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EXTRACTION OF TIN FROM WASTE PRINTED CIRCUIT BOARD IN HYDROMETALLURGICAL PROCESS

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Abstract*-This era of electronics is creating an ambivalent situation for human civilizations. The waste stream coming through this pipeline causing hazardous environment and performing the role of secondary resources of value metals. The printed circuit board is the point of attraction as it acts as the brain of the whole system. Thus it has to carry the elements those have good electrical and mechanical properties. However, to satisfy the requirement, the value and hazardous elements are used there at the same time. When Gold, Silver, Copper etc. are used mostly for their conductivity, Tin is mostly used as a soldering material. As energy sources are fixed for planet earth, resources should be taken care of. Recycling of used appliances is a great option where value metal like Tin can be extracted and reused. In this study, hydrometallurgy process is used. Dissolving PCBs into strong nitric acid media and cemetation by Zn powder may yield 86% Tin of pure form. Hydrometallurgical routes are found to be the most efficient to recover value metals.*

Keywords: E-waste, PCBs, Aqua regia, Leaching, Oplinger method, Electrodeposition.

1. INTRODUCTION

More efficient but with a shorter life span electronic devices come onto the market that causes installment of more than millions of electronic devices per year. On the other hand, significant numbers of old electronic devices are being scrapped. According to Cui & Forssberg, six million tons of Waste Electrical and Electronic Equipment (WEEE) were generated in west Europe in 1998. Printed circuit boards (PCBs) are the most essential part of almost all the electric and electronic equipment (EEE). Both technological innovation and short life span accelerate the replacement of EEE, which increase waste PCBs (Cui et al. 2003). However, most electronic companies do not devote any effort to treat their waste. They think from the business perspective more, sell new products and find it more effective than spending money and resources on treating discarded equipment. Waste PCBs has been attracting the attention by its environmentally harmful materials and abundant valuable metals listed in table 1 (Wang et al. 2005).

Table 1. The chemical composition of PCBs (Wang et al. 2005)

Elements	Amount	Elements	Amount
Copper	19.66%	Calcium	1.13%
Aluminum	2.88%	Silver	500 ppm
Lead	3.93%	Gold	300 ppm
Zinc	2.10%	Palladium	33 ppm
Nickel	0.38%	Indium	500 ppm
Iron	11.47%	Manganese	9700 ppm
Tin	3.68%	Cobalt	300 ppm

The nonmetallic materials of PCBs mainly consist of thermosetting plastics (TS), thermoplastics (TP), glass fibers and ceramic fractions. Thermosets cannot be remelted or reformed because of their cross-linked polymeric structure. Incineration is not the best method for treating nonmetallic materials because of the presence of inorganic fillers such as glass fiber, which significantly reduces the fuel efficiency. Disposal in a landfill is the main method for treating non-metallic materials of PCBs, but it may cause secondary pollution and resource-wasting. If those printed circuit boards are improperly disposed of, hazardous materials could cause serious environmental problems and numerous valuable metals will be lost. Mechanical (Shigeki et al. 1997, Zhang et al. 1998, Veit et al. 2006, 2007), pyro metallurgical (Hennie et al. 1994, Chiang et al. 2007) and hydrometallurgical (Baba et al. 1987, Macaskieet et al. 2006, Vegliò et al. 2003) routes are available to recover metals. The mechanical processes like shredding, milling, mesh analysis etc. are pre-treatment before pyrometallurgy and hydrometallurgy. The pyrometallurgical process can be efficient but this high-temperature process causes serious health and environmental problems, especially air pollution. Hydrometallurgy may be more efficient and more easily controlled comparing with pyrometallurgy (Andrews et al. 2000).

In this study, efficient recovery of Tin from waste PCBs in hydrometallurgical extraction process was focused. This is more suited to lab-scale experiments and much more environmentally friendly than pyrometallurgy. This study aims for the hydrometallurgical recovery procedures of tin from mobile phone printed circuit board. The methodology of this research work comprised of a systematic laboratory experimental research performed in the following sequence: i) Collection of e-wastes from local market and local industries; ii) Characterization by AAS/XRF of elements present in the selected e-wastes(PCBs), iii) The e-wastes were subjected to an acid leaching process for TIN recovery using various process parameters.

2. SAMPLE SELECTION & CHARACTERIZATION

To recover tin form waste PCB, PCBs of mobile phones were collected from local market of Dhaka. The collected PCBs were dismantled manually. The different component parts were carefully separated and main PCB boards were taken. We collected 1kg PCB of mobile. To find out the valuable metals present in PCB boards, Atomic Absorption Spectroscopy (AAS), (Model: Varian AA 240 Fs) analysis was done which determined concentration of elements in liquid phase. At first PCBs were dissolved into aqua regia solution. As it is a toxic process, precautions were taken. The solution was then dark brownish green color. And complete dissolution was achieved. The solution was then filtered using filter paper. Figure 1. shows acid digestion of PCB samples under the fume hood.

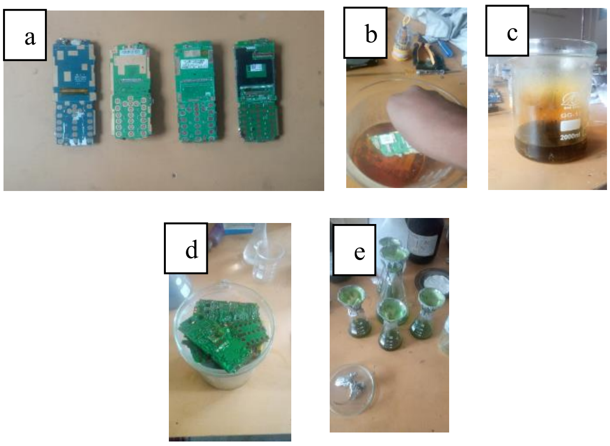

Fig. 1: (a) Dismantled PCBs (b) dissolving PCB into aqua regia (c) solution after complete dissolution (d) PCB taken out after dissolution (e) filtering the solution

3. CHARACTERIZATION OF WASTE PCBs

The PCBs used in this study were prepared for chemical analysis by digestion with aqua regia. After digestion, the sample was filtered, and dilutions were made according to the element to be analyzed and the analysis method used: atomic absorption spectrometry (AAS). Leaching analyses were performed according to the Environmental Protection Agency (EPA) SW-846 test method. Table 2. shows the concentration of elements in the chosen samples analyzed by AAS techniques.

Table 2. AAS analysis of mobile PCBs

Sample	Element	Concentration (mg/L)
	Aluminium (Al)	753 mg/L
	Arsenic (As)	Less than 0.05 mg/L
	Cadmium (Cd)	0.18 mg/L
	Chromium (Cr)	278 mg/L
	Cobolt (Co)	9.04 mg/L
	Copper (Cu)	12823 mg/L
	Calcium (Ca)	79.9 mg/L
Mobile PCBs	Iron (Fe)	1528 mg/L
	Lead (Pb)	193 mg/L
	Manganese (Mn)	33.4 mg/L
	Mercury (Hg)	1.67 mg/L
	Nickel (Ni)	733 mg/L
	Molybdenum (Mo)	3.59 mg/L
	Silver (Ag)	33.3 mg/L
	Tin (Sn)	1150 mg/L

4. METHODOLOGY OF TIN EXTRACTION

500 gm of waste mobile PCBs were collected, cut into identical sizes (3cm X 3cm), washed and dried. At first, the samples were leached in 25% Nitric acid, 1000 mL leach solution was stabilized for 24 hrs. After filtering Metastannic Acid (H_2SnO_3) was found.

$$\mathbf{Sn + 4HNO_3 = H_2SnO_3 + 4NO_2 + H_2O}$$

The solid precipitation was preheated to 150ºC for 4 hrs. Then heated to 600ºC for removal of Pb and HCl was added for leaching.

$$\mathbf{H_2SnO_3 + 4HCl = SnCl_2 + Cl_2 + 3H_2O}$$

Zn was added then in leach liquor to cement tin.

$$\mathbf{SnCl_2 + Zn \xrightarrow{t^\circ C} Sn + ZnCl_2}$$

Tin(II) chloride react with zinc to produce tin and zinc chloride. This reaction takes place at a temperature of 200-300°C.

40 percent sodium hydroxide solution and 5 percent hydrogen peroxide (H_2O_2) were added at 60°C and stirred for 1 hour, Sodium stannate was found $Na_2[Sn(OH)_6]$.[69]

$$\mathbf{Sn + 2NaOH + 4H_2O \xrightarrow{t^\circ C} Na_2[Sn(OH)_6] + 2H_2}$$

Oplinger method was followed for electrodeposition of Sn. Sn deposited on the cathode. Deposited tin was separated and dried. Then the powder was characterized by X-Ray Fluorescence (Shimadzu Lab Center XRF-1800).

Electrodeposition Parameters:

Sodium stannate = 0.2375 mol/l

Sodium hydroxide = 1.0 mol/l
Hydrogen peroxide = 0.5 g/l
Anode = tin
Cathode = Graphite
Ratio of anode to cathode area = 3
Cathode current density = 30 A/f^2 or 322.9 A/m^2
E. M. F = 4.0 volts
Temperature of solution = 70ºC

Figure 2 shows the different stages of the tin extraction process. Figure 3 gives an outline of the extraction process.

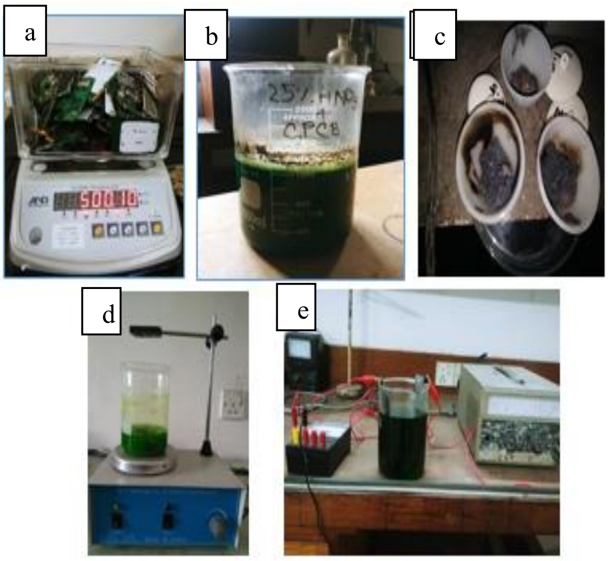

Fig. 2: Different stages of Tin extraction: (a) Sample preparing (b) Acid Dissolving (c) Burning at 600ºC (d) Leach liquor stirring in HCl and Zn (e) Electrodeposition process

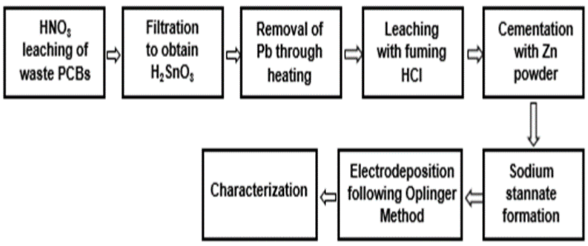

Figure 3. The process flow for Tin extraction

Table 3 shows XRF results of the sample. 86.5% Sn has been obtained from locally sourced mobile PCB sample. Some Copper is also present in the powder, which shows that not all the Copper had been removed from the leach liquor. Moreover, Copper is a highly reactive metal and tends to readily precipitate in reducing environment, thus accounting for its residual presence in the sample.

Analyte	Result %
Sn	86.5339 %
Cu	10.6859 %
Zn	1.4804 %
Si	0.7325 %

Table 3. XRF result of recovered Tin sample

5. FINDINGS

Tin is an important element used as lead-free solder material in commercial electrical and electronics. So loss that has already created a crisis, should be mitigated. The hydrometallurgical route can help to recover efficiently. As this route deals with concentrated acid media, precautions should be taken before the dissolving of PCBs. And also by products should be handled and managed properly. However, this can create value from extracted Tin that can be reused.

This study has successfully demonstrated the recovery of tin from mobile phone PCBs. Through hydrometallurgical process routes significant amount of tin were recovered. Tin showed corresponding metal recovery of 86.5%. Analysis by XRF has confirmed the recovery of this precious metal. The amount of metal obtained was used to approximate average yield of tin element from 1 tonne of waste PCBs. The result is summarised in Table 4.

Table 4. Comparison of yield value from experiment with reference value

Recovered Metal	1 ton PCBs (present study)	1 ton PCBs (Reference value)	Market Value (USD/gm)	Value Recovered (USD)
Tin	24 kg	30.84 kg (Vidyadhar, 2016)	0.03	$720

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