Recovery Of Copper From Printed Circiut Boards Through Electrolytic Process –A Case Study

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ABSTRACT

Printed Circuit Boards (PCBs) collected from local sources were used for recovering copper by electrolytic process, using a laboratory reactor setup of working volume 15 liters and nitric acid for dissolution. Copper plate was used as the cathode and graphite rod as the anode for the deposition process. Five durations were adopted both for the dissolution and deposition processes. Based on the above investigations it found that 5 hours for 132 gm copper has dissolved and the maximum copper deposited was 14.861 gm in 120 minutes, which is equal to 12% of maximum recovery of copper from the PCBs. The maximum power consumption is found to be 0.0214 kWh for 14.861 gm of copper recovered. The maximum copper (Cu) recovered in 120 minutes of the deposition process can be considered as the optimum for the 5 L of dissolved solution. There is scope to refine the process and scale it up, if proper funding and facilities are made available.

Keywords – E-waste management, electrolytic cell process, operating conditions, recovery of copper, recycling.

I. INTRODUCTION

Rapid technological progress made in electronics, especially in the last decade, has led to very frequent replacement of electronic equipment. Thus, used electrical and electronic equipment ended up as waste materials. Waste Electrical and Electronic Equipment (WEEE), popularly known as e-waste, is reported to be generated in the range of 20 to 50 million tones (MT), in the world (Heart, 2009). Printed Circuit Boards (PCBs) represent 3% of mass of global WEEE generated (Dalrymple et.al, 2007). E-waste in general contains hazardous substances, such as, toxic metals (Cadmium, mercury etc.) and persistent organic pollutants (e.g.: halogenated flame retardants). Due to significant risks to human health and environment posed E-waste, legislations have been enacted all over the world, for their collection, recycling and safe disposal. In spite of the existence of specific legislation, recycling activities are mostly carried out in poor working conditions, leading to adverse impact on human health and environment, especially, in countries like: China, India, Pakistan, Ghana and Nigeria (Huo et.al, 2007; Kuper and Hojsik, 2008 and Manhart, 2010).

PCB as a key component of WEEE, can be considered as a significant raw material due to its complex composition, mainly consisting of metals (40%), organics and ceramics (each 30%). Among the various metals that are typically present in PCBs, copper is available in large quantity (27%), which has considerable material value. Hence, efforts were directed to recover metals from PCBs, through best available technologies, which helps not only manage hazardous substances scientifically, but also, to reduce dependencies on primary metal resources.

Two major techniques, namely, Pyrometallurgical and Hydrometallurgical, were widely recognized for recovery of metal from e-waste (Cui and Zhang, 2008; Quinet et.al, 2005) and in the last decade the attention has moved to hydrometallurgical process. Several investigators have reported the feasibility of copper recovery by electrodeposition techniques (Oishi et.al, 2007; Masavetas et.al, 2009). However, it has also been reported that attention has been paid very rarely to the relationship between the applied electrolytic conditions and the recovered copper (Masavetas et.al, 2009). Hence, in this study recovery of copper from PCBs, using the electrolytic process has been investigated and an attempt has also been made to study the performance of the copper recovery process, based on the operational parameters such as: electrolysis duration, energy consumption etc.

II. MATERIALS AND METHODS

a) Printed Circuited Boards

Based on the available literature, it was found that there are no separate collection systems in India, and hence there is no authentic data available on the quantity generated and disposed-off every year, and the resulting environmental risk. However, a field survey conducted by the authors (Pradeep Kumar et al., 2013) on the IT industries located in Puducherry (India), revealed that the general awareness on the potential hazardous nature of e-waste is rather poor, and that no attempt has been made to recover metals, in spite of the fact that the total e-waste generation is 11.06 TPA (at present). Hence, waste PCBs were collected from various local sources and used as source material for the present study. The waste PCBs were used in “as is where is” basis, i.e. used in “as collected form”, without giving any pretreatment.

b) Electrolytic reactor setup

A glass reactor of working volume of 15L was used for electrolytic process. The setup consisted of a graphite rod of 25 mm diameter as the anode and stainless steel mesh of diameter 100 mm as the cathode for dissolution process. Copper plate of 40 mm width, 150 mm length and 10 mm thick was used in the recovery process as cathode and the same dimensional graphite rod was used as a anode in the recovery process. A direct current (DC) power supply and a multimeter was used to measure the current and voltage during the electrolytic process. The experimental setup adopted is shown in Fig. 1, which is based on the one reported by Zeljko Kamberovic et.al, (2011).

Fig.1. Experimental setup of the electrolytic process

c) Methodology

The experimental methodology has been carried out in three stages. The selection and preparation of source material (PCBs) as a first stage, followed by dissolution of metal present in PCBs into the prepared solution as a second stage and finally recovery of the dissolved metals from the solution by electrolytic process, at the third stage. Capacitors, ICs, joints, mountings, etc. were removed from the PCBs and sorted manually. The PCBs were then cut into pieces as small as possible, and the cut pieces were weighed. The weighed PCBs were then placed in the reactor. It was ensured that the cut pieces are in maximum contact with the graphite anode to enhance the dissolution of the metal in the PCBs by improving the conductivity. The anode set was connected to the positive terminal of the rectifier and stainless steel mesh was connected to the negative terminal of the rectifier (current 1 A and voltage 0-12V). Maximum possible current was set to carry out the experiment and the voltage was maintained such that to achieve maximum current and hence rate of dissolution. In the process, 5 liters of distilled water was taken in a container, then 500 ml concentrated nitric acid (HNO_3) was added first and after that 300 gm sodium nitrate ($NaNO_3$) was added. (Nitric acid was added as it can dissolve metals like lead, tin and copper, but it does not dissolve gold). Nitric acid is steadily consumed during the dissolution and hence it has to be added periodically. Sodium nitrate was added in the bath as it helps to maintain the electrical conductivity of the bath and hence the release of nitrate ions. Sulphuric acid could not be used as it does not dissolve copper, but, it reacts with lead forming lead sulphate, which is water insoluble. The probable chemical reactions involved in the dissolution process are given in Eqn. (1).

$$\mathbf{HNO_3 \longrightarrow H^+ + NO_3^-}$$
$$\mathbf{NaNO_3 \longrightarrow Na^+ + NO_3^-}$$
$$\mathbf{Na^+ + H_2O \longrightarrow NaOH + H_2 \quad \ldots (1)}$$
$$\mathbf{H_2O \longrightarrow H^+ + OH^-}$$
$$\mathbf{H_2O + 2OH^- \longrightarrow \tfrac{1}{2}\, O_2 + H^+}$$

Dissolution of metals present in PCBs takes place according to the following reactions: [Eqn. 2(a) to 2 (c)]

For Copper:

$$\mathbf{Cu + NO_3^- \longrightarrow Cu\,(NO_3)_2 + 2e^- \quad \ldots 2(a)}$$

For Lead:

$$\mathbf{Pb + NO_3^- \longrightarrow Pb(NO_3)_2 + 2e^- \quad \ldots 2(b)}$$

For Tin:

$$\mathbf{Sn + 2NO_3^- \longrightarrow Sn(NO_3)_2 + 2e^-}$$
$$\mathbf{Sn + 4NO_3^- \longrightarrow Sn(NO_3)_4 + 4e^- \quad \ldots 2(c)}$$
$$\mathbf{Sn(NO_3)_4 + H_2O \longrightarrow Sn(OH)_4 + HNO_3}$$
$$\mathbf{Sn(OH)_4 \xrightarrow{(Ignite)} SnO_2 \xrightarrow{(Fusion\ with\ alkali)} Na_2SnO_3}$$

The remains in the reactor were taken out, dried, weighed, and the weight loss in the scrap was calculated, which is equal to the amount of metals that have gone into solution. The current, voltage and time were measured so as to calculate the energy consumed for the dissolution of metals.

The copper plate was polished by emery paper, cleaned with acetone and after drying the plate, its initial weight was noted. This copper plate was connected to negative terminal (cathode) and graphite rod was connected to positive terminal (anode) of the rectifier. Both electrodes were dipped in solution and an external supply was given. The copper ions in the solution move to the cathode for deposition. The probable reactions at anode and cathode are given in Eqn. 3(a) to 3(c)

Reaction at Anode:

$$\mathbf{H_2O + 2OH^- \longrightarrow \tfrac{1}{2} O_2 + H^+ \quad \ldots (3a)}$$
$$\mathbf{2H^+ \longrightarrow H_2\uparrow \quad \ldots (3b)}$$

Reaction at Cathode:

$$\mathbf{Cu^{2+} + 2e^- \longrightarrow Cu\ (deposited\ on\ cathode) \quad \ldots (3c)}$$

A study was also conducted to analyze the governing parameters like: electrolysis duration both during for the dissolution and deposition processes. The study was also extended to understand effect of pH, energy consumption during both the dissolution and deposition processes, the relation between electrolysis duration with energy consumption for recovering the maximum percentage of copper.

III. RESULTS AND DISCUSSION

a) Effect of electrolysis duration on dissolution and deposition process

In the five sets of experiments that were conducted for the dissolution and deposition processes the duration for the dissolution process was 5, 4, 3, 2, 1 hours and the initial amount of PCBs taken for the dissolution process was 500 gm for every set of experiment. Weight of the dried sample of PCBs was noted after 5 hours of dissolution process and it was found that 132 gm was dissolved in nitric acid bath. The results obtained during the dissolution and deposition processes were presented in Figs 2 to 4. Based on the analysis of the results obtained, critical inferences are drawn as detailed below:

(i) Weight of PCBs dissolved goes on gently increasing, with the rate of increase being higher during initial stages, and stabilises at latter stages, within the range of duration considered.

(ii) However, the weight of copper deposited in the cathode plate almost increases linearly with time, barring the initial stage.

(iii) On the other hand, power consumption during the dissolution and recovery processes with time, almost exhibit the same trend.

Initial weight of the copper plate was noted for the deposition process and after the electro deposition of copper the deposited weight of copper in the cathode electrode was assessed by taking the weight. The duration for the deposition process was set as: 120, 90, 60, 30, 15 minutes. It was found that 14.861 gm of copper deposited during 120 minutes is the highest, among all the durations considered. It is found that the maximum copper (Cu) recovered was 12% and achieved after 120 minutes, in 5 L of dissolved solution.

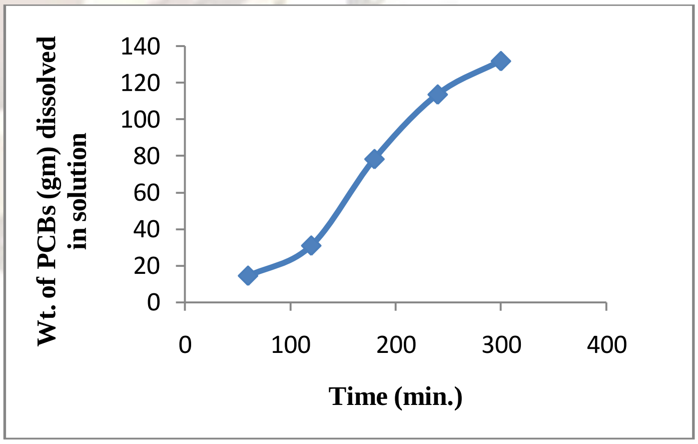

Fig.2. Time (min.) Vs Weight of PCBs dissolved in solution (gm)

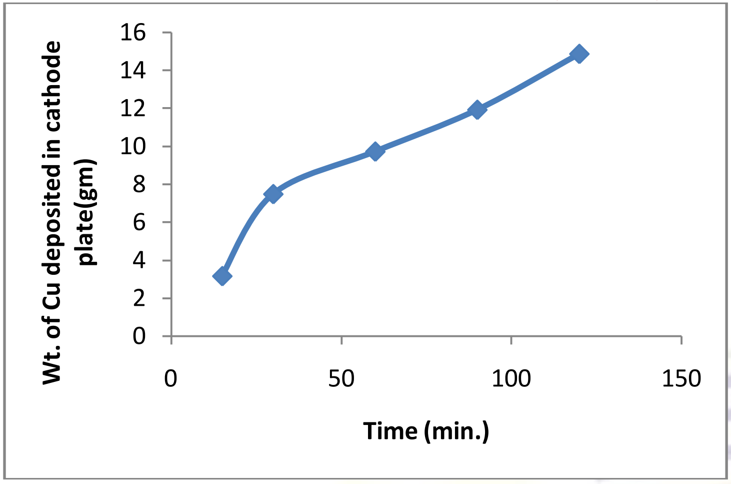

Fig.3 Time (min.) Vs Weight of Copper deposited in cathode plate (gm)

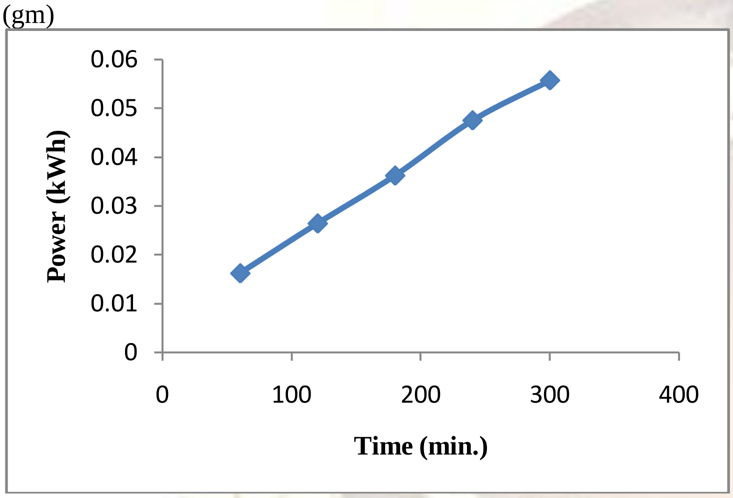

Fig.4 Time (min.) Vs Power consumption for dissolution process (kWh)

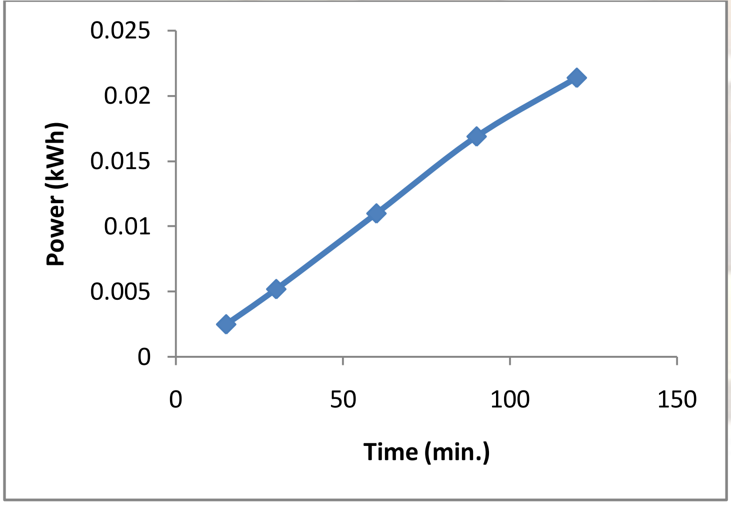

Fig.5 Time (min.) Vs Power consumption for recovery process (kWh)

b) Effect of pH

The pH of the solution i.e. in dissolution process and deposition process was 1.0 (i.e. very highly acidic), due to the usage of nitric acid for dissolution of metals. No addition of any buffer solution was made for the study of pH variation in the experimental investigations, as it would affect the reaction that is undergoing in the reactor. At the end of the electrolytic process, pH was reduced to near 'neutral', by adding Na_2 Co_3 and NaOH (i.e. 12 gm / 100 ml and 7.2 gm /100 ml of acidic solution), before it is disposed off, in an eco-friendly manner.

c) Energy consumption

Specific electrical energy consumption is defined as the amount of electrical energy consumed per unit mass of E-waste loaded and it was calculated in terms of kilo watt hour (kWh) one gram of copper recovered (kWh g^{-1} Cu). The maximum power or energy consumption was found to be 0.0214 kWh for 14.861gm of copper recovered (Figs. 6&7). It can be seen that as the power consumption increases drastically, as the weight of PBS dissolved in solution increases. However, the weight of copper deposited increases gently with increase in power.

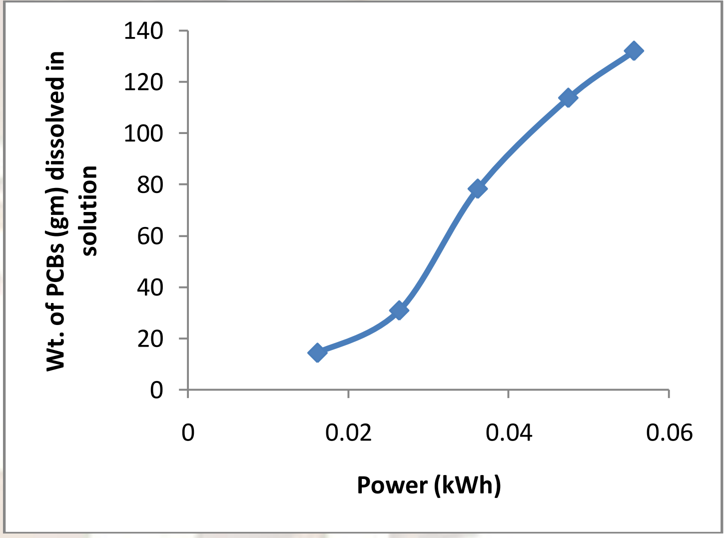

Fig.6 Power (kWh) Vs Weight of PCBs dissolved in solution (gm)

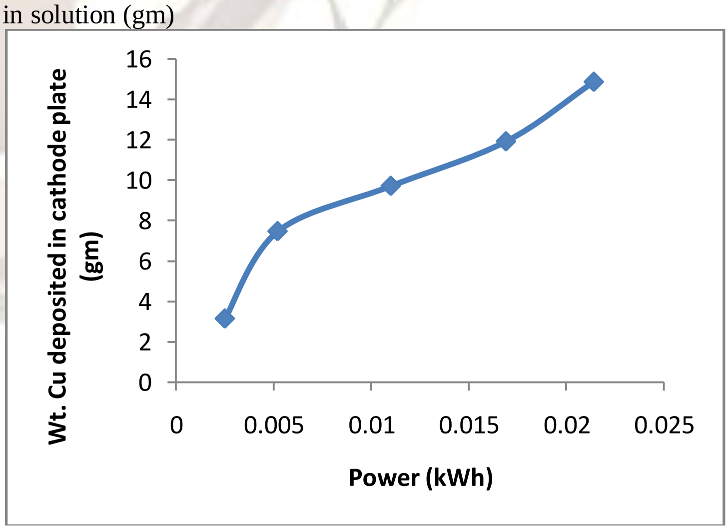

Fig. 7 Power (kWh) Vs Weight of Copper deposited in cathode plate (gm)

IV. CONCLUSION

i. For the recovery of copper from E-waste (PCBs), the maximum duration for the dissolution process was found to be 5 hours for the dissolution of 132 gm of PCBs compounds and the maximum duration of electrolysis for deposition of copper was 120 minutes for 14.861 gm.
ii. The maximum power consumption was 0.0214 kWh for 14.861 gm of copper recovered.
iii. Maximum copper (Cu) recovered is 12% and it was achieved in 120 minutes using 5 L of dissolved solution.
iv. The performance of the process seems to depend on the choice of the electrolyte, the initial state of PCBs, duration and power consumed duration the dissolution and deposition stages.
v. There is scope for improvement in the process and scaling it up, with the support for research from funding agencies, as laboratory investigation has its own limitations.

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