1979

Processing of copper refinery anode slimes

Shrirang Anant Kulkarni

Recommended Citation

Kulkarni, Shrirang Anant, "Processing of copper refinery anode slimes" (1979). *Masters Theses*. 3603.
https://scholarsmine.mst.edu/masters_theses/3603

PROCESSING OF COPPER REFINERY
ANODE SLIMES

BY

SHRIRANG ANANT KULKARNI, 1955-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

1979

Roger K. Clifford (Advisor) A E Morris

Charles A Sorrell

ABSTRACT

A study of commercial copper refinery anode slimes has been conducted to evaluate the separation of valuable metals contained in the slimes. The slimes contain substantial quantities of Ag, Sn, Au, Pb, and Cu. The values were present principally as AgCl, SnO_2, Au, $PbSO_4$, Cu and $CuSO_4$.

A Roast-Leach-Roast-Leach (RLRL) technique solubilized up to 91 pct of the Ag and 99 pct of the Cu from raw slimes.

The Pb-Sn separation was investigated using the following hydrometallurgical techniques: 1) DETA (diethylene triamine) leaching; 2) NaOH leaching; 3) $(NH_4)_2CO_3$ leaching; and 4) NaOH with Na_2S plus $NaNO_2$ leaching. The NaOH with Na_2S plus $NaNO_2$ leaching process was ineffective in Pb-Sn separation. The $(NH_4)_2CO_3$ leaching process involves two leaching operations plus the electrowinning operation to recover Pb, which makes this process expensive; also the Pb recovery was poor. DETA leaching and NaOH leaching have been found to be effective from a chemical standpoint. These processes have been able to separate the Pb and the Sn into two products: 1) a Pb concentrate assaying 86.1 pct Pb with 95.6 pct of the Pb reporting to the Pb product, and 2) a Sn product assaying 54.6 pct Sn which contained 97.6 pct of the Sn along with almost all of the Au from slimes.

A proposed flow sheet would call for an acid Roast-Leach-Roast-Leach followed by DETA leach and filtration to separate a Sn rich residue; PbS would then be precipitated from the filtrate and recovered by another filtration step. The DETA solution would then be regenerated by the addition of CaO to remove the sulfate.

ACKNOWLEDGEMENTS

The author wishes to express his deepest appreciation to Dr. Roger K. Clifford, my advisor, for his patience and guidance throughout this study. I would also especially like to thank Dr. A. E. Morris, who greatly aided in preparing the final manuscript.

The author gratefully acknowledges the financial support provided by the Institute of Chemical and Extractive Metallurgy and U.S. Bureau of Mines through Contract No. USDA 65184011.

Special thanks are given to Jean Kramme for her efforts in typing this thesis.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION

During the electrorefining of copper, an insoluble slime accumulates at the bottom of the cells. This slime contains a variety of metallic compounds having potential value, such as Ag, Sn, Pb, Cu and Au.

A study of anode slimes produced at an industrial copper refinery was done by the UMR Institute for Chemical and Extractive Metallurgy.[1] The assays of the raw slimes showed about 7.0 pct Cu, 35.0 pct Pb, 15 pct Sn, 900 troy oz Ag/st and 3 to 5 troy oz Au/st. The study showed that the metals of interest were Ag, Sn, Au, Pb and Cu. The Cu was found to be a mixture of metallic Cu and cupric ions as in $CuSO_4$. The Pb was mostly present as $PbSO_4$ and the Sn was mostly in the form of SnO_2. Most of the Ag was present as AgCl.

A. PREVIOUS INVESTIGATION

An investigation of a Roast-Leach-Roast-Leach process (RLRL) was carried out on these slimes by the Institute of Chemical and Extractive Metallurgy, University of Missouri-Rolla in 1976-1977.[1] The results showed that the process solubilized as much as 91.1 pct of Ag and 99.0 pct of the Cu. The process was essentially roasting the slimes at 530° C with 20 to 50 wgt pct addition of H_2SO_4 and leaching in hot water at 90° C. This procedure was repeated. The recovery of silver remained unchanged after a 24-hour leach in a 1 pct NaCN solution.

B. RESEARCH OBJECTIVES

The present study was initiated to evaluate different hydrometallurgical methods for separating the SnO_2 from the $PbSO_4$ found in the RLRL residues. The objective was to determine the most effective leaching technique(s) from a chemical and an economic standpoint. It was found that the slimes could be leached effectively from a chemical standpoint with DETA (diethylene triamine) or with NaOH; therefore, the research work was mainly concentrated on leaching of slimes with DETA and with NaOH.

The constraints on the project from an economic standpoint were the following:

1. Regeneration of reagents or low reagent costs, and
2. A low capital cost for the process equipment.

II. LITERATURE REVIEW

A. AMINE LEACHING

A procedure is described for Pb recovery from $PbSO_4$ which comprises the following steps:

1. Amine leach. Aqueous solutions of aliphatic amines solubilize $PbSO_4$. $PbSO_4$ is soluble in different amines such as EDA (ethylene diamine), PDA (propylene diamine), DETA (diethylene triamine), TETA (triethylene triamine), TEPA (tetraethylene pentamine) and MPADA (mixed polyalkylene diamine).

The solubility of Pb is almost directly proportional to the number of nitrogen atoms in DETA with a ratio Pb/N equal to 1/4. The Pb complexes with DETA up to about 600 g/ℓ Pb. In the alkylene amine group the diamines--e.g. ethylene diamine, propylene diamine, etc. have only two N atoms each, both of which form NH_2 groups, while the polyamines--e.g. diethylene triamine, triethylene tetramine, etc.--have three or more N atoms, two of which are present in NH_2 groups, with the remainder in NH groups. Therefore, as the solubility of Pb is directly proportional to the number of N atoms in alkylene amine, the solubility is higher in polyamines--(e.g. DETA, TEPA, etc.) than in diamines--(e.g. EDA, PDA, etc.). The solubility of Pb in different amines at 2 N-equivalents/ℓ is as follows:[2] 12.5 g/ℓ for PDA, 16.7 g/ℓ for EDA, 63.3 g/ℓ for MPADA and TEPA, 75 g/ℓ for TETA and 100 g Pb/ℓ for DETA.

The $PbSO_4$ leaching reaction goes as follows:[3]

$$PbSO_4 + DETA \longrightarrow [Pb(DETA)]\ SO_4 \qquad (1)$$

2. Carbonation. Typically, the next step after amine leaching would be carbonation as shown by the following reaction.[3]

$$6[Pb(DETA)]\ SO_4 + 10\ CO_2 + 14\ H_2O \longrightarrow 2\ [2PbCO_3 \cdot Pb(OH)_2] + 3\ DETA(H_2SO_4)_2 + 3\ DETA(H_2CO_3)_2 \qquad (2)$$

The CO_2 reacts with the Pb-DETA complex to produce a $2PbCO_3 \cdot Pb(OH)_2$ which is insoluble. Experiments showed that 100 pct of the Pb from the solution could be precipitated on addition of about 35 gCO_2/ℓ.[2]

3. Regeneration. The purpose of this operation is to remove from the system the SO_4^{--} and to regenerate an equivalent amount of free amine for recycling according to the following equations:[3]

$$DETA(H_2SO_4)_2 + 2\ Ca(OH)_2 \longrightarrow DETA + 2\ CaSO_4 + 4\ H_2O \qquad (3)$$

$$DETA(H_2CO_3)_2 + 2\ Ca(OH)_2 \longrightarrow DETA + 2\ CaCO_3 + 4\ H_2O \qquad (4)$$

The solution contains CO_3^{--} as well as SO_4^{--} and the objective is to cause CaO to react only with SO_4^{--}, producing $CaSO_4$ free of Pb, and of amine. In these experiments laboratory grade 'CaO', ground to 200 mesh should be used to ensure complete reaction.[2] F. A. Forward et al. state that regenerated solutions are found to be suitable for recycling.[2] The small CO_2 content of recycle solution has no adverse effect on leaching.

Haruo Mimura et al. state that the overall loss of DETA is supposed to be less than 5 pct in one extracting cycle, including diminution of its extracting power.[3] But C. Coekelbergs et al. state that the regeneration of amine solution is not very easy because it produces a $CaSO_4 \cdot 2H_2O$ residue which has to be discarded.[4]

4. Reduction. This is the final phase of the possible process, which leads to a metallic Pb product. The procedure is comprised of placing $2PbCO_3 \cdot Pb(OH)_2$ in a graphite crucible and heating to approximately 800° C. The carbon of the crucible served as the reducing agent. CH_4, CO or any other reducing gas may be substituted for carbon and reduction can be carried out at any convenient temperature. The reaction goes as follows:[2]

$$3C + 2[2PbCO_3 \cdot Pb(OH)_2] \xrightarrow{800^\circ C} 6Pb + 7CO_2 + 2H_2O \qquad (5)$$

As there are theoretically no impurities in the $2PbCO_3 \cdot Pb(OH)_2$ the resulting Pb metal should be very pure. The Pb metal produced is about 99.99+ pct Pb.[2]

Figure 1 shows a possible flow diagram for the production of high purity Pb by amine leaching.[2]

Some of the limitations of an amine leaching process have been stated by F. P. Haver et al.[5] They state that the $2PbCO_3 \cdot Pb(OH)_2$ was difficult to wash free from amine. The $2PbCO_3 \cdot Pb(OH)_2$, after drying was also very light and fluffy, making carbon reduction inefficient. They suggested another method for recovery of Pb, i.e. electrowinning from amine solutions using graphite electrodes. Pb was electrowon from a 10 pct DETA solution containing 100 g/ℓ Pb with a potential of 4.6 V at 25° C and a current density of 10 amp/ft^2 with a 1-1/2" spacing between electrodes. This method has also certain limitations; the Pb deposited as long dendritic needles which grew rapidly across the solution to the anode, causing short circuits. No gassing occurred at the anode because PbO_2 was formed at the anode. The PbO_2 formation at the anode can be prevented by use of a diaphragm cell. However this would further increase the voltage drop and did not correct other problems. Thus electrowinning does not seem to be a viable alternative.

B. $(NH_4)_2CO_3$ LEACH

F. P. Haver et al. have developed a process for recovering Pb, which involved the following steps:[5]

1. The $PbSO_4$ residue was treated with $(NH_4)_2CO_3$ solution to change the Pb to an acid soluble form and to obtain $(NH_4)_2SO_4$ as a byproduct:

$$PbSO_4 + (NH_4)_2CO_3 \longrightarrow PbCO_3 + (NH_4)_2SO_4 \qquad (6)$$

2. The $PbCO_3$ was dissolved in H_2SiF_6 at room temperature to complete the following reaction:

$$PbCO_3 + H_2SiF_6 \longrightarrow PbSiF_6 + H_2O + CO_2\uparrow \qquad (7)$$

3. The solution was electrolyzed to recover 99.9 pct-pure Pb metal and to regenerate H_2SiF_6. Electrolysis was conducted using a graphite plate as the anode and a Pb starting sheet at the cathode. Glue was

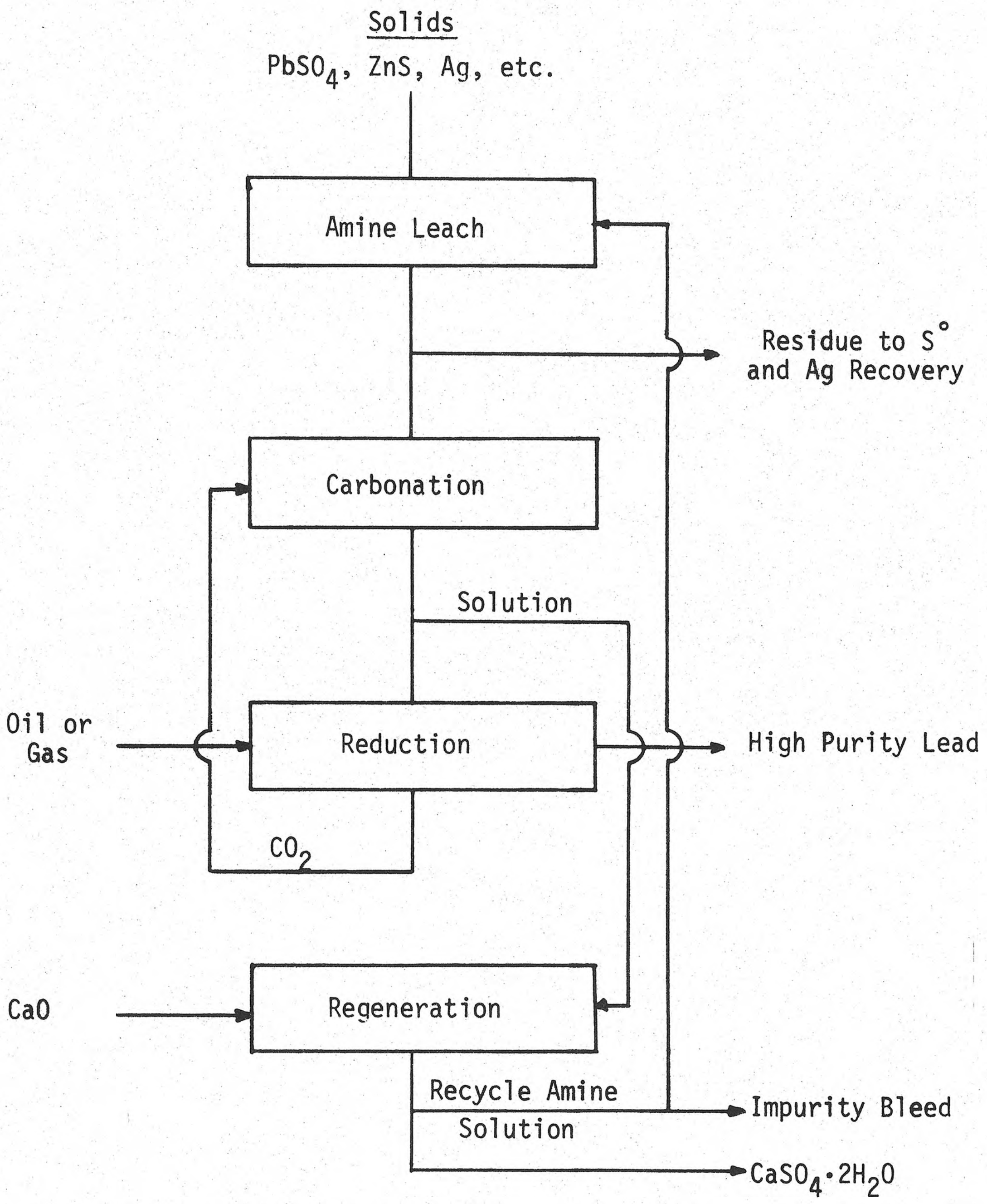

Figure 1. Flow Diagram for the Production of High Purity Pb by Amine Leaching

added to the electrolyte to prevent dendritic growth. A voltage of 2.6 volts was required along with a current density of 20 amp/ft^2, a 1-1/2" spacing between electrodes and an operating temperature of 40° C. These conditions gave a smooth, dense deposit of 99.97 pct Pb.[5]

Figure 2 shows a possible flow diagram for recovery of Pb from $PbSO_4$ using a $(NH_4)_2CO_3$ leach.[5]

C. LEACHING OF TIN BEARING MATERIALS

L. W. Pommier and Saul J. Escalera have proposed a process of leaching Sn bearing material (SnO_2, SnO and SnS) in a solution of NaOH, Na_2S and $NaNO_2$.[6]

The leaching solutions were mixtures of reagent grade NaOH and $Na_2S \cdot 9H_2O$ in proportions such that the ratio of the Na from the NaOH to the Na from the Na_2S was 3:1. The $NaNO_2$ was then added to the mixture. The mixture was then heated to 90° C and Sn bearing dust was added to it while stirring; heating continued during the 8-hour leaching operation. About 98 pct of the Sn was solubilized. The Sn went into the solution as SnO_3^{--} and SnS_3^{--}. Any Pb, Cu or Sb that went into the solution was precipitated as a sulfide because of their extremely slight solubility in basic solutions. Ag, Au and Bi were not soluble in basic solutions and also reported to the leach residue.[6]

The residue was then removed by filtration. The filtrate was reheated to 90° C and placed in an electrolytic cell which contained two anodes and one cathode, all made of steel. The current efficiencies were 98 pct and the chemical analysis of the recovered Sn met the specifications of AAA type Sn. The cathodic Sn had a smooth, shiny surface and no dendrites were observed.

The leaching reactions go as follows:[6]

$$SnO_2 + 2\ NaOH \longrightarrow Na_2SnO_3 + H_2O \tag{8}$$

$$SnO_2 + 3\ Na_2S + 2\ H_2O \longrightarrow Na_2SnS_3 + 4\ NaOH \tag{9}$$

During the electrowinning process, the cathodic reactions that take place for the Na_2SnO_3 and the Na_2SnS_3 are described as follows:[6]

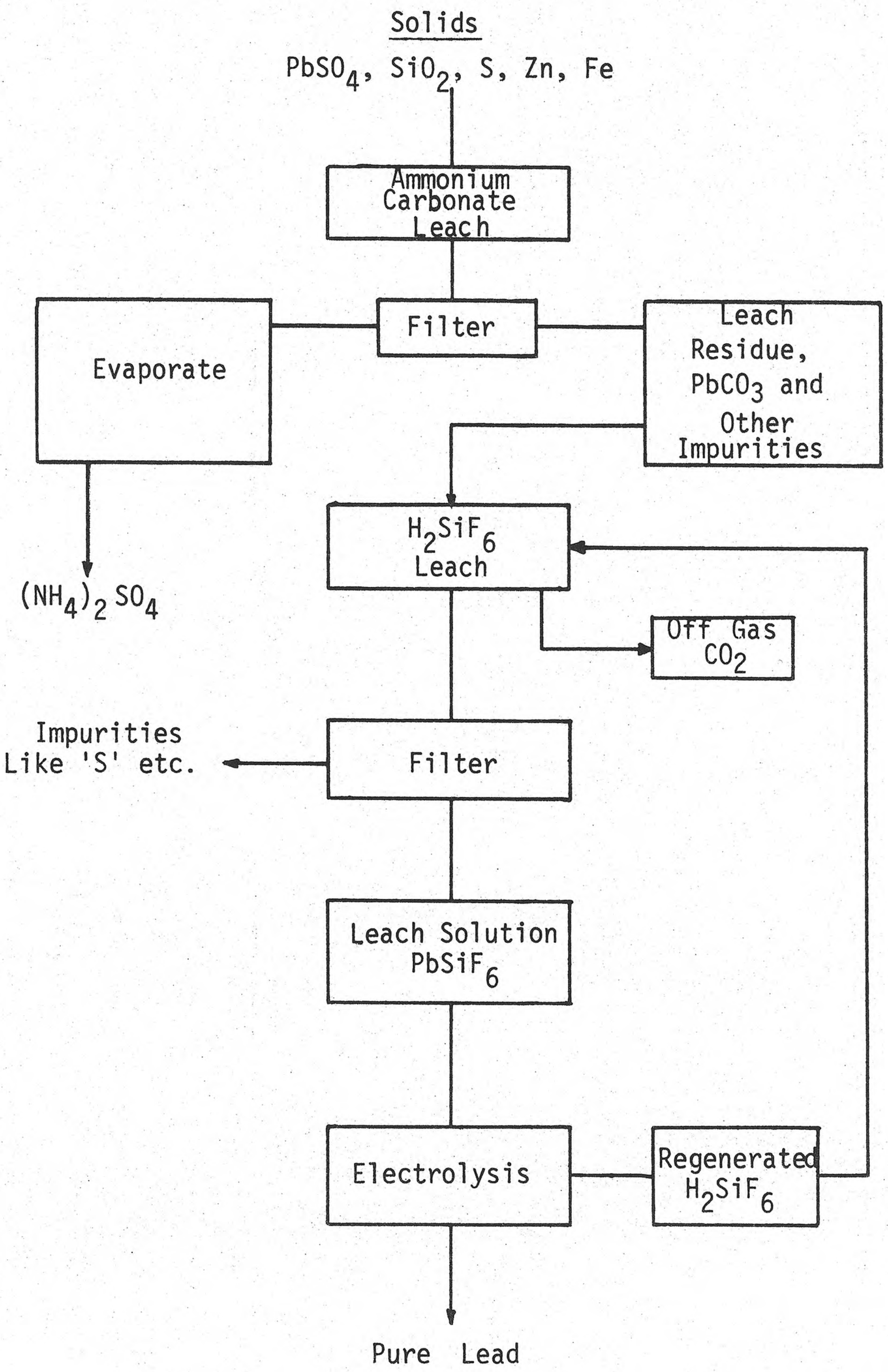

Figure 2. Flow Diagram for Recovery of Lead from $PbSO_4$ Using an Ammonium Carbonate Leach

$$Na_2SnO_3 + H_2O \longrightarrow 2NaOH + O_2 + Sn^\circ \tag{10}$$

$$Na_2SnS_3 + 2\ O_2 \longrightarrow Na_2S + 2\ SO_2 + Sn^\circ \tag{11}$$

Thus there is regeneration of both NaOH and Na_2S which are recycled with the evolution of O_2 and SO_2 at the anode.

III. EXPERIMENTAL DETAILS

A. MATERIALS

The materials used in this study are described as follows:

1. Characterization of Starting Materials. The assays of various samples used in this study are found in Table I. The Pb, Cu, and Sn analyses were obtained by wet chemical techniques; the Ag and Au assays were obtained by fire assay at the Iron King Assay Office, Humboldt, Arizona.

The raw sample used for the majority of study was dried at 120° C to drive off physically absorbed water; the sample assayed 7.00 pct Cu, 34.4 pct Pb, 15.5 pct Sn, 894.7 oz Ag/st and 3.42 oz Au/st. The raw slimes sample initially contained about 2 pct coarse material such as wood chips, rubber, dirt and a few large chips of elemental Cu which were removed from the sample prior to drying and assaying. The dried raw slimes were lightly ground with a mortar and pestle and screened through a -65 mesh screen and then mixed thoroughly. X-ray data indicated that most of the Ag was present as AgCl. Most of the Pb was present as $PbSO_4$ while the majority of the Sn was present as SnO_2.

2. Reagents. All reagents used were reagent grade, except for $PbSO_4$ which was prepared by reacting PbO with HNO_3 and precipitating it with Na_2SO_4 to produce $PbSO_4$. The $PbSO_4$ was then washed free from acids and then dried. It was then lightly ground with a mortar and pestle and screened through 100 mesh before use. H_2SiF_6 was a waste product containing 24.7 pct H_2SiF_6 along with 1.09 pct P_2O_5. The DETA and $Na_2S\cdot9H_2O$ were technical grade. $Na_2S\cdot9H_2O$ was in the form of flakes which were ground with a mortar and pestle before use. The $NaNO_2$ and NaOH were reagent grade. The RLRL and other leaching processes were performed using distilled water.

3. Equipment. A one liter capacity glass reactor was used for all the leaching reactions. An overhead motor driven stirrer was used to provide moderate agitation. A Thermolyne Corporation resistance type furnace, model no. F-A1738-1, was used for carbothermic reduction of $2PbCO_3\cdot Pb(OH)_2$. For hydrogen reduction of slimes a small Lindberg

TABLE I

ASSAYS OF AN INDUSTRIAL COPPER REFINERY SLIMES STARTING MATERIAL

Sample	Cu, pct	Pb, pct	Ag, oz/st	Au, oz/st	Sn, pct
Raw slimes dried at 120° C	7.00	34.4	894.7	3.42	15.5
Raw slimes dried as 200° C	--	--	901.3	3.210	--
Raw slimes washed and dried	4.5	36.37	974.2	--	--
Roasted slimes not decopperized	7.24	36.81	470.6	1.784	10.0
Roasted decopperized	0.24	38.88	352.3	5.488	17.0
AgCl sample	0.08	2.0	19,142.9	Trace	--

Hevi-duty tube type furnace, model no. 54032-A, was used. A vacuum pump filtering device was used for filtration. Whatman number 5 filter paper (Fisher brand) was used for all filtering operations except for NaOH solutions. For NaOH solutions Reeve Angel glass fiber filters were used. A Corning model no. 12 research pH meter was used for all pH measurements.

B. PROCEDURES

The procedures followed in this experimental work are as follows:

1. Roast-Leach-Roast-Leach (RLRL). The process involves roasting the slimes at 530° C in a resistance type furnace with 18 to 20 wgt pct addition of H_2SO_4 for 6 hours. The roasted slimes were leached in hot water at 90° C for 1 hour. One liter of hot water was used to leach 200 gm of slimes. This procedure was repeated.

2. DETA Leaching. RLRL slimes were leached in 2 pct, 5 pct, and 10 pct of DETA solution at 23° C with moderate agitation. The leaching was performed in a one liter enclosed glass reactor for 2 to 4 hours. The overhead stirrer was used to provide moderate agitation. Then the residue was filtered, washed, and dried. The solution was then treated with CO_2 or Na_2S. CO_2 was bubbled through the solution in a beaker which was covered with polythylene wrap. The CO_2 was bubbled in excess of the stoichiometric amount to ensure that no Pb remained in solution. The basic lead carbonate [$2PbCO_3 \cdot Pb(OH)_2$] was precipitated, filtered, washed free from DETA and then dried. The solution was then treated with double the stoichiometric amount of CaO for 2 hours at 23° C with moderate agitation. This was a DETA regeneration step.

The regeneration reactions were also performed in a one liter enclosed reactor, with moderate agitation at 23° C. The cycle time was 2 hours.

The alternative technique for precipitating Pb was treating the solution with $Na_2S \cdot 9H_2O$. The $Na_2S \cdot 9H_2O$ flakes were crushed in a mortar and pestle, and then reacted with the Pb bearing DETA solution in an enclosed reactor for 2 hours at 23° C with moderate agitation. Thus PbS precipitate was formed which was then filtered, washed and dried. Then regeneration of the DETA solution with CaO was performed as described above.

3. NaOH Leaching. NaOH pellets were dissolved in distilled water to make an 8 pct (2 molar) leaching solution.

The leaching, precipitating and regenerating procedures were the same as for DETA leaching.

4. Carbothermic Reduction of $2PbCO_3 \cdot Pb(OH)_2$. The $2PbCO_3 \cdot Pb(OH)_2$ powder was placed in a crucible and heated to 950° C in a resistance type furnace for 1 hour. The crucible temperature was about 925° C. Optimum Pb recovery was obtained at 950° C furnace temperature, 5 gm of charcoal/100 gm of $2PbCO_3 \cdot Pb(OH)_2$ and 3 gm of sodium borate flux/100 gm of $2PbCO_3 \cdot Pb(OH)_2$. A Pb button was obtained which was covered by slag. The slag was broken off and the Pb button was weighed and analyzed. Pb buttons of 99.9 pct purity were obtained with 100 pct recovery of Pb.

5. Hydrogen Reduction of Slimes. These experiments were performed in a tube furnace. Ten gm of RLRL slimes were reduced by passing H_2 over a crucible placed at the center of the tube furnace at 650° C. The cycle time was 2 hours. The excess H_2 coming out was passed through water and then burned by a flame at the opening to avoid explosion. The gas pressure was kept at 5 psi. The product was found to be metallic prills of a Pb-Sn alloy.

6. Selective Electrowinning of Ag and Cu from RLRL Solutions. The RLRL solutions were electrolyzed using a Cu cathode and a Pt anode at 23° C. At 1.4 V an Ag powder was recovered at the cathode which was fluffy and consisted of long crystals of metallic Ag. Ag powder was easily removed from the cathode by stirring the electrolyte. The Ag settled to the bottom of the beaker and the solution was then siphoned. This solution was then electrolyzed using the same electrodes to recover the Cu at a voltage of 2.9 V and a temperature of 23° C. The Cu which plated on the Cu cathode was rough and difficult to strip from the Cu starter cathode sheet.

C. EXPERIMENTAL STRATEGY

Initially leaching tests were performed on reagent grade SnO_2, $PbSO_4$ prepared at UMR labs, AgCl from an industrial copper refinery and elemental Cu, by treating them with different leaching reagents like

NaOH, DETA and $(NH_4)_2CO_3$. The cycle time, temperature, concentration of the leaching reagent and degree of agitation were varied to find the optimum solubility conditions. The evaluation of a particular success or failure was based upon the percentage of Pb solubilized and the recovery of Pb into the $2PbCO_3 \cdot Pb(OH)_2$. In these tests only one condition was varied at a time.

At the same time the recyclability of the leaching reagents and difficulties encountered in regeneration were studied. The evaluation of a particular success or failure of the recyclability of a leaching reagent was based upon its leaching efficiency after 5 cycles, the purity of the Pb product and the percentage of Pb recovered.

Recovery of Pb by electrowinning and by carbothermic reduction was studied and equally pure Pb products were obtained. In performing the carbothermic reduction tests a two level factorial statistical design was used to optimize the parameters of reduction time, amount of charcoal used, and the amount of sodium borate flux. The basis for success was the weight percent of Pb recovered.

Atomic absorption, wet chemistry and fire assaying techniques were used for assaying and analysis.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. TREATMENT OF RAW SLIMES

From the previous investigations it was found that the Roast-Leach-Roast-Leach process (RLRL) solubilized about 91.0 pct of the Ag and 99.0 pct of the Cu. It was found from the literature review and preliminary tests that the $PbSO_4$ in the slimes could be effectively leached from a chemical standpoint with DETA (diethylene triamine) to separate SnO_2 and $PbSO_4$.

To test the overall process on slimes, 1200 gm of raw slimes were processed by a Roast-Leach-Roast-Leach, a NaCN leach and DETA leach technique. The results of the tests are tabulated in Table II. Prior to processing, the slimes sample from an industrial Cu refinery was decanted and filtered to remove most of $CuSO_4$ solution.

The slimes were then dried overnight at 125° C and ground in a mortar and pestle to pass 65 mesh. Twelve hundred grams of slimes were mixed with 18 wgt pct H_2SO_4 and roasted for 6 hours at 530° C. They were then leached for 1 hour in 6 liters of water at 90° C. The residue was again roasted and leached in the same manner as above. There was a 20.5 pct weight loss at the end of the second leach. The residue was then leached in 4 liters of 1 pct NaCN solution for 24 hours with moderate agitation. No air or O_2 was bubbled. This was done in an attempt to remove any AgCl present after the RLRL treatment and before the DETA leach. The sample was again filtered and dried. The residue was then leached for 4 hours at 23° C in 3.5 liters of a 10 pct (100 g/ℓ) DETA solution. The residue was then filtered and dried; there had been a 72.2 pct weight loss at this point. The filtrate was reacted with CO_2 gas to precipitate $2PbCO_3 \cdot Pb(OH)_2$. Samples of the various products were analyzed.

Table II shows the assays of slimes and the cumulative weight pct removed after each treatment. The Roast-Leach-Roast-Leach process removed 1.8 pct Pb, 97.1 Cu, 0.0 pct Sn, 84.3 pct Ag and 12.6 pct Au. It was seen that a substantial amount of Cu and Ag was removed by

TABLE II

RESULTS OF PROCESSING Cu REFINERY SLIMES

Treatment	Temp., °C	Time, Hours	Cumulative Pct Weight Loss	Assays					Cumulative Weight Pct Removed				
				Pct			troy oz/ton						
				Pb	Cu	Sn	Ag	Au	Pb	Cu	Sn	Ag	Au
Feed	-	-	-	34.4	7.0	15.5	894.7	3.42	0.0	0.0	0.0	0.0	0.0
Roasted	530	6	0.0	-	-	-	-	-	-	-	-	-	-
H_2O Leach	90	1	16.3	39.9	1.93	-	386.6	3.65	2.9	76.9	-	63.8	10.6
Re-Roast	530	6	16.3	-	-	-	-	-	-	-	-	-	-
Re-Leach	90	1	20.5	42.5	0.26	-	176.2	3.76	1.8	97.1	-	84.3	12.6
1% NaCN Leach	23	24	24.4	43.3	0.23	-	114.4	1.66	4.8	97.5	-	90.3	63.3
10% DETA Leach	23	4	72.2	5.0	0.45	54.6	226.7	0.20	96.0	98.2	2.1	93.0	98.4
Aqua Regia Leach	65	1	76.7	Tr	0.20	59.0	209.3	0.42	100.0	99.3	11.3	94.6	90.2
$2PbCO_3 \cdot Pb(OH)_2$ from DETA	23	-	-	80.2	0.004	-	0.001	-	-	-	-	-	-
Pb Button by Carbon Reduction	925	1	-	99.99	0.004	-	0.005	-	-	-	-	-	-

Roast-Leach-Roast-Leach process. The NaCN leach was not very effective for Ag which increased the amount of Ag solubilized from 84.3 pct to 90.3 pct, but it was quite effective for Au which increased the amount of Au solubilized from 12.6 pct to 63.3 pct. Only 4.8 pct Pb and none of the Sn was removed by the end of this stage. The DETA leach removed 96.0 pct of Pb and only 2.1 pct of Sn. The results showed that the DETA leach process could produce a high purity $2PbCO_3 \cdot Pb(OH)_2$ which contained 80 pct Pb. The DETA leach residue contained 97.9 pct of the original Sn at a grade of 54.6 pct Sn which is equivalent to 69.1 pct SnO_2. An aqua regia leach was not effective in removing Ag and Au from the Sn residue.

The filtrate saved from the RLRL operation was electrolyzed to selectively electrowin Ag and Cu, using a Cu cathode and a Pt anode at 23° C; 350 ml of this solution was electrolyzed at 1.4 V for 6 hours. A fluffy Ag powder gathered at the bottom of the flask. No Ag powder was observed adhering to the Cu cathode. The initial solution concentration was 5.7 gm Ag per liter and essentially 100 pct of the Ag was recovered from the solution by electrowinning.

The same 350 ml solution from which Ag was removed was selectively electrolyzed at 2.9 V for 12 hours. The solution initially contained 13.6 gm Cu/ℓ and 90 pct of the Cu was recovered by electrowinning.

The important aspects of this preliminary work were: 1) the realization that about 91.0 pct of the Pb was solubilized in DETA, 2) the process could produce a high purity $2PbCO_3 \cdot Pb(OH)_2$, which contained 80 pct Pb (this could be reduced to produce 99.99 pct Pb metal), 3) the RLRL process solubilized about 97 pct of the Cu and about 84 pct of the Ag and 4) 90 pct of the Cu and 100 pct of the Ag could be recovered by selectively electrowinning the RLRL solutions.

B. DETA LEACHING

The following section deals with the study of process variables in leaching slimes with DETA, regeneration or recyclability of DETA and recovery of Pb from Pb concentrate.

1. Study of Process Variables. The raw slimes contained $PbSO_4$, AgCl, SnO_2, $CuSO_4$ and elemental Cu. Therefore the first step was to

determine the solubilities of these species in various concentrations of diethylene triamine (DETA) solutions. The results are shown in Figure 3. The results show that the $PbSO_4$ and Cu^{++} are very soluble, AgCl and elemental Cu are moderately soluble and SnO_2 is insoluble in DETA solutions. In 100 g/ℓ solutions of DETA the solubilities were 215 g/ℓ for $PbSO_4$, 115 g/ℓ for Cu^{++}, 40 g/ℓ for AgCl and zero g/ℓ for SnO_2 after 48 hours at 23° C with agitation. The solubilities were determined by a weight loss method.

Tests were performed to determine the effects of time, temperature, DETA concentration, agitation and pulp density on the leaching of pure $PbSO_4$. The test results showed that 100 pct of a $PbSO_4$ sample could be dissolved in 5 pct, 10 pct and 20 pct solutions of DETA in only 2 or 3 minutes at 23° C with moderate agitation, with a 50 pct excess of DETA over the stoichiometric requirement. Only 50 pct of a $PbSO_4$ sample dissolved after 24 hours with no agitation. This showed that moderate agitation is a necessity. Samples of pure SnO_2 showed no loss in weight after 48 hours of agitation in 10 pct (100 g/ℓ) solutions of DETA at 23° or 60° C.

2. <u>Regeneration or Recyclability of DETA</u>. This section deals with recycle leaching tests with DETA, the efficiency of DETA after each cycle and the regeneration or recyclability of DETA.

In a 10 pct DETA solution (100 g/ℓ) the solubility of $PbSO_4$ was found to be 215 g/ℓ, so the leaching experiments were started with 10 pct DETA solutions. Initially the recycle leaching tests were performed on $PbSO_4$ powder. One hundred gm of $PbSO_4$ was treated with 500 ml of 10 pct (100 g/ℓ) DETA for 4 hours at 23° C with moderate agitation. All of the $PbSO_4$ was dissolved in 2-3 minutes. The $PbSO_4$ leaching reaction goes as follows:[3]

$$PbSO_4 + DETA \longrightarrow [Pb(DETA)]\ SO_4 \qquad (1)$$

CO_2 was then bubbled through this solution to precipitate $2PbCO_3 \cdot Pb(OH)_2$. The CO_2 was passed through in excess so as to ensure that all Pb in solution was precipitated as $2PbCO_3 \cdot Pb(OH)_2$ as shown by the following reaction.[7]

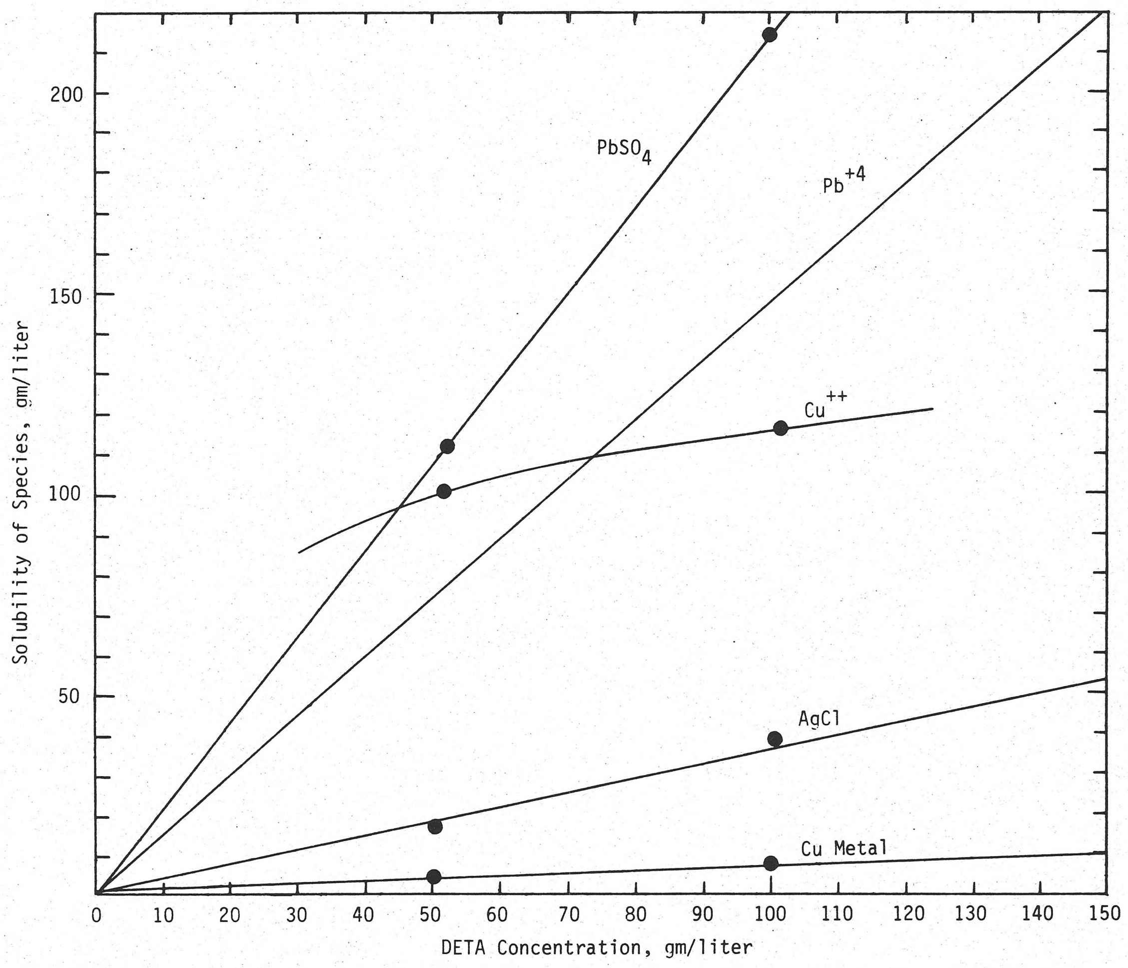

Figure 3. Solubilities of Metal Values in Various Concentrations of Diethylene Triamine (DETA) Solutions

$$6[Pb(DETA)]\ SO_4 + 10\ CO_2 + 14\ H_2O \longrightarrow 2\ [2PbCO_3 \cdot Pb(OH)_2] + 3\ DETA(H_2SO_4)_2 + 3\ DETA\ (H_2CO_3)_2 \qquad (2)$$

The $2PbCO_3 \cdot Pb(OH)_2$ precipitate was filtered, dried and weighed. The filtrate was then treated with CaO to remove SO_4^{--} from the system and to regenerate an equivalent amount of free amine (DETA) for recycling according to the following equations:[3]

$$DETA(H_2SO_4)_2 + 2\ Ca(OH)_2 \longrightarrow DETA + 2\ CaSO_4 + 4\ H_2O \qquad (3)$$

$$DETA(H_2CO_3)_2 + 2\ Ca(OH)_2 \longrightarrow DETA + 2\ CaCO_3 + 4\ H_2O \qquad (4)$$

In these experiments technical grade CaO, ground to 200 mesh was used to ensure complete reaction, with a 100 pct excess of CaO over the stoichiometric requirement. The $CaSO_4$ precipitate was filtered and the filtrate was used for recycling. Distilled water was added to the filtrate to make up the solution volume lost in the process. One hundred gm of $PbSO_4$ was again treated with 500 ml of filtrate and the same procedure was repeated for precipitating $2PbCO_3 \cdot Pb(OH)_2$ and regeneration of DETA. This was repeated up to 7 cycles to determine the recyclability of DETA and the recovery of Pb from the solution as a $2PbCO_3 \cdot Pb(OH)_2$ precipitate. Table III shows the pct $PbSO_4$ solubilized in each cycle ("leaching effiency") of DETA on that cycle and the pct of the solubilized Pb recovered from the solution in the $2PbCO_3 \cdot Pb(OH)_2$ product.

From the results it can be seen that by the third cycle the leaching efficiency of DETA had dropped to 46 pct from 100 pct. The Pb recovery was about 100 pct on the first cycle but it dropped to 80 to 86 pct for the next three cycles. From the results it can be seen that the recyclability of the DETA is not good. For checking the recyclability with actual slimes, experiments were again carried out with 10 pct (100 g/ℓ) DETA solutions.

Three hundred fifty gm of RLRL (Roast-Leach-Roast-Leach) slimes were treated with 1 liter of 10 pct (100 g/ℓ) DETA solution. The solution leached 97 pct of $PbSO_4$ on the first cycle and about 95 pct of

TABLE III

RESULTS OF RECYCLE LEACHING TESTS OF $PbSO_4$ POWDER USING 10 PCT DETA SOLUTIONS

Cycle	Pct $PbSO_4$ Solubilized	Pct of Solubilized Pb Recovered in Lead Product
1	100.0	99.17
2	62.0	80.68
3	46.6	82.16
4	24.5	86.33
5	21.3	52.39
6	13.0	81.37
7	7.0	100.00

the Pb was recovered in the Pb concentrate. On the second cycle the solubility of the $PbSO_4$ dropped to 17 pct and the Pb recovery remained the same at about 95 pct. These experiments showed that the recyclability was very poor when actual slimes were treated. The main reason for the lower DETA efficiency with slimes when compared to the $PbSO_4$ powder was the high volume of SnO_2 in the residue. The SnO_2 in the slimes remained un-leached and this residue might have adsorbed DETA and the DETA might have been lost on the SnO_2 residue when it was filtered. Thus the reason for low recyclability could be the adsorption of DETA on the SnO_2 residue, adsorption of DETA on the $2PbCO_3 \cdot Pb(OH)_2$ product and the $CaSO_4$ precipitate which was produced during the regeneration step.

A set of experiments was performed with 2 pct (20 g/ℓ) DETA solutions to determine whether the recyclability of DETA could be increased by using lower concentrations of DETA solutions. Initially the recycle leaching tests were performed using $PbSO_4$ powder. The procedure consisted of 1) a DETA leach, 2) filtration, 3) CO_2 precipitation of $2PbCO_3 \cdot Pb(OH)_2$ and 4) CaO regeneration of the solution.

The solubility of the $PbSO_4$ dropped to only 83 pct from 100 pct on third cycle and 100 pct of the Pb was recovered as $2PbCO_3 \cdot Pb(OH)_2$. These results were good when compared to the results of the 10 pct DETA leach in which the solubility of $PbSO_4$ dropped to 46 pct on third cycle. Thus lower DETA concentrations were found to have better recyclability than did the higher concentration solutions. The experiments were continued on actual slimes using 2 pct DETA solutions.

Fifty gm samples of RLRL slimes were leached in 625 ml of 2 pct DETA solutions for 2 hours at 23° C. The slurries were then filtered to yield a residue assaying 54.6 pct Sn, 5.0 pct Pb and 0.76 pct Ag and containing 4.4 pct of the Pb, 97.9 pct of the Sn and 96.6 pct of the Ag from the feed. The filtrate was treated by bubbling CO_2 to precipitate a $2PbCO_3 \cdot Pb(OH)_2$ product which was recovered by filtration. The Pb product assayed 80.2 pct Pb, 0.004 pct Sn and 0.000 pct Ag and contained 96.6 pct of the original Pb. CaO was then added to the solution to precipitate $CaSO_4$ so that the DETA could be recycled. Table IV shows the pct $PbSO_4$ solubilized in each cycle on a particular

TABLE IV

RESULTS OF RECYCLE LEACHING TESTS ON RLRL SLIMES USING 2 PCT DETA SOLUTIONS FOLLOWED BY CO_2 AND CaO REGENERATION

Cycle	Pct of $PbSO_4$ Solubilized from Slimes
1	100
2	64
3	36
4	25
5	20

cycle. The solution only leached at 64 pct efficiency on the second cycle and at about 20 pct efficiency on the fifth cycle. Although the DETA leaching efficiencies were found to be higher than those observed in the case of the 10 pct DETA, it was still not high enough to make the system economically viable. Thus other methods for regeneration of the DETA were attempted.

In the first method, Na_2S was used to precipitate Pb from the solution as PbS instead of using CO_2. The tests used identical leaching conditions as were previously described (CO_2 plus CaO regeneration) so that the DETA leach residues were similar. The Pb was then precipitated from the filtrate by the addition of Na_2S to precipitate a very high grade PbS assaying 86.12 pct Pb (pure PbS is 86.6 pct Pb), 0.4 pct Sn and 0.008 pct Ag. Tables V and VI show that the DETA solutions with Na_2S regeneration leached at 67 pct efficiency on the third cycle; however, they leached at 87 pct efficiency when the sulfate was also removed by the addition of CaO. This shows that CaO plays an important role in improving the DETA leaching and recycling efficiency. Nearly 100 pct of the Pb was recovered from the solution as the PbS product.

Thus if we compare different DETA regeneration techniques, from a regeneration and recyclability point of view, the Na_2S and CaO regeneration method seems to be the best.

Haruo Mimura et al. state that the overall loss of DETA is supposed to be less than 5 pct in one extracting cycle, including diminution of its extracting power.[3] But experimentally it was found that at the end of the fifth cycle the loss was about 55 pct. As discussed before the reason for the higher diminution of extracting power seems to be adsorption of DETA on the un-leached SnO_2 residue, $2PbCO_3 \cdot Pb(OH)_2$ or PbS product and $CaSO_4$ precipitate which is produced during regeneration step. So the next set of experiments was conducted to determine if the DETA which is adsorbed on these residues could be removed by washing the residues with water and if this wash water could be used for leaching slimes.

Initially the residues were washed with cold water (room temperature). Samples of 100 gm of RLRL slimes were treated with

TABLE V

RESULTS OF RECYCLE LEACHING TESTS ON RLRL SLIMES USING 2 PCT DETA SOLUTIONS FOLLOWED BY Na_2S REGENERATION

Cycle	Pct of $PbSO_4$ Solubilized from Slimes
1	100.0
2	87.4
3	66.4

TABLE VI

RESULTS OF RECYCLE LEACHING TESTS ON RLRL SLIMES USING 2 PCT DETA SOLUTIONS FOLLOWED BY Na_2S AND CaO REGENERATION

Cycle	Pct of $PbSO_4$ Solubilized from Slimes
1	100.0
2	95.76
3	85.5
4	54.94
5	44.43

2.5 liters of wash water for 12 hours with moderate agitation. The solubility of the $PbSO_4$ was found to be less than 2.6 gm/liter, which was negligible. The residues were then washed and stirred in hot water. One hundred gm of $PbSO_4$ was treated with 500 ml of the hot wash water for 12 hours with moderate agitation. The solubility of $PbSO_4$ in this DETA wash solution was found to be only 14.62 gm/liter. From these experiments it was clear that taking the trouble of washing the residues is not worth the effort from a recyclability point of view. Distillation of wash water to recover and recycle DETA was also attempted, but was not very successful either.

Cu was also solubilized along with $PbSO_4$ in DETA solutions. It was felt that some of the Cu which was being complexed by the DETA could be electrowon to regenerate the tied up DETA from the DETA solutions. However, the solubility of the $PbSO_4$ decreased from 107 g/ℓ to 60 g/ℓ after removing Cu by electrowinning. This was probably due to the DETA breaking down while electrolyzing the solution.

To avoid adsorption of DETA onto the $2PbCO_3 \cdot Pb(OH)_2$ product or the PbS product and onto the $CaSO_4$, Pb was electrolyzed directly from the Pb bearing DETA solution in one series of tests. Electrowinning of Pb was accomplished using a Pb cathode and a C anode. High purity Pb was recovered at the cathode but the leaching efficiency of the DETA decreased to 6 pct from 100 pct on the second cycle of this test. Thus electrowinning proved to be an unsuccessful process for regeneration of the DETA. Amongst all the regeneration methods tried, the Na_2S plus CaO regeneration scheme seemed to be the best.

3. Recovery of Pb. Up to this point the process variables in DETA leaching and regeneration of DETA have been discussed. At this stage one obtains a Pb product which is either $2PbCO_3 \cdot Pb(OH)_2$ or PbS. A PbS product could be sold directly to a lead smelter. This section deals mainly with the reduction of $2PbCO_3 \cdot Pb(OH)_2$. It also deals with the direct recovery of Pb from DETA solutions by the electrowinning technique.

a. Reduction of $2PbCO_3 \cdot Pb(OH)_2$ to Elemental Pb. A series of statistically designed tests was performed to determine the effects of temperature, time, charcoal addition, and sodium borate flux addition on the carbothermic reduction of $2PbCO_3 \cdot Pb(OH)_2$ to elemental Pb.

The first set of experiments was carried out to determine the optimum reduction temperature. In these experiments pure $PbCO_3$ was used instead of $2PbCO_3 \cdot Pb(OH)_2$. One hundred gm of $PbCO_3$ was reacted with 5 gm of charcoal for 2 hours at 500° C, 750° C and 950° C furnace temperatures. At 500° C and 750° C the $PbCO_3$ compound remained unreduced; only at 950° was the $PbCO_3$ reduced and a Pb button obtained. Thus a furnace temperature of 950° C was found to work well which was a 925° C crucible temperature.

Additional experiments were conducted at 950° C for 60 minutes to determine the effect of the quantity of charcoal and sodium borate flux used. One hundred gm of $PbCO_3$ was treated with different quantities of charcoal and sodium borate flux. Table VII shows the results of these tests.

Trial Number 4 showed the best results; 87.24 pct Pb was reduced. This was obtained with high (4 gm) charcoal and high flux (3 gm) level. The individual factor effects of charcoal and flux were positive and the combined factor effect of charcoal-flux (x_1x_2) was also positive. This showed that increased charcoal and flux gave higher Pb recovery.

Another series of reduction experiments was performed using a larger amount of charcoal, but keeping the cycle time (60 minutes) and temperature (950° C) constant. Table VIII shows the results of these tests.

Trial Number 7 showed the best results when 100 pct of the Pb was reduced at the low charcoal (5 gm) level and high flux (3 gm) level. Individually the factor effect of charcoal was negative. This showed that the low charcoal (5 gm) level was better. The flux factor effect and the combined charcoal-flux effect were positive, so the high flux (3 gm) level was better.

Finally to determine the optimum cycle time, charcoal addition, and flux addition, a series of statistically designed tests were performed and a two-level factorial design was formed for these three variables and the results are shown in Table IX. From the table it can be seen that Trial Number 5 gave 100 pct Pb recovery. In this particular trial the cycle time was 60 minutes (low level), the

TABLE VII

TWO-LEVEL FACTORIAL DESIGN RESULTS FOR THE REDUCTION OF LEAD CARBONATE USING CHARCOAL AND SODIUM BORATE FLUX AT 950° C FOR 60 MINUTES

Trial	x_1	x_2	x_1x_2	Mean	Wt Pct Reduced
1	-	-	+	+	44.32
2	+	-	-	+	62.88
3	-	+	-	+	64.04
4	+	+	+	+	87.24
Effect	+20.88	+22.08	+4.64	64.62	

Factor	Level	
	Low (-)	High (+)
x_1 - charcoal	3.0 gm	4.0 gm
x_2 - flux	0.0 gm	3.0 gm

TABLE VIII

TWO-LEVEL FACTORIAL DESIGN RESULTS FOR THE REDUCTION OF LEAD CARBONATE USING CHARCOAL AND SODIUM BORATE FLUX AT 950° C FOR 60 MINUTES (LARGER CHARCOAL ADDITIONS)

Trial	x_1	x_2	x_1x_2	Mean	Wt Pct Reduced
5	-	-	+	+	89.91
6	+	-	-	+	43.04
7	-	+	-	+	100.00
8	+	+	+	+	70.87
Effect	-38.0	+18.96	+8.870	75.955	

Factor	Level Low (-)	 High (+)
x_1 - charcoal	5.0 gm	10.0 gm
x_2 - flux	0.0 gm	3.0 gm

TABLE IX

TWO-LEVEL FACTORIAL DESIGN RESULTS FOR THE REDUCTION OF LEAD CARBONATE USING CHARCOAL AND SODIUM BORATE FLUX AT 950° C FOR 60 MINUTES AND 90 MINUTES

Trial	x_1	x_2	x_3	Wt Pct Pb Reduced	x_1x_2	x_2x_3	x_3x_1	$x_1x_2x_3$	Mean
1	-	-	-	89.91	+	+	+	-	+
2	+	-	-	78.60	-	+	-	+	+
3	-	+	-	43.04	-	-	+	+	+
4	+	+	-	78.99	+	-	-	-	+
5	-	-	+	100.00	+	-	-	+	+
6	+	-	+	81.18	-	-	+	-	+
7	-	+	+	70.87	-	+	-	-	+
8	+	+	+	98.19	+	+	+	+	+
Effect	+8.54	-14.4	+15.18		+23.1	+8.34	-4.28	-0.03	79.97

Factor	Level Low (-)	Level High (+)
x_1 - time	60 min	90 min
x_2 - charcoal	5.0 gm	10.0 gm
x_3 - flux	0.0 gm	3.0 gm

charcoal addition was 5 gm (low level), and the flux addition was 3 gm (high level). This can be justified by observing the individual factor effects and the interactions. Factor effects for charcoal addition and the interaction of time-flux were negative. But individually the factor effect of flux was positive, having a higher value than the effect of time.

This shows that low level for time cycle, low level of charcoal addition and high level for flux addition are beneficial. The optimum conditions were to react the $PbCO_3$ for 60 minutes at 925° C with a 5 pct charcoal addition and a 3 pct sodium borate flux addition. The result was a 100 pct conversion of the $PbCO_3$ to Pb metal of 99.99 pct purity.

b. Recovery of Pb by Electrowinning. The electrowinning technique was tried in an effort to recover Pb metal directly from DETA solutions. Ten gm of $PbSO_4$ was dissolved in 250 ml of 2 pct DETA and then it was electrolyzed using a Pb cathode and a C anode. The voltage was kept at 4.6 V and the cycle time was 8 hours. Pb was recovered at the Pb cathode until dendritic needles which grew rapidly across to the anode caused short circuits. Besides this problem the leaching efficiency of DETA decreased to 6 pct from 100 pct on the second leaching cycle after Pb electrowinning and this made the technique impractical.

C. NaOH LEACHING

This section deals with the leaching of slimes with NaOH solutions. The results from the leaching tests showed that the solubility of $PbSO_4$ in 2 molar NaOH solution is 40.5 g/ℓ at 23° C and at 80° C. The solubility of SnO_2 was found to be very small (0.3 g/ℓ) at 23° C and at 80° C. The solubilities were determined by weight loss method. Thus this method could be quite effective for the separation of SnO_2 and $PbSO_4$. Therefore the further experiments were carried out with 2 molar NaOH (8 pct) solution at only 23° C.

The recycle leaching tests were performed on RLRL slimes using 2 molar NaOH solutions and recovering Pb as a $2PbCO_3 \cdot Pb(OH)_2$ product by bubbling CO_2 through the NaOH solution. Fifty gm of RLRL slimes were leached for 2 hours in one liter of an 8 pct NaOH (2 molar) solution at 23° C. Approximately 89 pct of the Pb was solubilized and was subsequently recovered by bubbling CO_2 through the filtrate to precipitate a $2PbCO_3 \cdot Pb(OH)_2$ product. Ninety-two pct of the Sn and 96.5 pct of the Ag stayed behind as solids in the original leach residue which was 42.7 pct of the original weight. The NaOH solution was only regenerated to 15 pct of its original strength when CaO was added to remove the sulfate and the solution was recycled to leach the second batch of RLRL slimes. The reason for the poor regeneration was that Na_2CO_3 also precipitated when the $2PbCO_3 \cdot Pb(OH)_2$ was precipitated, lowering the strength of the NaOH solution. This also lowered the assay of the Pb concentrate to 71.0 pct Pb. An experiment was carried out to determine the neutralizing effect on a NaOH solution due to the amount of CO_2 bubbled during Pb precipitation. Figure 4 shows the relationship between the percentage Pb remaining in solution and the amount of CO_2 added. It also shows the relationship between hydroxide ion concentration and the amount of CO_2 added. The results showed that four times the stoichiometric amount of CO_2 was required to precipitate the Pb from the filtrate and that the hydrogen ion concentration decreased from 2.0 to 1.3 moles per liter with the CO_2 addition. The subsequent CaO addition also precipitated $CaCO_3$ as well as the intended $CaSO_4$ precipitate. Thus, the regeneration of NaOH solution only leached 15 pct of the quantity of slimes on the second cycle as it did on the first cycle.

The recyclability of the NaOH solution by the CO_2 plus CaO regeneration method was found to be very poor, so additional recycle leaching tests were performed using Na_2S to precipitate the lead as PbS. Twenty gm of RLRL slimes were leached with 500 ml of 8 pct (2 molar) NaOH at 23° C for 2 hours. The Sn residue was 39.7 pct of the original weight, assayed 41.0 pct Sn and contained 3.6 pct of the original Pb, 96.0 pct of the Sn, and 98.7 pct of the Ag. The filtrate was then treated with Na_2S to precipitate 9.3 gm of PbS concentrate which assayed 75.5 pct Pb and contained 84.1 pct of the original Pb. Experiments were carried for five cycles. Table X shows the percentage $PbSO_4$ solubilized after each cycle. It shows that the recycled NaOH solution worked at 67 pct efficiency after the fifth cycle. In the next set of experiments, after precipitating PbS, CaO was added to

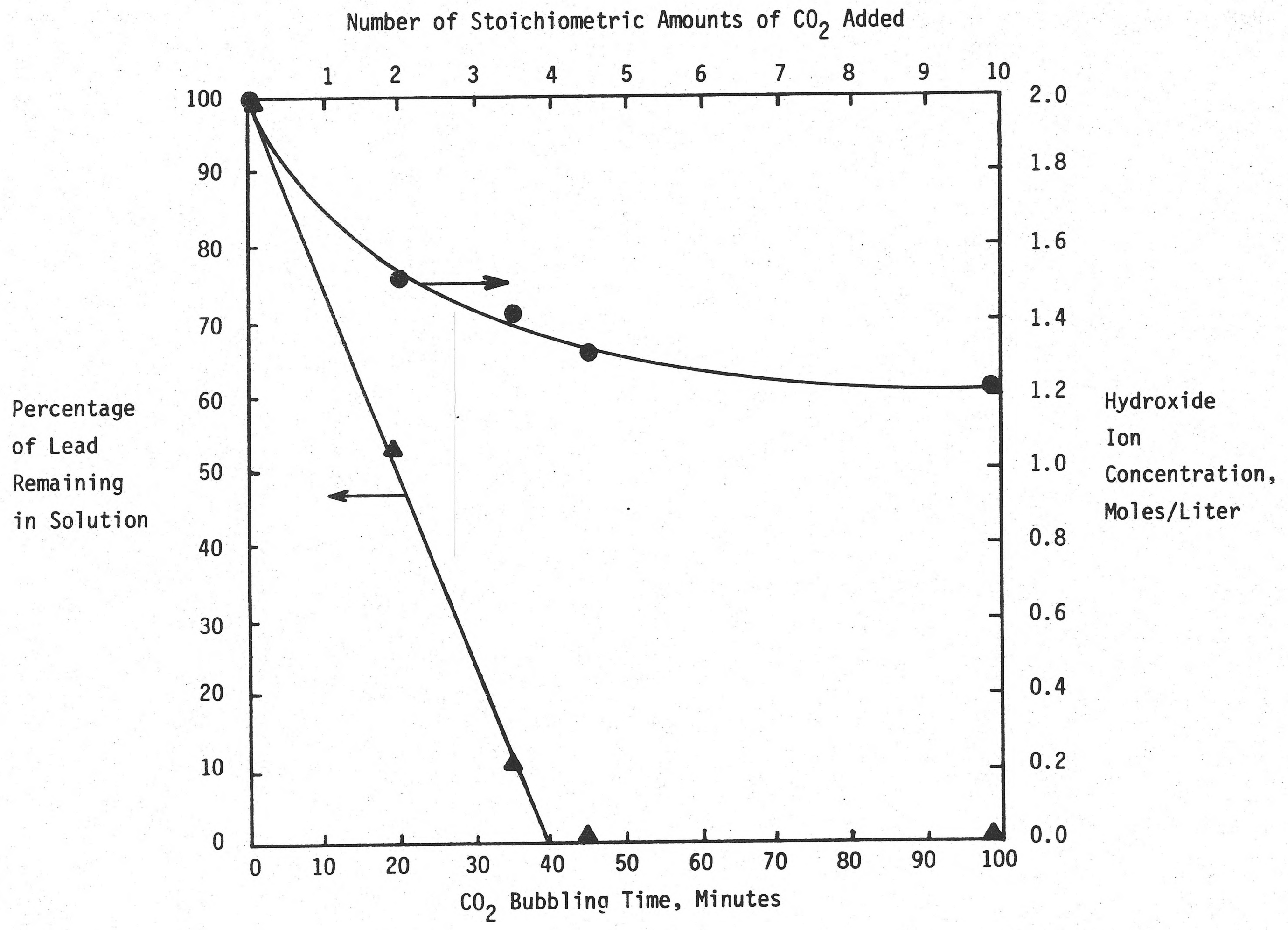

Figure 4. Results of Precipitating $2PbCO_3 \cdot Pb(OH)_2$ from a NaOH Solution Used to Leach RLRL Slimes

TABLE X

SOLUBILITY OF $PbSO_4$ IN 2 MOLAR NaOH SOLUTIONS REGENERATED WITH Na_2S

Cycle	Pct of $PbSO_4$ Solubilized from Slimes
1	100.00
2	98.71
3	84.29
4	90.91
5	67.76

remove the sulfate and to regenerate the NaOH solution. Table XI shows that after the addition of CaO, the solution leached at 85 pct efficiency after five cycles. Thus it can be seen that the NaOH leaching technique with Na_2S plus CaO regeneration seemed to be the best technique with respect to recyclability.

Table XII shows the results of several different NaOH leaches of RLRL slimes.

D. COMPARISON OF VARIOUS LEACHING METHODS

This section deals with the comparison of various leaching and regeneration methods which were discussed in section B and section C. The results of some of the better tests are summarized in Table XIII. The assay of the RLRL slimes used as feed for these tests is listed under Method E, which would be to sell the slimes after the RLRL treatment. Method C appears to be the best of Methods A through D. Method C yielded the highest grade Pb and Sn products through a DETA leach with Na_2S plus CaO regeneration of the solution. The Pb product of Methods C and D contained 95.6 pct of the original Pb which is quite high compared to Method A (88.7 pct) and Method B (84.1 pct). Thus the highest Pb recovery was obtained by Method C.

Figure 5 shows the percentage of $PbSO_4$ from RLRL slimes which was solubilized after the leach solution was regenerated. This compares the recyclability of various leaching and regeneration methods. Method B seemed to have better recyclability compared to Method C. Methods A and D seemed to have very poor recyclability.

E. PRELIMINARY ECONOMIC EVALUATION AND MATERIALS BALANCE

This section deals with a preliminary economic evaluation of Methods A through E, discussed in previous sections, a flow sheet and a full materials balance for the best of Methods A through D. Table XIV shows the number of pounds of reagents required by Methods A through E to recover one pound of contained Pb. At the top of Table XV is listed the cost of each of the reagents (Feb. 1979) in terms of dollars per pound of reagent. Table XV also shows the cost of the individual reagents required to produce one pound of contained Pb in the Pb product. The last column shows the smelter value of one pound of

TABLE XI

SOLUBILITY OF $PbSO_4$ IN 2 MOLAR NaOH SOLUTIONS REGENERATED WITH Na_2S AND CaO

Cycle	Pct of $PbSO_4$ Solubilized from Slimes
1	100.00
2	100.00
3	90.84
4	89.10
5	85.90

TABLE XII

TIN RESIDUES FROM VARIOUS NaOH LEACHES OF RLRL SLIMES AT 23° C

Test	NaOH Conc., Pct	Leach Time, Hours	Pct Solids	Pct of Original Wt in Residue	Residue Assays, Pct Pb	Residue Assays, Pct Sn	Residue Assays, Pct Ag	Pct Remaining from Feed Pb	Pct Remaining from Feed Sn	Pct Remaining from Feed Ag
164 (1st cycle)	8	2	4	39.5	3.77	41.0	0.63	3.6	96.0	98.7
164 (5th cycle)	Recycle Solution	2	4	59.0	30.82	33.0	0.23	46.4	99.0	99.7
169	8	2	4	39.5	3.27	52.9	0.73	3.1	99.2	98.9
131	8	2	4.8	42.7	11.05	36.5	0.66	11.3	99.0	96.5

TABLE XIII

ASSAYS AND DISTRIBUTION OF PRODUCTS FROM THE LEACHING OF RLRL SLIMES

		Assays, Pct			Distribution,(2) Pct		
Method(1)	Product	Pb	Sn	Ag	Pb	Sn	Ag
A	Sn Residue	11.1	36.5	0.66	11.3	92.7	96.5
	Pb Conc.	71.0	0.5	0.032	88.7	1.0	3.5
B	Sn Residue	3.77	41.0	0.63	3.6	96.0	98.7
	Pb Conc.	75.7	0.5	0.003	84.1	1.4	1.3
C	Sn Residue	5.0	54.6	0.76	4.4	97.9	96.6
	Pb Conc.	86.12	0.4	0.008	95.6	1.11	3.4
D	Sn Residue	5.0	54.6	0.76	4.4	97.9	96.6
	Pb Conc.	80.2	0.004	0.000	95.6	0.00	0.0
E	Feed, RLRL	41.87	16.8	0.291	100.0	100.0	100.0

(1) Method A: NaOH leach with CO_2 + CaO regeneration
Method B: NaOH leach with Na_2S + CaO regeneration
Method C: DETA leach with Na_2S + CaO regeneration
Method D: DETA leach with CO_2 + CaO regeneration

(2) Note: The distribution of metal may not add to 100.0% as some metal may still be left in the filtrates from the leaching or precipitation steps.

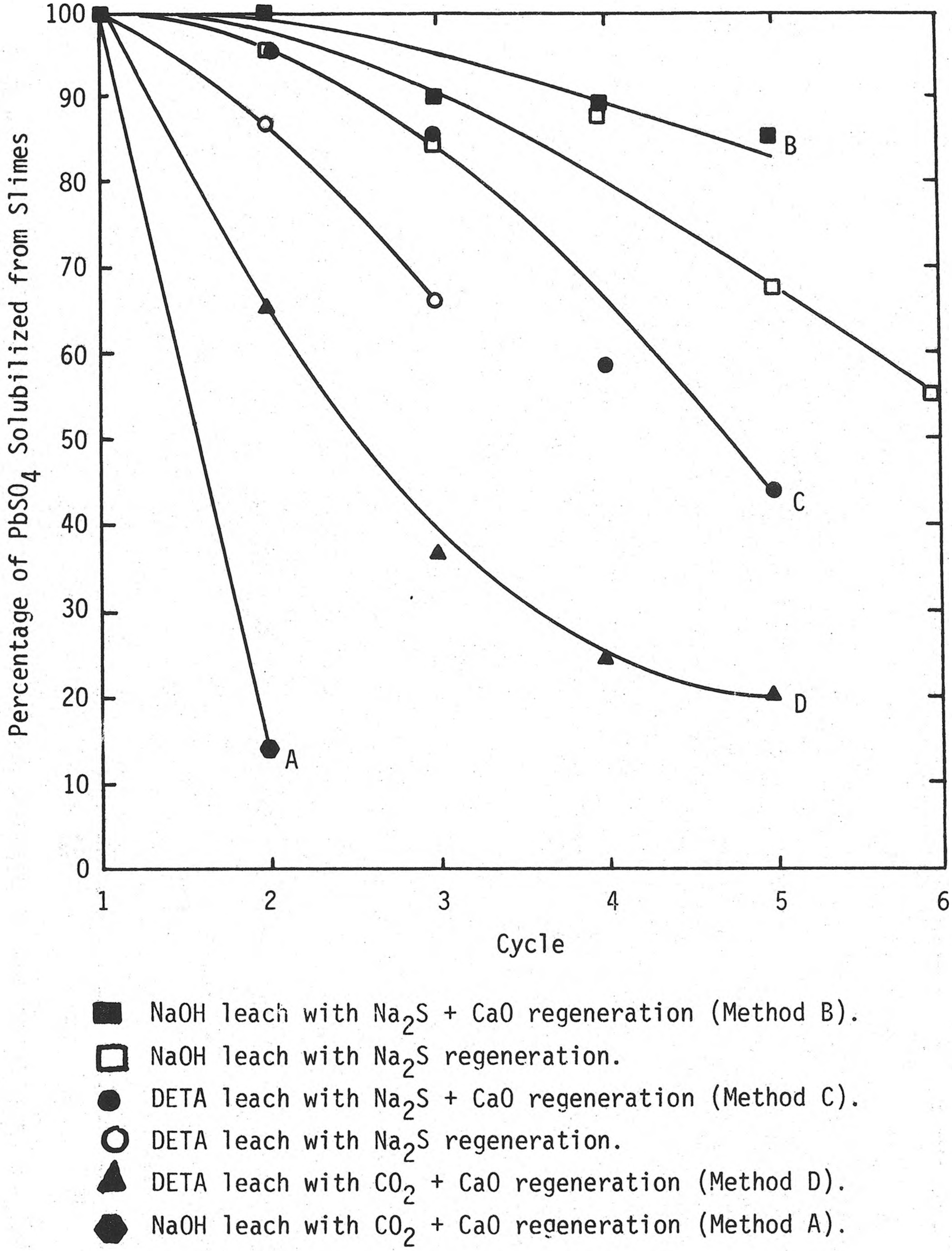

Figure 5. Percentage of $PbSO_4$ from RLRL Slimes Which Was Solubilized After the Leach Solution Was Regenerated

TABLE XIV

POUNDS OF REAGENTS REQUIRED TO PRODUCE ONE POUND OF LEAD METAL FROM RLRL SLIMES

Method	NaOH	DETA	Na_2S	CO_2	CaO
A	0.93	-	-	0.85	1.60
B	0.84	-	0.58	-	1.28
C	-	0.13	0.55	-	1.23
D	-	0.25	-	0.71	1.62
E	-	-	-	-	-

TABLE XV

REAGENT COSTS (FEB. 1979) TO PRODUCE ONE POUND OF LEAD METAL FROM RLRL SLIMES, DOLLARS

Method	NaOH at \$0.175/lb	DETA at \$0.973/lb	Na_2S at \$0.16/lb	CO_2 at \$0.077/lb	CaO at \$0.03/lb	Total Reagent Cost, \$	Smelter Value of Each Contained Pound of Pb, \$
A	0.163	-	-	0.065	0.048	0.276	0.339
B	0.147	-	0.093	-	0.038	0.278	0.343
C	-	0.126	0.088	-	0.037	0.251	0.351
D	-	0.243	-	0.055	0.049	0.347	0.347
E	-		-	-	-	0.000	0.291

contained Pb. A market value of $0.48 per pound for pure Pb metal was used in these calculations. Method D is the worst in that the reagent costs just equal the smelter value of Pb; Method E appears to be the best because the Pb is worth $0.29 per pound with no treatment after RLRL. Thus, even though the chemistry is interesting the economics for Pb recovery by Methods A through D do not appear to be favorable.

The total economic evaluation is not dependent solely upon Pb, however. Thirty-eight pct of the potential economic value of the RLRL slimes comes from Sn, 47.6 pct from Ag, and only 7.5 pct from the Pb. Table XVI lists the pounds of reagents required to process one pound of RLRL slimes and the total reagent cost per pound of slimes leached. The reagent costs range from $0.10 to $0.14 per pound of slimes and the maximum potential value of the slimes is $3.27 per pound.

Of the methods actually tested in the laboratory, Method E (no treatment) appears to be the most economical. But if the potential economic value of Sn is considered, Method C appears to be the best of the Methods A through D in which a Pb-Sn separation was actually made. Method C yielded the highest grade Pb and Sn products at the least cost through a DETA leach with Na_2S plus CaO regeneration of the solution.

A flowsheet for the leaching of one ton of RLRL slimes according to Method C is shown in Figure 6. Twelve and one-half tons (3,000 gallons) of 2 pct DETA solution would be used to leach one ton of RLRL slimes at 23° C for 2 to 4 hours. The slurry would then be filtered to yield 0.415 tons of a Sn residue assaying 5.0 pct Pb, 54.6 pct Sn, 0.764 pct Ag, and 0.45 pct Cu; the residue would contain 4.4 pct of Pb, 97.9 pct of the Sn, and 96.6 pct of the Ag, and 7.8 pct of the Cu. Figure 3 (section A) shows that Cu and Ag as well as Pb have a certain solubility in DETA solutions. The DETA filtrate in Figure 6 would then be treated with Na_2S to precipitate 0.465 tons of PbS concentrate assaying 86.12 pct Pb, 0.4 pct Sn, 0.008 pct Ag, and 0.02 pct Cu with 95.6 pct of the Pb reporting to the PbS product. A full material balance for the process is listed in Table XVII with the process stream numbers corresponding to those found in Figure 6. The worst problem in the scheme would probably be encountered in the

TABLE XVI

POUNDS OF REAGENTS REQUIRED TO PROCESS ONE POUND OF RLRL SLIMES ASSAYING APPROXIMATELY 41 PCT LEAD

Method	NaOH	DETA	Na_2S	CO_2	CaO	Total Reagent Cost per lb RLRL Slimes, $
A	0.344	-	-	0.349	0.590	0.105
B	0.310	-	0.214	-	0.472	0.103
C	-	0.052	0.221	-	0.494	0.101
D	-	0.101	-	0.285	0.651	0.140

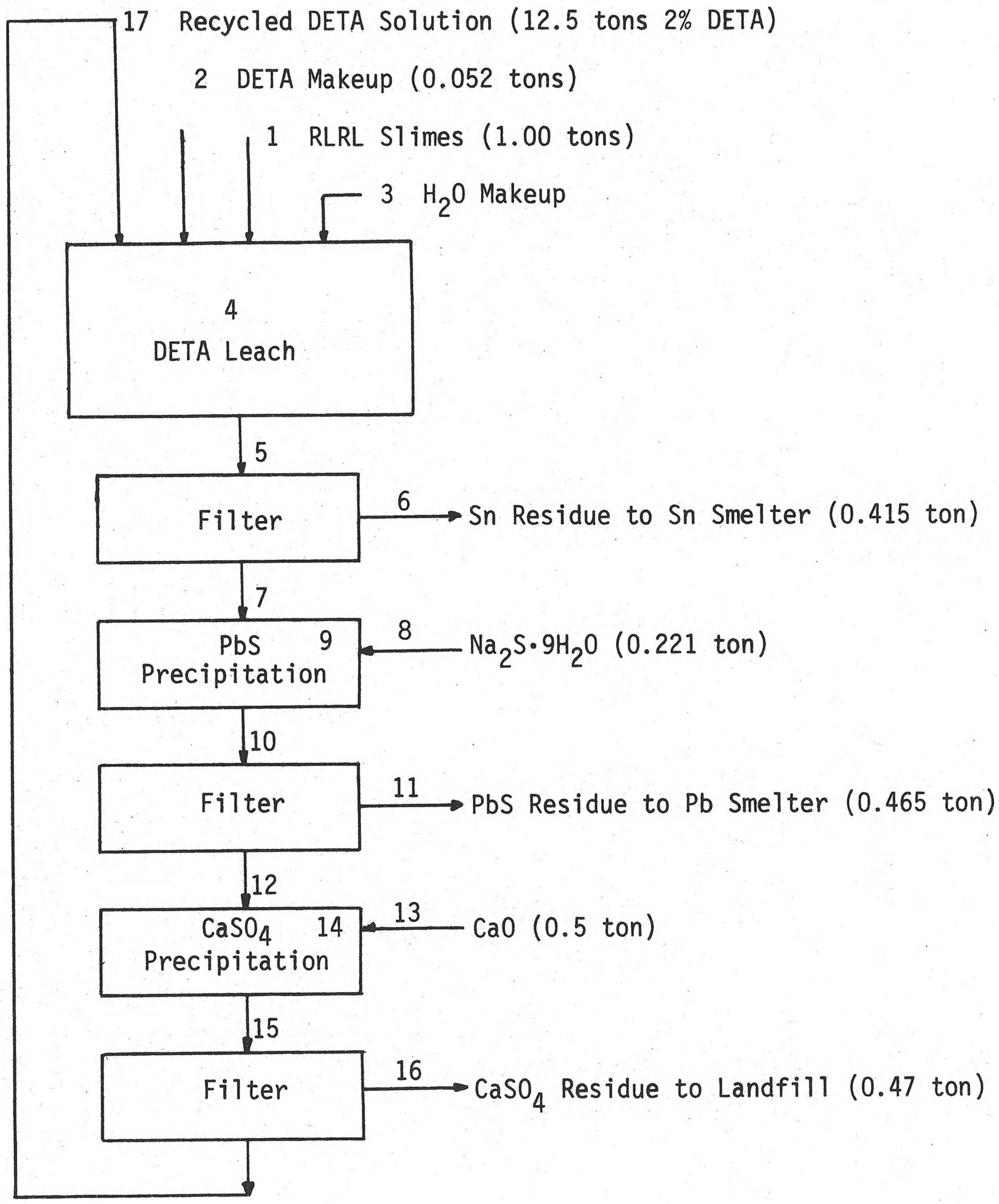

Figure 6. Possible Flowsheet for DETA Leaching of RLRL Slimes

TABLE XVII

MATERIALS BALANCE ON DETA LEACH OF ONE TON OF RLRL SLIMES AT 23° C

Stream	Description	Weight, tons		Pct Solids	Time, Hours	Assay, Pct				Distribution, Pct			
		Solids	Liquids			Pb	Sn	Ag	Cu	Pb	Sn	Ag	Cu
1	RLRL Slimes	1.000	0.00	100.0	--	41.9	16.8	0.594	0.26	100	100	100	100
2	DETA Makeup	0.000	0.052	0.0	--	--	--	--	--	--	--	--	--
3	H_2O Makeup	0.000	0.10	0.0	--	--	--	--	--	--	--	--	--
4	DETA Leach (2%)	1.000	12.50	7.4	4	3.1	1.24	0.044	0.02	100	100	100	100
5	Filter Feed	0.415	13.09	3.1	--	--	--	--	--	100	100	100	100
6	Sn Residue	0.415	0.06	85.0	--	5.0	54.6	0.764	0.45	4.4	97.9	96.6	71.8
7	Filtrate	0.000	13.03	0.0	--	3.07	0.03	0.00	0.00	95.6	2.1	3.4	28.2
8	Na_2S Addition	0.221	--	100.0	--	--	--	--	--	--	--	--	--
9	PbS Precipitation	--	--	--	1	3.02	0.03	0.00	0.00	95.6	2.1	3.4	28.2
10	Filter Feed	0.465	12.80	3.51	--	3.02	0.03	0.00	0.00	95.6	1.1	3.4	28.2
11	PbS Residue	0.465	0.07	85.0	--	86.12	0.40	0.008	0.02	95.6	1.1	3.4	28.2
12	Filtrate	0.000	12.70	0.0	--	0.00	0.10	0.00	0.00	0.0	1.1	0.0	0.0
13	CaO Addition	0.500	0.00	0.0	--	--	--	--	--	--	--	--	--
14	$CaSO_4$ Precipitation	--	--	--	1	0.00	0.10	0.00	0.00	0.0	1.0	0.0	0.0
15	Filter Feed	0.470	12.60	3.5	--	0.00	0.10	0.00	0.00	0.0	1.0	0.0	0.0
16	$CaSO_4$ Residue	0.470	0.07	85.0	--	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0
17	Recycle DETA	0.000	12.50	0.0	--	0.00	0.10	0.00	0.00	0.0	1.0	0.0	0.0

filtration of the slime leach residues and precipitates. This has been accomplished in the laboratory without major problems, but it would be more difficult on a commercial scale. Countercurrent decantation of liquids and solids would probably help greatly with the filtration problem. The estimated capital cost for the equipment to process 0.7 tons per day of RLRL slimes would probably range from $50,000 to $100,000, depending upon the exact equipment used.

F. OTHER TESTS

Since it appears that DETA and NaOH leach systems are expensive, some alternative methods were examined. Samples of the RLRL slimes were reduced to metal in a furnace at 650° C using hydrogen. A metallic alloy of Pb and Sn was produced. It may be possible to sell this alloy directly to the makers of solder. It was also found that the metallic Sn dissolves in hot H_2SO_4 while Pb remains insoluble or precipitates as $PbSO_4$. Carbothermic reduction of the RLRL slimes was also attempted, but it was not successful.

Some other leaching techniques were also tried. Samples of SnO_2 and $PbSO_4$ were leached in aqua regia solutions at 65° C. Only 10.7 pct of the $PbSO_4$ was soluble in 2 hours while 0.0 pct of the SnO_2 was soluble.

F. P. Haver[5] et al. indicated that $PbSO_4$ could be converted to $PbCO_3$ by the use of $(NH_4)_2\ CO_3$ solutions according to the reaction:[5]

$$(NH_4)_2CO_3 + PbSO_4(S) \rightleftarrows (NH_4)_2SO_4 + PbCO_3(S) \qquad (6)$$

The $PbCO_3$ could then be reduced with hydrogen or carbothermically as described in section B of DETA leaching. Samples of $PbSO_4$, SnO_2 and AgCl were reacted for 2 hours at 23° C with 200 g/ℓ solutions of $(NH_4)_2\ CO_3$. One hundred pct of the $PbSO_4$ was converted to $PbCO_3$, 2 pct of the SnO_2 was lost, and 7.5 pct of the AgCl dissolved. The SO_4^{--} was then removed by filtration while the metal values which are solids remained in the filter cake. Hydrogen reduction of the residue could yield a Pb-Sn solder. Alternatively the $PbCO_3$ could be leached with H_2SiF_6 and would possibly be electrowon from solution. Electrowinning of the Pb was carried out in the laboratory, but the C anode deteriorated rapidly. Also PbO_2 was produced at the anode while metallic Pb was being deposited at the cathode. Thus all of the Pb did not report to the cathode.

A leaching test was performed using NH_4OH plus $NaNO_3$ solution. A 40 gm sample of RLRL slimes was leached for 2 hours at 75° C in 500 ml of a solution containing 8 pct NH_4OH and 0.8 pct $NaNO_3$. Only 10 pct of the slimes dissolved in this test which meant that neither the SnO_2 nor the $PbSO_4$ were selectively leached from the slimes.

L. W. Pommier and Saul J. Escalera have proposed a process of leaching Sn bearing material (SnO_2, SnO, SnS) in a solution of NaOH, Na_2S and $NaNO_2$.[6] This process was attempted in the laboratory using reagent grade SnO_2. Twelve gm samples of reagent grade SnO_2 were leached for 8 hours in 100 ml of 2 molar (8 pct) solutions of NaOH. To the leach solutions various amounts of Na_2S and $NaNO_2$ were added. Leaching was performed at 23° C as well as 90° C; but none of the reagent grade SnO_2 leached. L. W. Pommier[6] et al. state that Sn-containing materials would go into solutions as SnO_3^{--} and SnS_3^{--} which are very soluble in the solution. But the results of these tests seem to be contradictory to this. It has also been stated that any Pb, Cu, Ni or Sb that went into solution would be precipitated as a sulfide because of their extremely low solubility in basic solutions. To observe the effects of NaOH, Na_2S and $NaNO_2$ on the leaching of RLRL slimes, statistically designed tests were performed. Eighty-three gm samples of RLRL slimes were leached for 8 hours in 1.000 liter of NaOH solution (80 gpl) at 90° C. Four tests were conducted to observe the effects of the Na_2S and the $NaNO_2$ additions. The NaOH and Na_2S were added to the beakers and diluted with 1.0 liter of water. The solution was heated to 90° C and then the slimes were added. The $NaNO_2$ was added immediately after the slimes addition.

Table XVIII shows the statistical model. Table XIX shows the factor effects and Table XX shows the results of the test.

Test Number 3 seemed to be the best. Forty-six pct of the Pb was present in residue as PbS, but 23.8 pct of Sn was also present in the residue and 12.8 pct Sn was solubilized. So this process does not seem to be very good for a Pb-Sn separation.

TABLE XVIII

STATISTICAL MODEL FOR LEACHING OF RLRL SLIMES USING NaOH, Na_2S AND $NaNO_2$ SOLUTIONS AT 90° C FOR 8 HOURS

Test	x_1	x_2	Pct Solubilized
1	-	-	58.7
2	+	-	16.3
3	+	+	12.4
4	-	+	57.38

Factor	Level	
	Low (-)	High (+)
x_1 - $Na_2S \cdot 9H_2O$	0.0 gm	85 gpl
x_2 - $NaNO_2$	0.0 gm	30 gpl

TABLE XIX

TWO-LEVEL FACTORIAL DESIGN RESULTS FOR LEACHING OF RLRL SLIMES USING NaOH (80 gpl), Na_2S AND $NaNO_2$ SOLUTIONS AT 90° C FOR 8 HOURS

Effects	Mean	x_1 $Na_2S \cdot 9H_2O$	x_2 $NaNO_2$	x_1x_2
Wt pct of slimes solubilized	36.2	-43.7	-2.61	-1.29
Pct Sn solubilized	9.4	5.4	2.2	-0.80
Pct Pb solubilized	42.8	-85.5	-0.75	0.75
Pct Ag solubilized	0.75	- 0.17	-0.28	0.26
Assay Sn in residue, pct	37.9	-26.7	-1.3	-0.20
Assay Pb in residue, pct	30.71	-34.0	-1.0	-2.03
Assay Ag in residue, pct	0.75	- 0.17	-0.28	0.26
Assay Sn in filtrate, gpl	2.19	1.64	1.19	0.30
Assay Pb in filtrate, gpl	7.92	-15.83	-0.10	0.09
Assay Ag in filtrate, gpl	0.0030	0.000	-0.0005	0.0015

TABLE XX

ASSAYS AND PERCENTAGE OF METAL SOLUBILIZED OF PRODUCTS FROM THE LEACHING OF RLRL SLIMES USING NaOH, Na_2S AND $NaNO_2$ SOLUTIONS

Test No.	Wt Pct Solubilized	Assays of Residue, Pct			Pct Solubilized			Assays of Filtrate, gpl		
		Sn	Pb	Ag	Sn	Pb	Ag	Sn	Pb	Ag
1	58.7	51.8	13.22	1.07	5.2	86.3	1.1	0.93	15.93	0.004
2	16.3	25.3	49.22	0.53	11.4	0.01	0.67	2.27	0.0018	0.0025
3	12.4	23.8	46.17	0.50	12.8	0.003	0.65	3.75	0.0016	0.0035
4	57.38	50.7	14.22	0.88	8.2	84.8	0.56	1.82	15.74	0.0020

Overall the alternative methods discussed in this section seemed to be expensive and impractical, so further investigations were not done.

V. CONCLUSIONS

The copper refinery anode slimes have been leached effectively from a chemical standpoint with DETA (diethylene triamine) and with NaOH to separate the Pb and the Sn into two products: 1) a Pb concentrate assaying 86.1 pct Pb with 95.6 pct of the Pb reporting to the Pb product, and 2) a Sn product assaying 54.6 pct Sn which contained 97.6 pct of the Sn along with most of the Au from the slimes. The NaOH with Na_2S plus $NaNO_2$ leaching and $(NH_4)_2\ CO_3$ leaching processes were not suitable for Pb-Sn separation.

The recyclability of the DETA solution was found to be poor. The Na_2S plus CaO regeneration method worked best from the regeneration point of view. Still, at the end of the fifth cycle the loss of the DETA's extracting power was about 55 pct. The reasons for the loss of the DETA's extracting power were 1) adsorption of DETA on the SnO_2 leach residue, 2) adsorption on $2PbCO_3{\cdot}Pb(OH)_2$ or PbS product, and 3) adsorption on $CaSO_4$ precipitate which was produced during the regeneration step. The recyclability of NaOH solution was higher when compared to the recyclability of the DETA solution; the NaOH lost only 15 pct of its extracting power at the end of the fifth cycle. But the quantity of NaOH required is very high which makes the process expensive. The cost of reagents equals 80 pct of the value of the Pb removed from the Sn concentrate, so that it would probably not be economically feasible to use either process commercially.

A proposed flow sheet would process Roast-Leach-Roast-Leach (RLRL) slimes by leaching with DETA solution which would solubilize Pb and separate the Sn residue by filtration. This residue would then be sold to a tin smelter. The filtrate would then be treated with $Na_2S{\cdot}9H_2O$ to yield a high grade PbS product. This product would then be filtered, dried and sold to a lead smelter. Following removal of the Pb product, the DETA solution would be regenerated by treating it with CaO. The $CaSO_4$ residue formed would then be filtered and the filtrate (DETA solution) would be recycled.

BIBLIOGRAPHY

1. J. M. Keating, "Recovery of Copper and Silver from Copper Refinery Anode Slimes." Report submitted to Institute of Chemical and Extracting Metallurgy, University of Missouri-Rolla.
2. F. A. Forward, H. Veltman and A. Vizsolyi, "Production of High Purity Lead by Amine Leaching." International Mineral Processing Congress, IMM London, 1960, p. 823-837.
3. Haruo Mimura, Choku Imai, Atsushi Nagai and Ziro Hirano, "Laboratory Tests on Extraction of Lead Diethylene Triamine (DETA) for Industrial Use." Nippon Kogyo Kaishi, Vol. 83, 1967, p. 36-42.
4. C. Coekelbergs and A. L. Delvaus, "Lead Sulfates Processing at Metallurgie Hoboken - Overpelt Present Practice and Future Developments." TMS Paper Selection A-79-33. AIME Meeting - New Orleans, February 1979.
5. F. P. Haver, K. Uchida and M. M. Wong, "Recovery of Lead and Sulfur from Galena Concentrate Using Ferric Sulfate Leach." United States Department of Interior, Bureau of Mines, Report of Investigations 7360, March 1970.
6. Luis W. Prommier and Saul J. Escalera, "Processing of Tin from Impure Raw Materials, Journal of Metals, April 1979, p. 10-12.

VITA

Shrirang Anant Kulkarni was born in Dharwar, India on August 5, 1955. He completed his schooling at Fergusson College, Poona, India.

In January 1977, he graduated from the College of Engineering Poona, University of Poona, Poona - Metallurgical Engineering Department from which he obtained the degree of B.E. in Metallurgical Engineering.

He has been enrolled in the Graduate School of the University of Missouri-Rolla since January 1978 and has held the position of Graduate Research Assistant for the Institute of Chemical and Extractive Metallurgy at the University of Missouri-Rolla from May 1978 to December 1978 and the USDI Fellowship from January 1979 to August 1979. He is also concurrently enrolled for a dual master's degree in the Department of Engineering Management as well as the Department of Metallurgical Engineering.