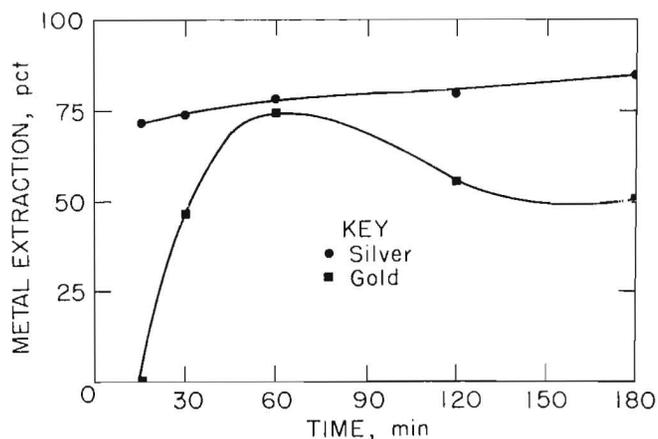


FIGURE 6. - Effect of time on gold and silver extraction.

TABLE 5. - Typical pregnant thiourea leach solution analysis

	Conc, ppm
Ag.....	146
Au.....	.18
Fe.....	670
Zn.....	90
Pb.....	46
As.....	36
Cu.....	9
Mn.....	2
Cd.....	1
Co.....	<1

TABLE 6. - Typical thiourea leach residue analysis

	Conc, pct
Ag.....	.18
Au.....	1.03
Pb.....	36
Zn.....	7.8
Fe.....	5.9
As.....	.78
Cd.....	.15
Mn.....	.12
Cu.....	.082
Co.....	.014

<sup>1</sup>oz/st.

Thiourea consumption is a problem that was not resolved; however, a recent investigation by Schulze (13) has shown that the addition of  $SO_2$  to the thiourea leach substantially reduces thiourea consumption.

#### Brine

Brine leach tests were conducted to study the effects of pulp density, acid concentration, and leach time on  $PbCl_2$  solubilization from the thiourea leach residue. Brine leach solution was prepared by adding 250 g/L NaCl to acidified water and heating to 55° C. Sufficient residue from the thiourea leach was added to the hot leach solution to vary the pulp density from 2 to 8.2 pct solids. The slurry was mixed for a specified time and filtered through a hot Buchner funnel. The solution was cooled to ambient temperature, and the  $PbCl_2$  crystals were filtered. Both the brine solution and

PbCl<sub>2</sub> crystals were saved for later use as feed to the cathode compartment of the electrolytic cell. The residue was saved for further treatment to recover the remaining silver and other valuable metals.

The effect of pulp density on PbCl<sub>2</sub> solubilization from the thiourea leach residue is listed in table 7. At a 2-pct pulp density, the contained PbCl<sub>2</sub> was completely solubilized. Increasing the pulp density to near 5.8 pct resulted in 95 pct of the PbCl<sub>2</sub> being solubilized, and at a pulp density of 8.2 pct, only 81 pct was solubilized from the thiourea leach residue. The contained lead chloride is between 24 and 36 g/L at these pulp densities.

TABLE 7. - Effect of residue pulp density on PbCl<sub>2</sub> solubilization<sup>1</sup>

Solids, pct	Lead, pct
2.0.....	99.6
3.9.....	99.5
5.8.....	95.3
8.2.....	81.5

<sup>1</sup>250 g/L NaCl plus 50 mL conc HCl/L; 3 h leaching time at 55° C.

Additional tests were carried out to determine the effect of acid concentration on PbCl<sub>2</sub> solubilization. All tests were conducted as described above, except the slurry contained 3.9 pct solids and the acid concentration was varied. Results listed in table 8 show that

TABLE 8. - Effect of acid strength on PbCl<sub>2</sub> solubilization and impurity content in brine solution

	HCl conc per mL of solution			
	0 mL	0.16 mL	0.50 mL	5.0 mL
Solubilized Pb <sup>1</sup> .....pct..	97.6	98.8	97.9	99.5
Metal content, <sup>2</sup> ppm:				
Ag.....	4	4	4	6
Fe.....	12	30	50	141
Zn.....	11	17	35	50

<sup>1</sup>250 g/L NaCl; 3 h, 55° C; 3.9 pct solids.

<sup>2</sup>Impurity content in brine solution.

PbCl<sub>2</sub> solubility increased slightly with increased acid strength, as did the impurity level of zinc, iron, and silver in the leach solution. Little advantage was gained by increasing acid concentration.

The time required to solubilize PbCl<sub>2</sub> from the thiourea leach residue was less than 15 min. Tests conducted from 15 min to 2 h resulted in over 99-pct PbCl<sub>2</sub> recovery. Iron and zinc impurities in the brine leach solution increased with time, as shown in table 9.

Tables 10 and 11 list analyses of representative brine leach solution (minus crystallized PbCl<sub>2</sub>) and residues, respectively. The only impurities in the pregnant brine solution of concern are silver, copper, and arsenic. Because of their position in the electromotive series (14), these metals will contaminate the lead metal produced during electrolytic recovery of byproduct lead. If necessary, these impurities can be

TABLE 9. - Effect of leach time on impurity content in brine solution<sup>1</sup>

Time, min	Metal content, ppm	
	Zn	Fe
15.....	18	88
30.....	24	120
60.....	43	167
120.....	61	217

<sup>1</sup>250 g/L with 50 mL/L HCl; 55° C; 3.9 pct solids.

TABLE 10. - Typical pregnant brine leach solution analysis<sup>1</sup>

	Conc, ppm
Ag.....	3.6
Au.....	<.01
Fe.....	46
Zn.....	34
As.....	<5
Cu.....	1
Mn.....	1
Cd.....	<1
Co.....	<1
Pb.....	<sup>2</sup> 8.8

<sup>1</sup>More than half of the PbCl<sub>2</sub> crystallized prior to solution analysis.

<sup>2</sup>g/L.

TABLE 11. - Typical brine leach residue analysis

	<u>Conc, pct</u>
Ag.....	115
Au.....	1<.01
Zn.....	18
Fe.....	10
Pb.....	4
As.....	1.47
Cd.....	.29
Mn.....	.22
Cu.....	.152
Co.....	.014
<hr/>	
oz/st.	

removed by passing the solution over lead shot (11). The brine leach residue contained small amounts of lead, which can be recovered with a second brine leach. Recovery of the remaining silver will be more difficult. A second thiourea leach was not effective in recovering silver, as discussed in the thiourea leach section. Additional work should be done to recover the remaining silver, zinc, and other metals.

#### SILVER AND GOLD RECOVERY FROM THIOUREA

Only minimal effort was expended to recover gold and silver from the thiourea leach solution. Previous work by Simpson (15) showed that gold and silver could be recovered from the thiourea leach solution with cation exchange resins, aluminum powder cementation, or electrolysis. The resin AG-50W-8X from Bio-Rad Laboratories successfully recovered the gold and silver with loadings on the resin of over 1,000 oz/st Ag and 100 oz/st Au. The resin was contacted with an acidified thiourea solution to strip the silver and with a caustic cyanide solution to strip the gold. Gold and silver were electro-won from their respective strip solutions on steel wool cathodes.

Aluminum powder (6 Al:1 Ag) added to thiourea leach solution containing 60 ppm Ag lowered the silver content to about 1 ppm. An acid leach will separate the silver from the aluminum-silver precipitate.

#### BYPRODUCT LEAD RECOVERY AND SPENT $\text{FeCl}_3$ LEACH SOLUTION RECYCLE

Figure 7 shows the electrolytic cell used to recover lead from the brine solution and reoxidize the spent  $\text{FeCl}_2$ - $\text{FeCl}_3$  leach solution. The cell, similar to one discussed by Kramer (16), was constructed of Plexiglas and polypropylene, with the anode and cathode compartments separated by an Ionics anion transfer membrane (17). Each compartment was 4.5 cm square with the anode compartment closed at the bottom. The cathode compartment was open at the bottom and had side holes for free flow of electrolyte between the cathode compartment and the 1,500-mL containment beaker. Cathode material was 6.35- by 3.18-cm pure lead foil, and the anode was a platinum basket (1.27 cm diam by 5.08 cm).

In nearly all tests, the catholyte consisted of a 250-g/L NaCl brine solution containing 27 g/L  $\text{PbCl}_2$  and 0.6M HCl, and the anolyte was spent  $\text{FeCl}_3$  leach

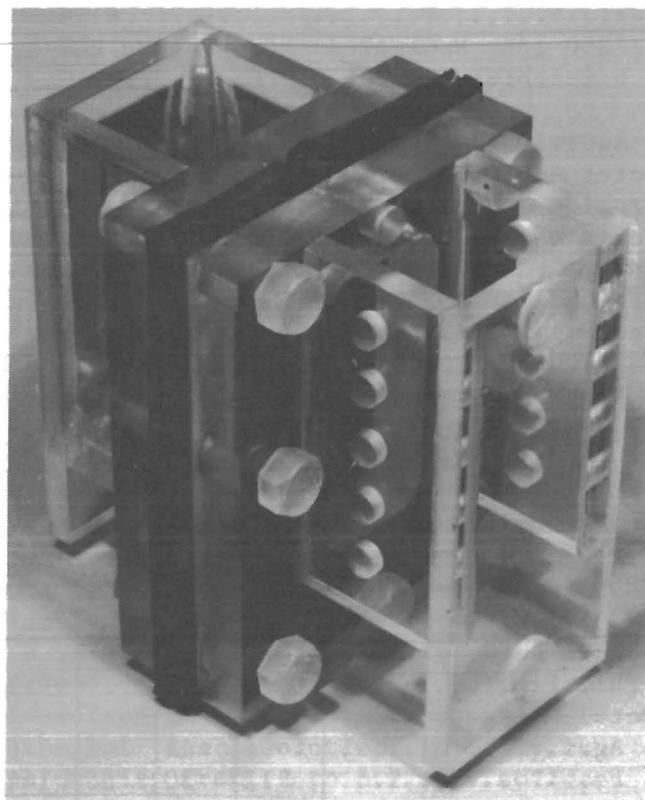


FIGURE 7. - Diaphragm electrolytic cell.

solution (table 3). Batch and semicontinuous experiments were conducted. All tests were initiated by adding 90 mL of spent  $\text{FeCl}_3$  leach solution (heated to  $55^\circ$  to  $60^\circ$  C) to the anode compartment, setting the cell into a 1,500-mL glass beaker, and adding 750 mL catholyte to the beaker. The platinum anode was put in the anode compartment, the power supply voltage was increased to slightly above 1 V, the lead cathode (precleaned with plastic scouring pad and washed with acetone) was placed into the cathode compartment, and the amperage was increased to give a current density of  $100 \text{ A/m}^2$ . The voltage was varied between 1.75 and 2.5 V. Usually, tests were conducted for 1.25 h. Cell agitation in the cathode compartment was supplied either by a magnetic stir bar or by nitrogen sparging. The only difference between semicontinuous and batch tests was that for semicontinuous tests anolyte was pumped from a beaker containing hot, spent  $\text{FeCl}_3$  leach solution into and out of the anode compartment at about 0.8 to 1.0 mL/min, and the catholyte was recirculated between a second beaker containing hot catholyte and the cell. Periodically,  $\text{PbCl}_2$  was added to the catholyte to maintain a relatively constant lead concentration

during electrowinning. Following the test, the cathode was removed from the cell, washed with deionized water, and then dried with a lint-free tissue.

Operating parameters such as current density, leveling agent addition (bone gelatin and calcium lignin sulfonate), lead and acid concentration, agitation rate, and nitrogen sparging were investigated. The bone gelatin used in this investigation was the same as described by Cole (18). Cathode current efficiency remained above 95 pct with all tests; therefore, most of the effort was directed toward improving cathode surface.

Dendritic growth on the edges of the cathode was dramatically decreased by ensuring the cathode dimensions were larger than the anode dimensions, and by increasing solution agitation from minimal to moderate (enough to suspend any insoluble  $\text{PbCl}_2$  or additives).

The results of varying the current density (CD) from 50 to  $248 \text{ A/m}^2$  with moderate catholyte agitation, no additive addition, and for 0.25 A·h are shown in table 12 and figure 8. Dendritic growth decreased as the CD decreased from 248 to  $100 \text{ A/m}^2$ . At lower CD, the cathode formed an oxidized coating.

TABLE 12. - Effect of current density on lead cathode quality

Current density, $\text{A/m}^2$	Current, A	Average voltage	Time, h	Cathode description
248.....	0.5	2.9	0.50	Dendritic growth; non-adherent over entire surface.
149.....	.3	2.4	.83	Dendritic growth over 75 pct of surface; nonadherent except bottom 25 pct.
100.....	.2	2.3	1.25	Dendritic growth over 50 pct of surface; nonadherent except bottom 50 pct.
75.....	.15	1.9	1.67	Dendritic growth over 50 pct of surface; nonadherent except bottom 50 pct; rough.
50.....	.10	1.6	2.50	Middle of cathode free of dendrites; considerable oxidized material--yellow brown in color.

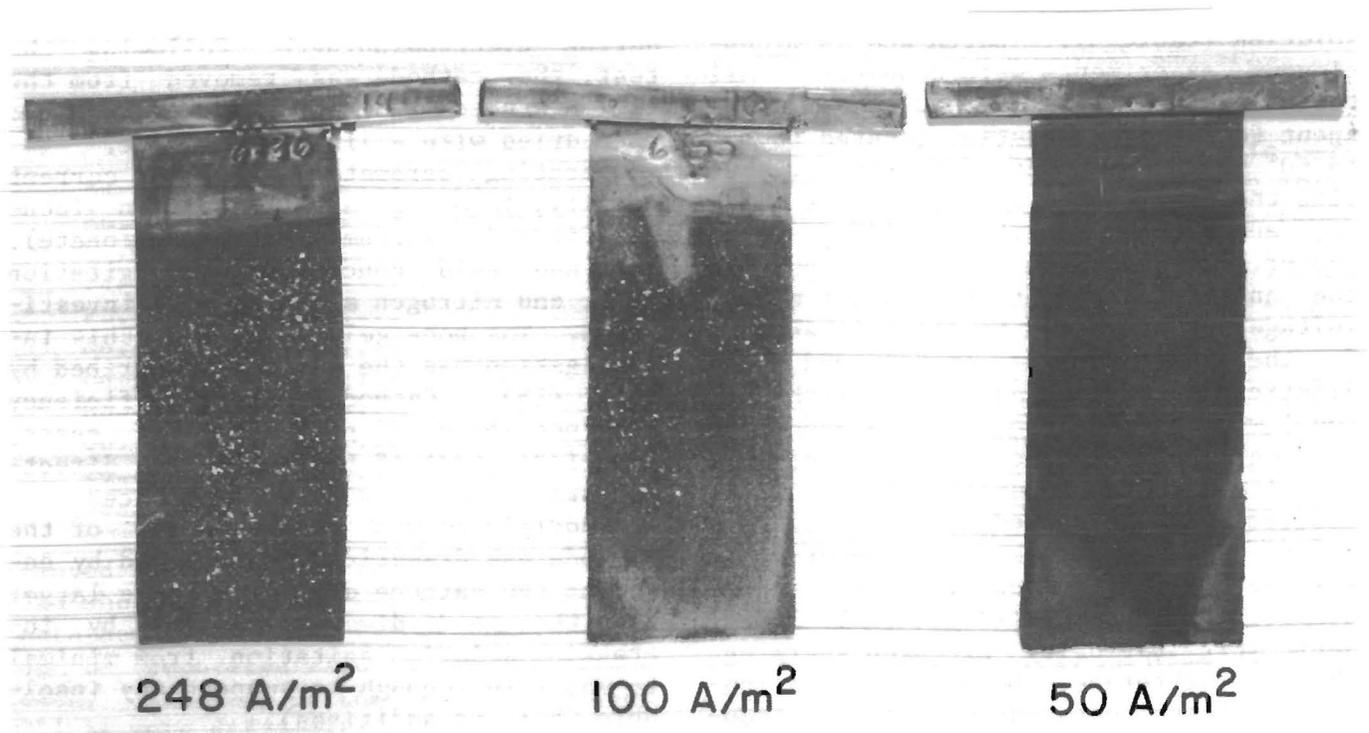


FIGURE 8. - Effect of current density on lead cathode quality.

Although reducing the CD decreased dendrite formation, the deposit was not acceptable. Others (18-20) have shown that organic compounds, referred to as leveling agents or additives, reduced dendrite formation and produced smooth lead deposits in a fluosilicic acid electrolyte and in chloride electrolytes (16). Animal glue, bone gelatin, and calcium lignin sulfonate were among the organics used. Preliminary tests with a  $PbCl_2$ -NaCl electrolyte showed bone gelatin to have a slight advantage over animal glue. Calcium lignin sulfonate produced loosely adhering lead deposits when used with or without glue, but the dendrites were nodular rather than long and flat. Therefore, further testing was discontinued with calcium lignin sulfonate but continued with bone gelatin.

Bone gelatin addition to the catholyte eliminated dendrite formation and resulted in a smooth, shiny lead deposit as shown in figure 9 and table 13. All tests were conducted at  $100 A/m^2$  for 0.25 A·h. Bone gelatin concentration was varied from 0.1 to 2 g/L. Deposit

quality increased with bone gelatin concentrations between 0.1 and 0.2 g/L, then decreased with increasing concentration. Effect on cell voltage was not significant.

TABLE 13. - Effect of bone gelatin on lead cathode quality

Bone gelatin, g/L	Average voltage	Cathode description
0.1.....	2.3	Surface free of dendrites; slightly rough appearance; shiny.
.2.....	2.4	Surface free of dendrites; smooth and shiny.
.5.....	2.4	Surface free of dendrites; slightly rough toward middle.
1.0.....	2.4	Surface free of dendrites; grainy appearance.
2.0.....	2.4	Surface free of dendrites; portions non-adherent; rougher.

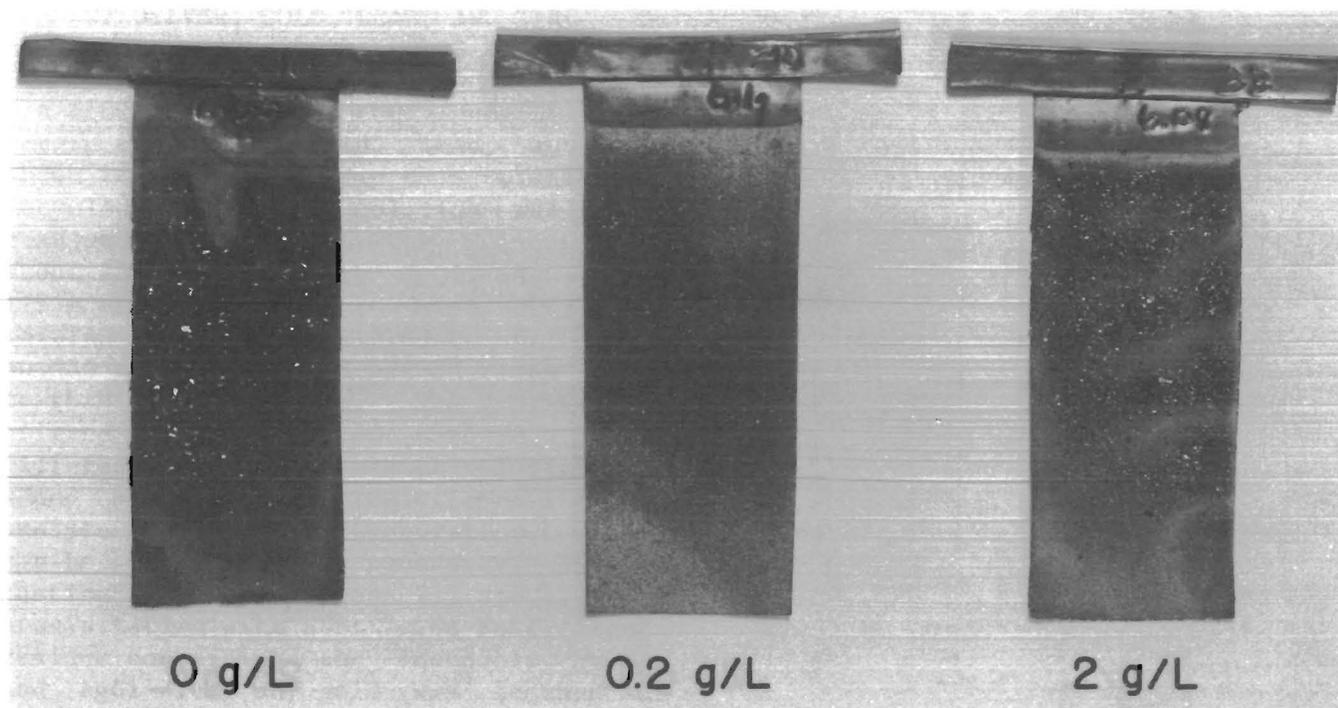


FIGURE 9. - Effect of bone gelatin concentration on lead cathode quality.

Results given in table 14 and figure 10 show the effects of  $PbCl_2$  concentration in the catholyte with 0.2 g/L bone gelatin at 100 A/m<sup>2</sup> for 0.25 A·h. At lower  $PbCl_2$  concentrations, the deposit was rough with short dendrites appearing over the entire cathode surface. As the  $PbCl_2$  concentration increased to 20 g/L, the dendrites disappeared, and finally, at 25 g/L  $PbCl_2$ , a smooth, shiny, dendrite-free deposit was produced.

TABLE 14. - Effect of  $PbCl_2$  concentration on lead cathode quality

$PbCl_2$ , g/L	Average voltage	Cathode description
7.....	2.4	Short dendrites over entire surface.
13.....	2.3	Short dendrites over entire surface.
20.....	2.3	No dendrites; slightly rough appearance; portion not adherent.
25.....	2.4	No dendrites; smooth and shiny.

Some additional testing was conducted to determine the effect of acid strength

and nitrogen sparging. Nearly all tests were conducted with 0.6M HCl, but a test conducted with no acid addition resulted in an equally good cathode. These results indicate that acid may not be required for good cathode quality; however, this question has not been fully resolved. Kramer (16) reported that nitrogen sparging under the cathode decreased dendrite growth considerably. Tests without glue addition and nitrogen sparging resulted in rough deposits with some dendrites on the edges. Glue addition with nitrogen sparging produced smoother deposits.

Semicontinuous tests were conducted to determine the cathode quality over several hours. All tests were conducted at 100 A/m<sup>2</sup> and with 0.2 g/L bone gelatin added to the  $PbCl_2$ -NaCl catholyte. Lead chloride was added at 3-h intervals to keep the  $PbCl_2$  concentration between 22 and 25 g/L. The spent  $FeCl_3$  leach solution (18 g/L  $Fe^{2+}$  and 5 g/L  $Fe^{3+}$ ) was pumped through the anode compartment at 0.96 mL/min for 6 h and 45 min. Lead deposits were free of dendrites and shiny, but the surface was rough and nodular, as shown in figure 11.

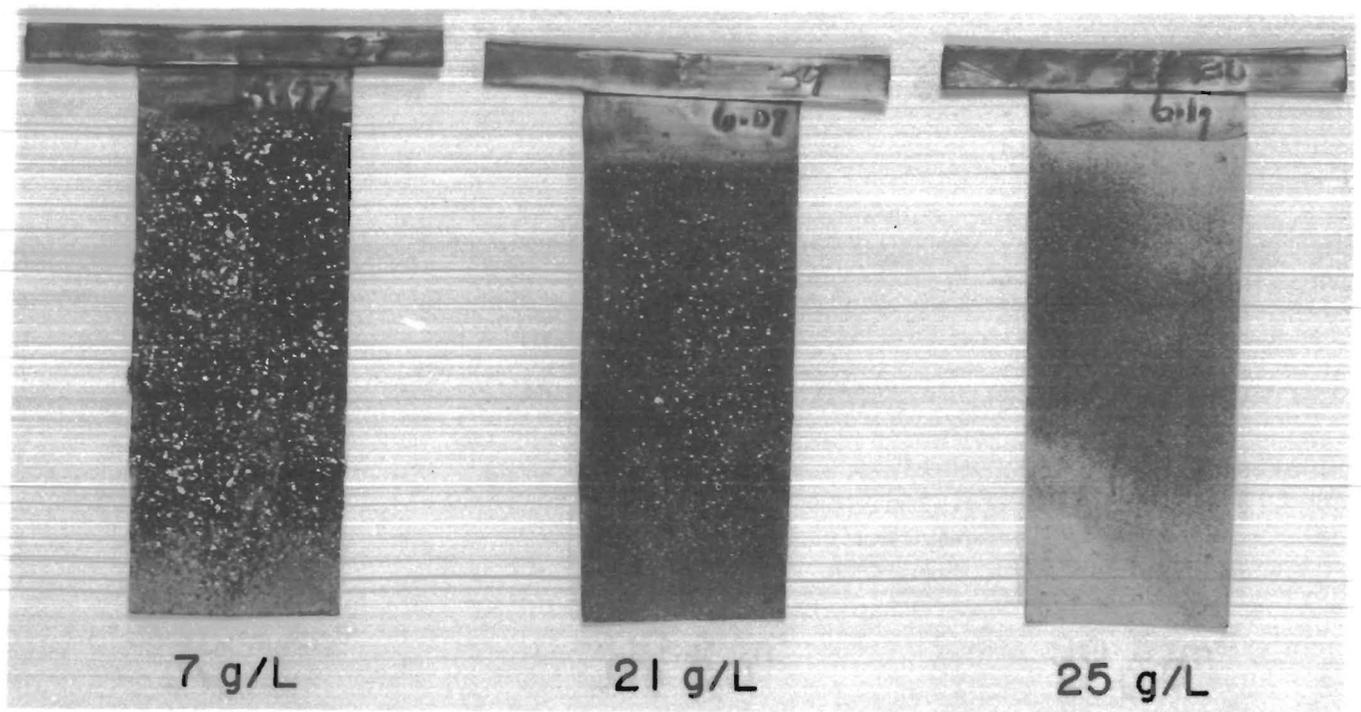


FIGURE 10. - Effect of  $PbCl_2$  concentration on lead cathode quality.

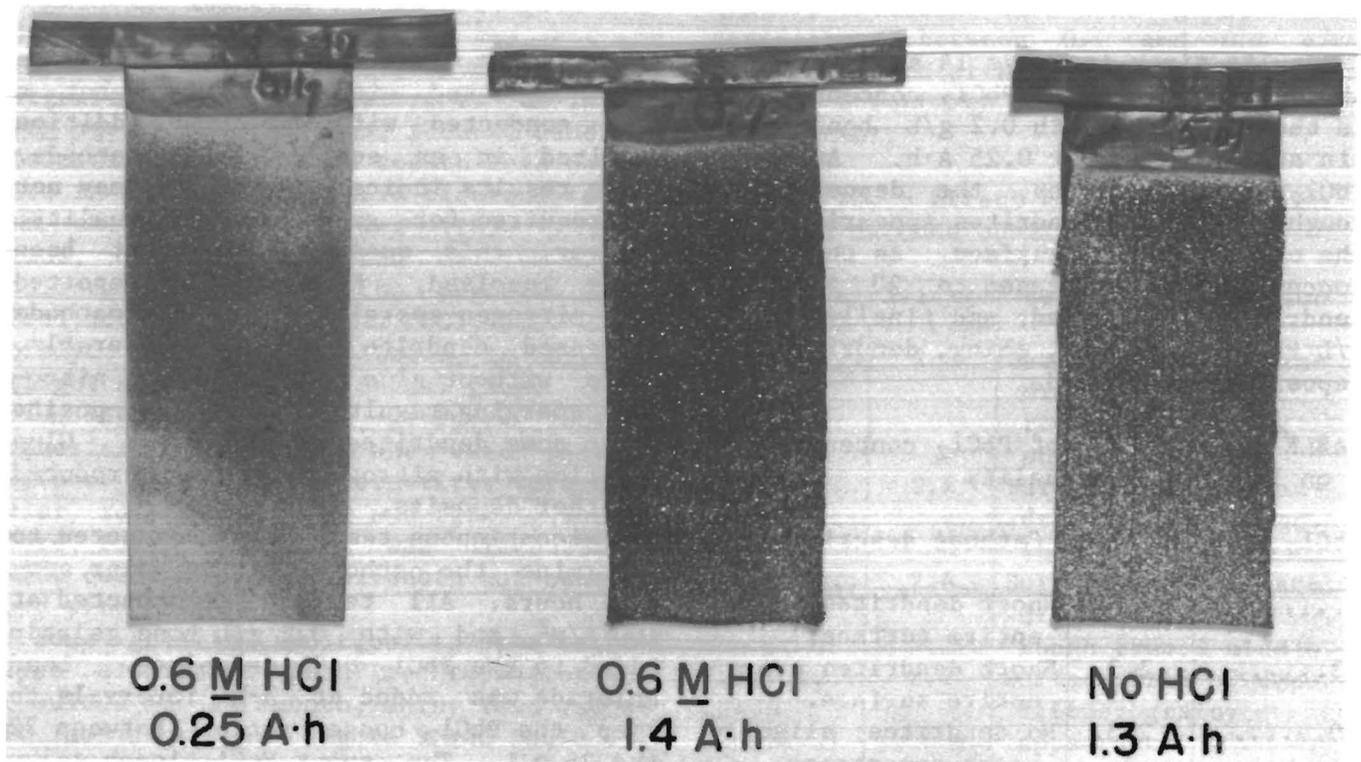


FIGURE 11. - Lead cathode from semicontinuous cell operation.

PROPOSED PROCESS FOR RECOVERING  
OF SILVER, GOLD, LEAD, AND ZINC  
FROM COMPLEX ORES

A flow diagram for the integrated recovery of silver, gold, lead, and zinc shown in figure 12. In this process, a recycled  $\text{FeCl}_3$  leach solution was first readjusted to pH 0.5 with HCl and to about 23 g/L  $\text{Fe}^{3+}$  with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; then 175 g of 90-pct minus 200-mesh ore, containing 50 oz/st Ag, 0.03 to 0.1 oz/st Au, 36 pct Pb, and 18 pct Zn, was added to this leach solution. The slurry was stirred and heated at 40° C for 6 h, then filtered. The spent leach solution was added to the lead electrolytic cell as an anolyte for solution regeneration. Zinc can be recovered, if necessary, by adjusting the pH to between 3.5 and 4, then precipitating with  $\text{H}_2\text{S}$ . The  $\text{FeCl}_3$  leach residue containing the insoluble  $\text{PbCl}_2$  and  $\text{AgCl}$  plus any gold was leached at about 40° C for 3 h with about 1,400 mL of 20-g/L thiourea solution adjusted to pH 1.5 with  $\text{H}_2\text{SO}_4$ . After filtration, the gold and silver can be either precipitated with aluminum powder, electrowon, or adsorbed on Bio Rad AG-50W-8X cation exchange resin (15). The thiourea leach residue, which contained the  $\text{PbCl}_2$ , was leached for 1 h at 55° to 60° C with about 3,000 mL of acidified 250-g/L NaCl brine solution to solubilize the  $\text{PbCl}_2$ . The residue was either discarded or re-leached to recover other metal values.

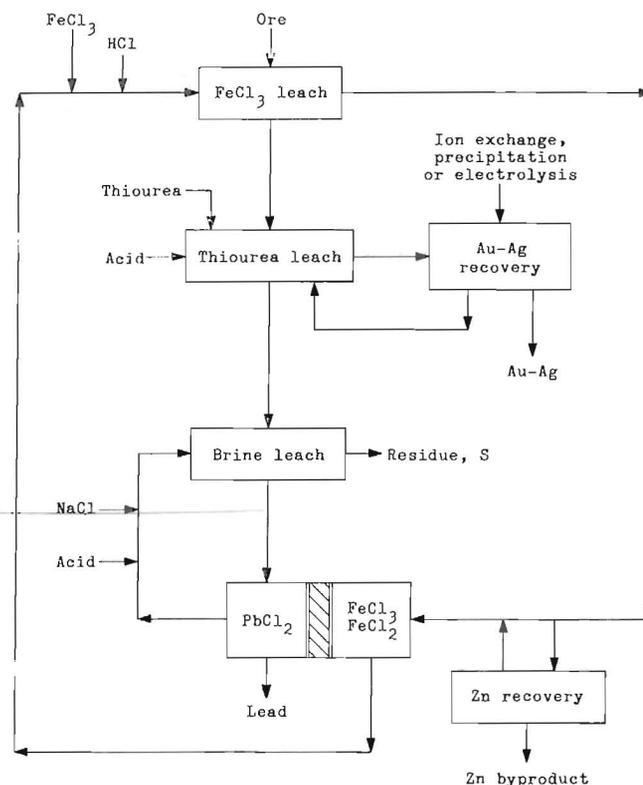


FIGURE 12. - Flow diagram for silver, gold, lead, and zinc recovery from a complex sulfide ore.

Lead was recovered from the hot  $\text{PbCl}_2$ -NaCl brine solution in the anion permselective membrane electrowinning cell. Lead current efficiency was greater than 99 pct with a CD of 100  $\text{A}/\text{m}^2$  using 0.2 g/L bone gelatin addition. Ferrous oxidation at the anode was 75 to 99 pct at a cell temperature of 55° C.

### CONCLUSIONS

Silver, gold, lead, and zinc were extracted from a complex lead-zinc sulfide ore sample with a sequential  $\text{FeCl}_3$ , thiourea, and brine leach.  $\text{FeCl}_3$  extracted about 50 pct of the zinc and formed insoluble chlorides of silver and lead; thiourea extracted nearly 85 pct of the gold and silver, and an NaCl brine solution solubilized the  $\text{PbCl}_2$ . Silver and gold were recovered from the thiourea leach solution by aluminum precipitation,

cation-exchange resin, or direct electrowinning. Lead was recovered from the brine solution with a two-compartment anion permselective membrane electrolytic cell. Lead metal was recovered at the cathode, and spent  $\text{FeCl}_3$  was regenerated at the anode. Cathodic current efficiency was greater than 95 pct, and anodic current efficiency ranged from 75 to 99 pct.

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