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Ultra-Fine Purification of Scrap Lead by Electrolysis

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Abstract

Various uses of corrosion resistant Lead, such as pipes, pewter and paint, has been identified in known history. Many applications in modern days use lead e.g., to prepare lead glazes for pottery and, in insecticides, hair dyes and as an anti-knocking additive for petrol. Lead is still widely used for pigments, ammunition, cable sheathing, weights for lifting, and weight belts for diving, leads crystal glass and in some solders. There are applications where lead is required in its refined form, such as background radiation reduction by providing lead shielding of environmental samples in High Purity Germanium (HPGe) spectroscopy. Pure lead is also required as a starting material for fabrication of plates of lead accumulator in battery industry. In present study, ultra-fine purification of scrap lead has been investigated by electrolysis. Electrolysis was done using different electrolytes, different electrodes and with varying interelctrode distances. One electrolyte used was lead dissolved in hexafluorosilic acid and the other was lead dissolved in tartaric acid and nitric acid. Stainless steel and graphite were used as cathode respectively while scrap lead is used as anode material. The results were compared by purification of scrap lead by hydro-metallurgical process and vacuum distillation techniques and it was deduced that by the electrolysis technique, the amount of pyrometallurgical process steps can be decreased dramatically.

Key Words: Electrolysis, Pyrometallurgy, Hexaflorosilicic Acid

1. Introduction

Lead is playing its role for a long time in human lives. Sources of primary lead are depleting quickly per different studies. Without recycling at present, the industrial growth rate primary sources of lead, can meet the needs of lead industry for only next 15 years [18]. Moreover, recycling of this metal is also necessary because discarded lead products are toxic and cannot be disposed of easily.

Different refining processes like pyrometallurgy, hydrometallurgy and electrowinning have been used for purification of lead and more techniques are still under study [2, 18, and 4]. Lead has already been purified using secondary refining methods which mainly include pyro-metallurgical route [12, 17]. This process has already been under criticism by environmental authorities owing to the emission of highly toxic gasses, liquid effluents and particulates [3]. In this process, lead is refined in three steps namely copper drossing, softening and caustic refining [12, 8]. Lead formed by this method is pure enough for use in different applications. Other methods in general practice for purification of lead are hydrometallurgical leaching and electrokinectic process. These methods produce lesser waste but at an expense of cost and hindered production rate [7]. Special applications like radiation shielding specifically when used for reducing background radiation field while gamma spectroscopy of environmental samples is being done using HPGe detector, require ultra-high purity lead metal [17, 11].

Per another study, refining process for lead that has been used earlier is sulfide co-precipitation method [12]. The process indicates that silver, iron, molybdenum and copper are intensely concentrated in precipitate and separated out efficiently. The other elements that are not removed are bismuth, cadmium, antimony, tin and zinc which stay in solution or are equally distributed between the two phases [10, 13].

Vacuum distillation of lead investigated in another research shows that all the impurities stay in the initial and final distillate of such method, except for bismuth and antimony [9, 15, 2].

The emerging methods that are becoming popular for ultra-refining are zone refining, vacuum distillation and electrolysis. [14] The present study is directed towards improvement in electrolysis technique for scrap lead purification using different electrolytes to obtain 99.99% pure lead.

2. Experimental Work

Electrolysis was done using different electrolytes and by changing the voltage across the electrodes to compare the results.

2.1 Electrolyte Preparation

Three types of electrolytes were prepared.

2.1.1 Electrolyte 1(E1)

30 grams of lead was dissolved in 100ml of nitric acid and heated at 40°C for 4.5hours. The nitric acid

was completely evaporated and then hexaflorosilicic acid was added in the same beaker and filtered to get the electrolyte. 14.9cmx8.9cm stainless steel plate was taken as cathode while 10.2cmx5.0cm Scrap lead plate was used as anode material.

2.1.2 Electrolyte 2(E2)

The second electrolyte was prepared by dissolving 50grams of lead stripes in 105 ml of hexafluorosilic acid and heating the solution at 80℃ for 4 hours below the boiling point of hexaflorosilicic acid. 10.4cmx3.2cm stainless steel plate was used as cathode while 10.4cmx3.1cm scrap lead plate was used as anode material. The anode was sonicated and dried in oven at 105℃ for 2 hours.

2.1.3 Electrolyte 3(E3)

The other electrolyte solution prepared was 7.75grams of lead stripes dissolved in 6grams of tartaric acid and75ml of nitric acid and heated at 40℃ for 8hours, stirred and then filtered. The cylindrical graphite electrode with diameter 1.143cm and length 7.21cm was used as cathode while 4.62 cmx2.54cm scrap lead plate was used as anode. The anode was sonicated and dried in oven at 105℃ for 2 hours.

2.2 Experimental Procedure

Terminals were attached to make the plates as anode and cathode. For E1, the distance between the cathode and anode was 5.0 cm and an applied voltage of 0.4V was given to get the current values. The height of anode and cathode dipped in electrolyte were 3.0cm for both electrodes.

For E2, the distance between the cathode and anode was 3.6 cm and an applied voltage of 0.5V was given in this case getting the current values. The amount of scrap lead deposited on anode was removed after every half an hour because previously when the experiment was run for 6 hours the deposited metal on cathode goes back in the electrolyte and dissolved in nitric acid again and the anode (scrap lead) was completely dissolved in it. The height of anode and cathode dipped in electrolyte were 3.7cm for both electrodes and the dipped area was181.65 A/cm^2.

For E3, the distance between the cathode and anode was 3.6 cm and 0.5V was applied which was reduced to 0.4V slowly when the experiment was run for 3hours. The same conditions were followed changing the applied voltage to 0.45V and running the experiment for almost 2.5 hours. The height of anode and cathode dipped in electrolyte were 2.3cm and the dipped area was 174.00A/cm^2 for both experiments. The deposited metal (lead) was removed from cathode and analyzed for characterization.

The concentration of lead dissolved in electrolytes was measured by atomic absorption spectroscopy.

The weight of lead deposited on cathode for all experiments was measured and calculated by Faraday’s Law of Weight Deposition given by:

$$m = \frac{ItM}{nF}$$

Where
m= mass Deposited
I= Current (A)
M= Molar Mass (g/mol)
t= total time
F =Faradays Constant (96500C/mol)
n = amount of substance Liberated (moles)

Figure 1 shows the deposition of metal from anode towards graphite cathode. While figure 2 shows the deposition of metal from anode towards stainless steel cathode. The deposition on cathodes has been shown in figure 3. Figure 4 shows the electrochemical cell setup.

The scrap lead was analyzed by ICP technique before performing experiments which has been shown in Table 2. It shows that the scrap lead was 97% pure with a major impurity of antimony 2%.

3. Results and Discussion

3.1 Atomic Absorption Spectroscopy (AAS)

To increase lead concentration in free acid, scrap lead chips were dissolved in hexaflorosilicic acid and left for 3 day for dissolution then the concentration of lead dissolved in each electrolyte was analyzed using atomic absorption spectroscopy. Five standard solutions of 10,20,30,50 and 70 ppm were prepared for calibration curve formation then electrolyte solutions were tested as unknown sample after dilution up to 200 times. Per Beer-lambert’s Law absorbance and concentration are directly proportional to each other, therefore, concentration was measured using calibration curve shown in Figure 5.

The concentration found for all three electrolytes was around 60 ppm which has a difference to the literature value of 70-75 g/L. This difference in value is since during the preparation of electrolyte, researchers have used additives mainly lignin sulphonate for dissolution of lead in hexaflorosilicic acid [1]. During these experiments, no additive has been used and lead was directly allowed to dissolve in hexa-florosilicic acid. Figure 5 shows the calibration graph obtained from AAS.

3.2 Current vs., Time Graphs

The change of current with the passage of time has been shown in figure 6 & 7. In figure 6, the graph shows decreasing behavior because the experiment was started at 0.5V and then decreased to 0.4V so the lead from electrolyte was transfering towards cathode. Then the increase in graph shows the deposition of metal on cathode from anode. The figure 7 shows increase in current with the passage of time because the same electrolyte was used, the one which was used at 0.5-0.4V, showing again the transfer of material from anode towards cathode rather than from elctrolyte to cathode.

3.3 Inductively Coupled Plasma Analysis (ICCP) of Feed and Lead after Electrolysis

The ICP analysis of scratched layer of lead deposited on SS cathode from anode (scrap lead) was done after electrolysis and was 99.94% pure at voltage of 0.39V and 99.98% at 0.45V. The results are shown in table 4. It shows that antimony was not detected in both experiments. High purity is obtained at lower voltage and less purity at high voltage. This is due to the reason that at high voltage the impurity mainly antimony may deposit on cathode as the reduction potential of antimony is 0.541V.

3.4 X-Ray Diffraction Analysis

A powder X-ray diffractometer armed with Cu anode and photo scintillation detector has been used to record the diffraction patterns of the scrap lead before electrolysis and the samples deposited on cathode after electrolysis. Scan was performed over an angular range (2θ) of 10-90° at the rate of 0.01°/sec. The pattern of scrap lead before analysis shows peaks of lead along with some minor impurities as quoted earlier by ICP analysis. The diffraction peaks obtained after electrolysis depicts only lead peaks confirming the deposition of pure lead on cathode during electrolysis. The results have been shown in figure 8.

4. Conclusions

A study of all available data on vacuum distillation of lead indicated that except for bismuth and possibly antimony, impurities should remain in initial and final distillate of such process [3].

Pyrometallurgy is a three-step process naming smelting, copper drossing and refining. It's a time consuming and environmentally unfriendly. [2]

Hydrometallurgical methods of lead have been done using sulphuric and hydrochloric acids. A major drawback of this technique is low solubility of lead sulphate and chloride. [16]

Electrolysis of scrap lead proved out to be cheap and economical process rather than performing electrolysis of galena (lead sulfide).

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Table 1: Table showing Electrolysis Experiment Conditions

Variables	**E1**	**E2**	**E3**
Anode	Scrap Lead	Scrap Lead	Scrap Lead
Cathode	Stainless Steel	Graphite	Stainless Steel
Electrolyte	Scrap Pb +HNO_3 (Evaporated) + H_2SiF_6	Nitric Acid + Tartaric Acid + Lead	Hexaflorosilicic Acid + Lead
Distance between Electrodes	5 cm	3.6 cm	3.6 cm
Voltage	0.4V	0.50 V	0.45V & 0.39V
Maximum Current	0.20A	0.17A	0.58A & 0.30A
Weight Deposited On Cathode	0.01grams	Deposited Weight dissolves in Electrolyte	0.93 g & 4.65g
Cell Area	None	181.65 A/m^2	174A/ m^2

Table 2: ICP Analysis of Feed & After Electrolysis Sample

Element	**Feed (Scrap Lead) %**	**Sample Percentage 0.4V**	**Sample Percentage 0.45V**
Pb	97	99.944	99.984
Sb	2.422	ND	ND
S	0.254	0.056	0.016
Sn	0.179	ND	ND
As	0.088	ND	ND
Si	0.029	ND	ND
Cu	0.018	ND	ND
Bi	0.017	ND	ND

ND = Not Detected

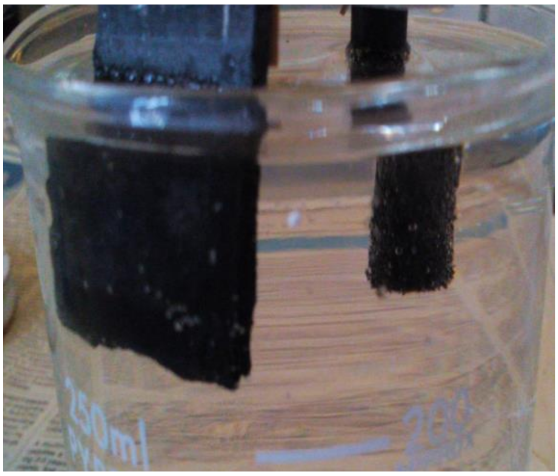

Figure 1: Nitric Acid + Tartaric Acid + Lead as Electrolyte

Figure 2: Hexaflorosilicic Acid + Acid + Lead as Electrolyte

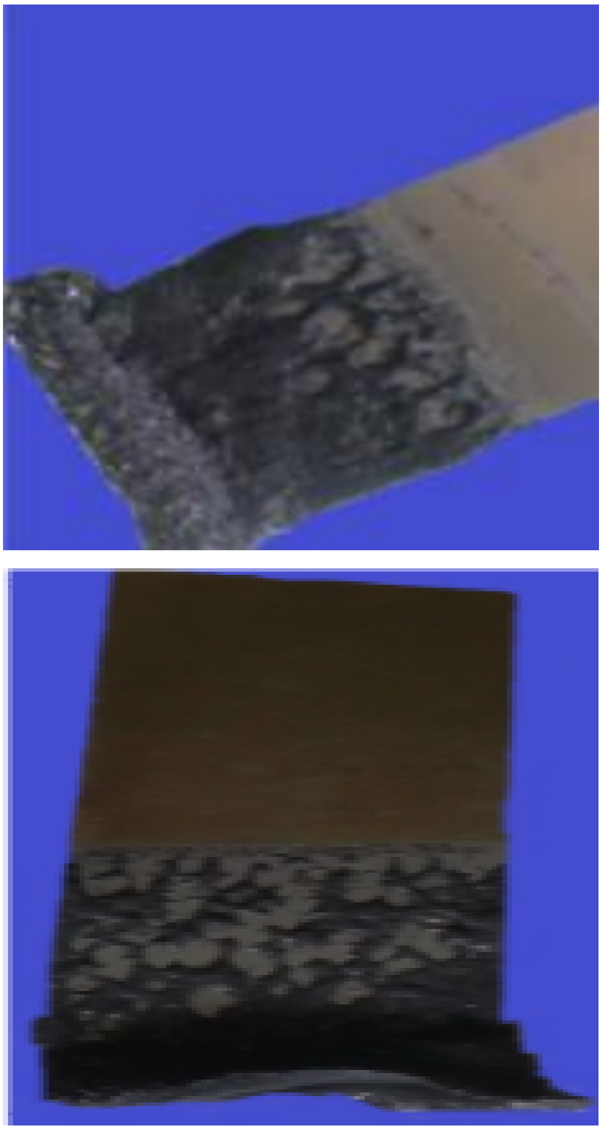

Figure 3: After electrolysis at 0.5 and 0.45V

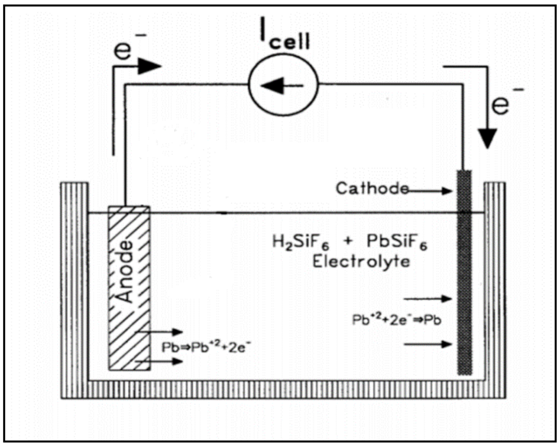

Figure 4: Electrochemical Cell Setup

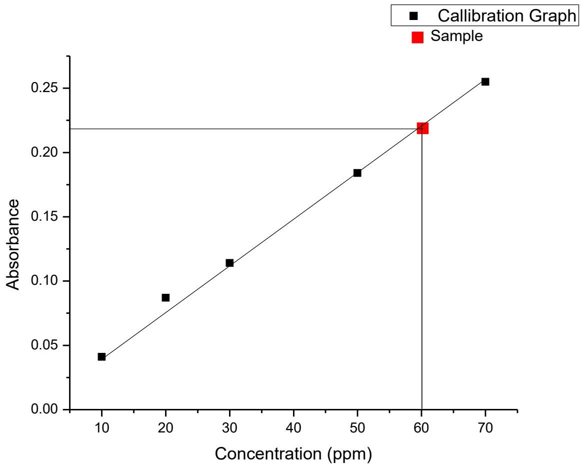

Figure 5: Calibration Curve from AAS

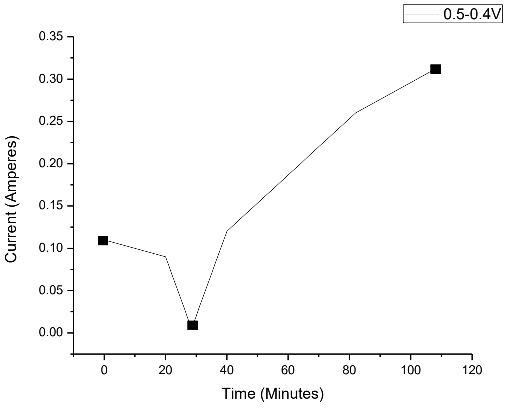

Figure 6: Current vs. Time for 0.4V

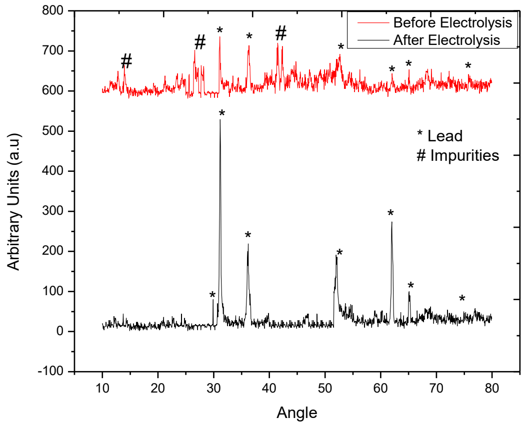

Figure 8: XRD Pattern of Scrap Lead before and after Electrolysis

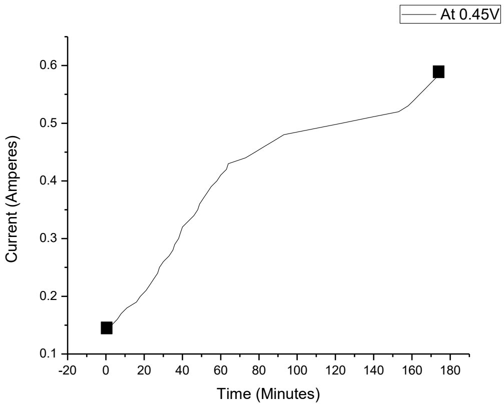

Figure 7: Current vs. Time for 0.45V