ELECTROLYTIC RECOVERY OF COPPER FROM WASTE PRINTED CIRCUIT BOARDS USING AMMONIACAL COPPER SULPHATE SOLUTION

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Abstract

There has been an exponential growth in the waste Printed Circuit Boards (PCB) and other electronic circuit scraps every year. These electronic and PCB scraps can be recycled so as to effectively regenerate the metal from the waste non-degradable components. This paper provides a methodology for simple, optimal, economical and efficacious recovery of copper from printed circuit boards that are found in almost all electric-electronic equipments and concludes that electrolytic process is an ecofriendly and efficacious with a minimal discharge of effluents. The paper also envisages on etching rate and various other parameters affecting the rate of copper recovery.

Keywords: PCB, Copper, Copper recovery, etchant, Ammoniacal copper sulphate.

I. INTRODUCTION

For the past few decades there has been a rapid worldwide growth in the electronic and semiconductor industries generating a large amount of electronic scraps. Printed circuit boards are part of these electronic scrap and are found in almost all electronic equipments. Printed circuit boards conventionally used generally contains 10–30% copper as well as plastics, fiberglass and other metals [1]. Copper is a versatile metal extensively used in various engineering, automotive and electronics applications. Its wide usage is due to its excellent electrical and thermal conductivity, high corrosion resistance, easy fabrication, and good strength and fatigue properties [2]

These unique features have made copper as an active metal in the design of PCBs, which involves several technical processes. However copper from waste or utilized PCBs poses serious environmental threat if not disposed properly. Regenerating copper from such PCB scraps and electronic industrial waste is very effective from the economical and environmental perspective. So recovery of copper from waste PCBs is a very vital study that has to be performed. The two commonly employed methods to recover copper are pyrometallurgical and hydrometallurgical process. The method incorporated in the experiment is the hydrometallurgy process that involves the utilization of an etchant (chemical solution) to remove copper from obsolete electronic PCBs by a controlled dissolution technique and recovery of high purity copper from etchant by using electrochemical method.

The reaction that takes places in the copper etching process is as follows.

$$Cu^{2+} + Cu^{0} \longrightarrow 2Cu^{+} \quad (1)$$

The unwanted waste copper in the PCB and electronic scrap are dissolved by the action of cupric (Cu^{2+}) ion, which converts it to cuprous (Cu^{+}) ion. The ideal etchant solution must have high etching rate, economical recovery of etched copper, low toxic fumes, minimum undercut and maximum dissolved copper capacity. Etching can be accomplished either with an acid or base. In general, the etchants used for copper recovery process are 1) Alkaline etchants 2) Acidic cupric chloride 3) Ferric chloride etchants. Alkaline etchants are the most commonly used etchant in copper etching process, because of its high dissolved copper capacity [2, 3]. In alkaline etchants two types of copper etchants are used, namely ammoniacal cupric chloride and ammoniacal cupric sulphate, and in specific ammoniacal cupric chloride etchants are the one most widely used, because of its high etching rate. The major limitation of this type of etchant is that the waste produced is difficult and expensive to treat moreover the etchant baths are usually operated on a feed and bleed type system thus occupying large volumes. Electrolytic attempts to recycle or regenerate such baths have been largely unsuccessful due to the corrosive nature of the material and the large amounts of chlorine gas evolution, so it has to use a divided cell for eliminating chlorine evolution. Though ammoniacal cupric sulphate etchant has a slower etching rate than ammoniacal cupric chloride it do not pose any waste treatment problems and are easily regenerated using electrolytic regenerating techniques. In ammoniacal cupric sulphate etchants the electrolysis can be conducted in a simple undivided cell. The etching of copper with ammoniacal cupric sulphate etchant can be expressed by the following reaction:

$$Cu(NH_3)_4SO_4 + Cu^{0} \longrightarrow 2\,Cu(NH_3)_2SO_4 \quad (2)$$

Very few literatures are available for recovery of copper from PCB by using ammoniacal cupric sulphate etchant, and no systematic scientific study on the effect of the different processing parameters are available in open literature. The present study is conducted to optimize the recovery of high purity copper from obsolete PCBs and electronic scraps by using ammoniacal cupric sulphate etchants. This study involves two steps i.e. Optimization of etchant based on better etching rate and Optimization of copper recovery from the optimized etchant to yield a better cathodic efficiency.

II. EXPERIMENTAL

The etchant (Ammoniacal cupric sulphate solution) is prepared from cupric sulphate (99.0%&Merck), ammonium salts (99.8%&Merck), ammonia gas and deionized millipore water. 100 gpl of copper and its corresponding sulphate ion concentration which had been set at a pH value of 9.0 by bubbling ammonium gas in were taken as the initial concentration of the etchant. To avoid oxidation or corrosion and enhance the passivity of the anode sides of the bipolar electrodes 5gpl of phosphate (as Ammonium di hydrogen ortho phosphate) was added [4]. It also acts as a brightener [5]. The etching rate of copper is studied at a temperature of 40°C. Specimen copper particles of dimension 1mm thickness and specific area 10mm×60mm were added to the etching solution and the corresponding etching rate is determined. Fresh etchants are prepared and used for each experiment. This procedure is performed to study the effect of various parameters affecting the copper-etching rate. The experiments also envisages on copper electrodeposition that is performed after optimizing the etching solution. The experiment for copper recovery is performed in a single compartment small cell. Various parameters like Current density, Temperature, and Time duration effects were studied to optimize the copper recovery. Based on the optimized result of a single cell the experiment is extended to a bi-polar cell made of acrylic sheet with 4 compartments. In the bipolar system, one face of the electrode acts as a cathode while the opposite face acts as anode. Polished Stainless steel 316 is used as an electrode. The bi-polar cell constructed for the experiment is equivalent to 4-monopolar cells. The total volume of the electrolyte is 5 liters. The 4 cells are compactly packed to form a closed loop system. The cell has an auxiliary tank in which a Titanium cooling coil is immersed. The cell is operated in a closed atmosphere, so that no ammonia gas escapes outside. The temperature of electrolyte is maintained high despite of greater loss of ammonia as the conductivity of electrolyte increases with increase in temperature. The cell is operated at 50°C at which the ammonia loss is higher. The evaporated ammonia is redissolved into the auxiliary tank, thus minimizing the ammonia loss. Intense care is taken throughout the experiment to avoid the leakage of current, so as to yield maximum cathode efficiency. A provision is incorporated in the auxiliary rectangular vessel to place the electronic scraps and PCBs for etching and synchronous recovery of copper. A schematics diagram of the Experimental Setup for Copper recovery is shown in Fig.1.

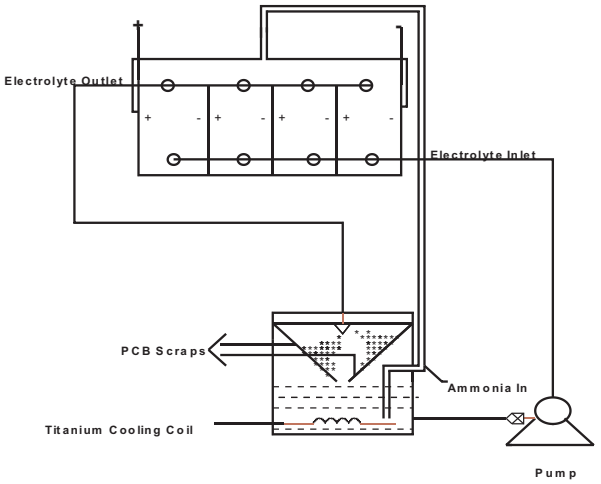

Fig. 1. Experimental Setup for Copper recovery

III. RESULTS AND DISCUSSIONS

Optimization of Etching solution:

There is a disadvantage associated with ammoniacal cupric sulphate etching solution which in comparison to the ammoniacal cupric chloride etchant has about a 30% slower corrosion rate [5] (Bernd Lindinger, 2000). Inserting an accelerator to the etchant considerably raises the etching rate. 100 gpl of copper with its corresponding sulphate ion and pH of 9 are taken as initial concentration of the etchant. In this experiment etchant optimization is vital because it is the one that favors both copper etching rate and electrodeposition. Etching rate increases with increase in copper concentration but above a critical point the etching rate drastically reduces; at the same instant higher concentration may also redissolute the deposited copper leading to the decrease of cathodic efficiency. Considering this perspective into account copper concentration was optimized to 100 gpl.

Effect of various additives

The addition of sulphate ion (as ammonium sulphate) to ammoniacal copper sulphate etchant increases the etching rate. The effect of sulphate concentration in the range of 100gpl to 225gpl was studied keeping other parameters constant i.e. etching temperature (maintained at 40°C, Copper concentration (maintained at 100gpl, 5 gpl of phosphate and pH 9.0). The results are shown in the

fig.2. From the results it was inferred that the etching rate increases with an increase in sulphate concentration, but this incremental gain decreases above 200gpl. At the same time high sulphate ion addition could also create a corrosive environment. The addition of a small quantity of chloride (as ammonium chloride) to ammoniacal copper sulphate also accelerates the copper-etching rate [6]. The chloride ion concentration in etchant is varied from 1 to 5gpl and the etchant rate was studied with other parameter constant i.e. etching temperature is 40°C, copper concentration is 100gpl at pH 9.0 with 200gpl of sulphate ion. The results are shown in the fig.3. From the results it was inferred that the etching rate increases with an increase in chloride ion concentration, but with high chloride ion concentration there is a possibility for chlorine evolution during copper recovery. So the chloride concentration is maintained lower.

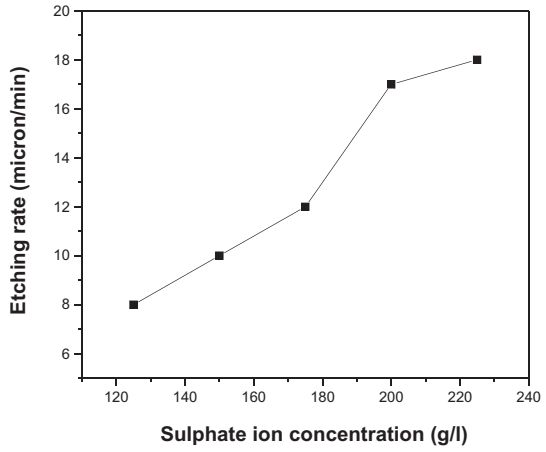

Fig. 2. Effect of Sulphate ion concentration on Etching rate.

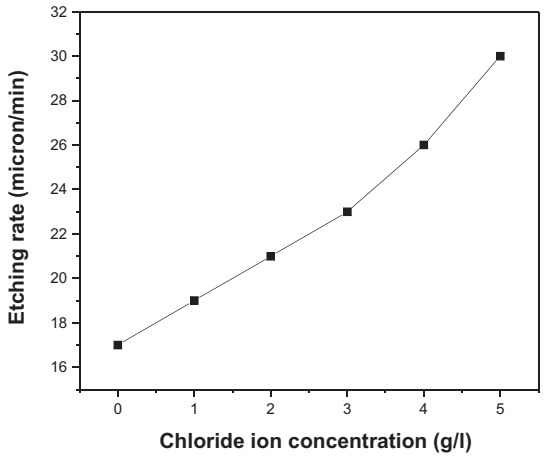

Fig. 3. Effect of Chloride ion concentration on Etching rate.

Effect of pH

The etching rate depends on pH based on the experiment it is illustrated in the table1. As the pH increases the etching rate also increases but after a particular pH level (i.e. 12 or higher), Cu $(OH)_2$ is formed and deposited as a stable film on copper surfaces that decelerates the etching rate.

Table 1. Effect of pH on Etching rate at 40°C

Solution PH	Etching rate (μm/min)
9	30
10	32
11	33
12	25

Effect of Temperature

The etching rate is directly proportional to temperature; the etching temperature for any etchant provides advantage in any metal etching process [2, 7]. Fig.4 shows the effect of temperature on etching rate of ammoniacal cupric sulphate solution. A typical etchant composition is shown in the table 2.

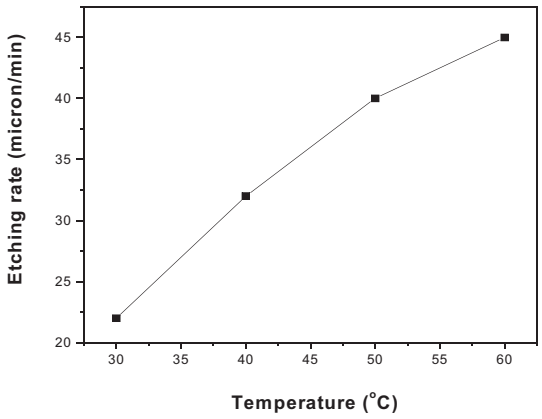

Fig. 4. Effect of Temperature on Etching rate.

Table 2. Typical composition of spent etching solution

Copper	100 g/lts
Sulphate	200 g/lts
Chloride	5 g/lts
Phosphate	5 g/lts
pH	10
Temperature	50°C
Etching rate	40μm/min

Electrolytic recovery of copper

The process consists of electrolyzing the spent etchant in an electrolytic cell with stainless steel electrodes. During electrolysis, the cupric ion gets reduced to cuprous ion and finally to metal. After optimizing the etchant, the experiment for copper recovery is performed in a single compartment small cell. Various parameters like Current density, Temperature, and Time duration effects were studied to optimize the copper recovery. Based on the optimized result of a single cell the experiment is extended to a bi-polar cell made of acrylic sheet with 4 compartments.

Effect of Current Density

For studying the effect of current density on recovery of copper from ammoniacal cupric sulphate etchant, The current density is varied from 500 A/cm^2 to 3000 A/cm^2, at the optimized temperature of 50^{o}C and results are presented in Table 3. From the results it is inferred that there is a decreasing trend in cathodic efficiency above 1500 A/m^2. This may be due to the fact that at higher current density there is more hydrogen and oxygen evolution at the cathode and anode side respectively [8].

Table 3. Effect of Current densities in Cell Efficiency

Current density (A/m^2)	Cell Efficiency (%)
500	45
1000	68
1500	78
2000	65
2500	40
3000	25

Effect of Temperature in Copper Recovery: -

The temperature plays an important role in the mass transfer and conductivity of the electrolyte. The advantage of operating the cell at an elevated temperature is to increase the conductivity of the electrolyte. The experiments are carried out at various temperatures and the results are shown in table 4. It is perspicuous from the table 4 & Fig.1, that as the temperature increases the current efficiency and etching rate also increases. But there is significantly a greater ammonia loss at temperature above 50^{o}C. It is also inferred that there is no much difference in current efficiency between the temperature ranges of 50^{o}C to 60^{o}C. So 50^{o}C is optimized as a favorable temperature for copper etching and electrodeposition.

Table 4. Effect of Temperature in Cell Efficiency

Temperature (^{0}C)	Current efficiency (%)
30	65
40	68
50	78
60	80

Effect of Duration in Copper Recovery: -

The Duration effect is also an important factor; since the electrolyte is an etchant and it can easily redisolve the deposited copper. So the duration effect also studied and the results are shown in the Table 5. The efficiency decreases with increase in the duration .The efficiency is high for duration of 4 hours, which is clear from the results. There is a considerable reduction in efficiency for the duration above 8 hours. So the experiment is performed in the interval of 4 to 8 hours, so as to have a maximum efficiency.

Table 5. Effect of Duration in Cell efficiency

Time duration (Hrs)	Current Efficiency (%)
4	78
8	77
12	55
16	40
24	25

IV. CONCLUSION

The methodology employed in this article provides an optimal and simple technique to reprocess the local electronic waste streams and thus regenerating value added copper products. It can be inferred that various additives like sulphate and chloride plays a very important role in copper etching rate at the same time pH and temperature also have their own impact. Except the pH all the parameters are directly proportional to etching rate. The optimum etchant combination is, copper 100 gpl, phosphate 5 gpl, sulphate 200 gpl, chloride 5 gpl, pH at 10 and the etching temperature 50^{o}C. After optimized the etchant, high purity copper was recovered from the etchant and the etchant was regenerated. The effects of various parameters, namely current density, process temperature and durations, influenced in current efficiency were investigated. At lower current density, the current efficiency is around 45% to 68% and it increases upto 78% at 1500A/m^2. Increasing the current density beyond that results in decreasing the current efficiency. Hence the optimum current density is fixed at 1500A/m^2. Temperature

and durations are also play a major role in cathodic efficiency, if temperature increases copper etching rate and cathodic efficiency also increases. But there is significantly a greater ammonia loss at temperature above 50°C, at the same time there is no much different in cathodic efficiency above 50°C. So the processing temperature of 50°C is favorable for both copper etching and recovery. The duration effect also influences the cathodic efficiency of copper recovery. Duration effect is negatively correlated with cathodic efficiency. There is a considerable reduction in cathodic efficiency for the duration above 8 hours. So the experiment is performed in the interval of 4 to 8 hours to get maximum efficiency.

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