

## Extraction of copper from small electronic devices populated on discarded PCBs

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**Abstract** : With the technological development, the demand for electric and electronic equipment (EEE) is increasing rapidly worldwide. Printed circuit boards (PCBs) is one of the essential parts of all the EEEs which contains large number of small components for different applications. Huge amount of such small components are generated during PCBs production as well as after its end of life. Recycling and reuse of these devices from waste circuit boards is essential to conserve the resources and avoid environmental problem. Present study shows the recovery of valuable copper from small electronic devices such as capacitor, LED, MOSFET etc. populated on discarded PCBs. The crushed samples were leached using nitric acid. 99% copper dissolution was observed at elevated temperature, pulp density of 15 g/L in 60 min with stirring speed of 300 rpm. The metals or its salt can be further produced from the leach liquor by the process of precipitation, evaporation, solvent extraction etc.

**Keywords** : Recycling, printed circuit boards, copper, leaching.

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### Introduction

In electrical and electronic equipments (EEEs), printed circuit boards (PCBs) has an important role. The manufacturing of PCBs requires large number of small components in which capacitor, LED, MOSFET etc. are used for different applications such as control temperature, power management, load switches, battery chargers, notebooks etc. The global market for electronic chemicals for the production of printed circuit boards (PCBs) and semiconductor packaging materials was estimated at \$10–15 billion in 2009. This diverse, highly specialized, technology-driven global market is projected to grow at an average annual rate of almost 5% through 2014<sup>1</sup>. The replacement of electrical and electronic equipments (EEEs) is necessity with faster rate with technological innovation and improvement of quality<sup>2,3</sup>. This results in generation of electronic wastes which are piling up in landfills and pose potential environment and health threats. E-wastes are also a special kind of resource, for example typical E-waste PCBs usually contain epoxy resin, fiberglass, copper, nickel, iron, aluminum and a certain amount of precious metals such as gold and silver<sup>4</sup>. The recovery of these metals are usually by hydrometallurgical process as

it is more efficient in comparison to the pyrometallurgical process. The process includes different treatments at high temperatures : incineration, melting etc. and it generates atmospheric pollution due to evolution of toxic dioxins furans gases, carcinogenic compounds<sup>5</sup>. Copper from waste printed circuit and other resources have been recovered by leaching using different medium as electro-generated chlorine in hydrochloric acid, nitric acid etc.<sup>6,7</sup>. The copper was reported to be leached to about 98.3% from waste printed circuit board in 3 mol/L nitric acid at 60 °C in 5 h<sup>8</sup>. In this paper, experimental work focuses on the optimisation of process parameters for the recovery of copper from small electronic devices populated on discarded PCBs. Various process parameters such as acid concentration, temperature, time, pulp density, etc. were studied for copper leaching. Based on the obtained result the leaching of copper from sample was validated. The results obtained from laboratory scale studies will be helpful to develop a non-toxic copper recovery from waste.

### Experimental

*Material and sample method* :

Small electronic device of PCBs get separated after

desolderization by thermal process then crushed in a grinding machine (Vibrating Cup Mill Pulverisette, Germany) with a speed 1000 rpm for 5 min then screened sample in sieve shaker.

#### *Leaching procedure :*

The leaching of the crushed small electronic devices of PCBs sample was carried out in closed three necked Pyrex glass reactor fitted with condenser on a hot plate maintained desired elevated temperature. When using stirrer the slurry was mixed which was adequate to ignore the mass transfer effect on leaching. Sample was taken in regular time interval for metal analysis after dissolution in acid using Atomic Absorption Spectrometer (AAS) (Perkin-Elmer model, Analyst 200; USA). Chemical reagent used for experiment where laboratory reagent grade (Grade : GR, supplied by Merck, India).

#### **Results and discussion**

The crushed sample of small electronic devices of PCBs after de-solderization contains maximum amount of copper i.e. 67% along with other metals as shown in Table 1.

#### *Leaching studies :*

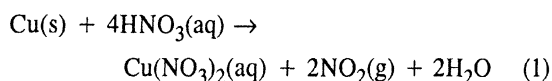
To recover copper from the crushed small electronic devices. A hydrometallurgical process followed by acid leaching has been considered suitable.

#### *Leaching of copper with different acidic solutions :*

The performance of the copper leaching using different acid solutions such as sulfuric acid, hydrochloric acid and nitric acid in different time intervals as shown in Fig. 1. When metal dissolve in the acid that depends on the chemical and physical character of the material to be leached, selectivity, reagent cost and its ability to be regenerated. This is important from the diffusion of reactants on the surface of the solid materials. Recovery of copper obtained was 99.99% with 6 M nitric acid solution at 90 °C in 60 min while only 0.4% and 11.2% copper dissolution observed in case of 6 M sulfuric acid and 6 M hydrochloric acid respectively in 60 min. This may be because of hindrance provided by formation of precipitates in case of sulphuric and hydrochloric acid.

#### *Effect of acid concentration :*

Dissolution of copper from sample was observed at different concentration of HNO<sub>3</sub> over a range of 5–6 M keeping pulp density of 15 g/L in different time interval. The results presented in Fig. 2 indicate that at 90 °C, equilibrium copper leaching of 98.2% and 99% is attained from the crushed small electronic devices of PCBs with 5 M and 6 M HNO<sub>3</sub> respectively in 30 min. It was observed that subsequent increase in acid concentration to 6 M, increased the copper recovery after 30 min it was constant in all cases. Increases the flux of H<sup>+</sup> ion across the particle boundaries due to increase in acid concentration and hence increased the rate of reaction<sup>9</sup>. Reaction in the time of leaching as given below<sup>10</sup> :



#### *Effect of pulp density and leaching time :*

Pulp density is the very important factor in the time of leaching as it increases the available surface area per unit volume of the solution and hence more metal is recovered from solution within specific time. Copper recovery from crushed small electronic devices of PCBs was studied in the range of 15 g/L to 30 g/L pulp density under the conditions : 90 °C, 5 M HNO<sub>3</sub>, stirring speed 300 rpm as shown in Fig. 3. From this figure it was noticed that pulp density was inversely proportional to the metal extraction with time. 99% copper recovered when using 15 g/L and 97.2% copper recovered when using 30 g/L pulp density within 45 min. Copper recovery increases to 99% with increased in time from 10 to 60 min as shown in Fig. 3.

#### *Effect of temperature :*

Leaching experiment was done by varying the temperature from 30–90 °C using pulp density 15 g/L. Copper extraction increased with increases in temperature due to reactive activity of HNO<sub>3</sub>. Fig. 4 shows copper recovery from crushed small electronic devices of PCBs increased from 6.8 to 99% with increase in temperature 30 to 90 °C. It is due to increase in temperature has increased the mass transfer coefficient and the diffusivity.

**Table 1.** Analysis of the metallic content in crushed sample of small electronic devices of PCBs

Metal	Cu	Ni	Pb	Sn	Fe	W	Mo	Si	Ca	Others
Weight (%)	67.0	0.17	3.05	0.1	0.0154	0.0009	0.082	2.21	0.28	Balance

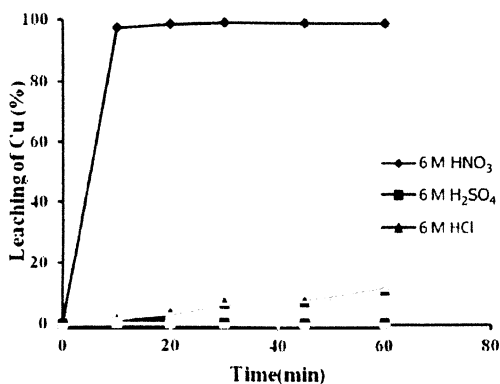


Fig. 1. Leaching of copper from crushed small electronic devices of PCBs at different acids [Experimental conditions : Temperature = 90 °C, Pulp density = 15 g/L, Time = 60 min, Stirring speed = 300 rpm].

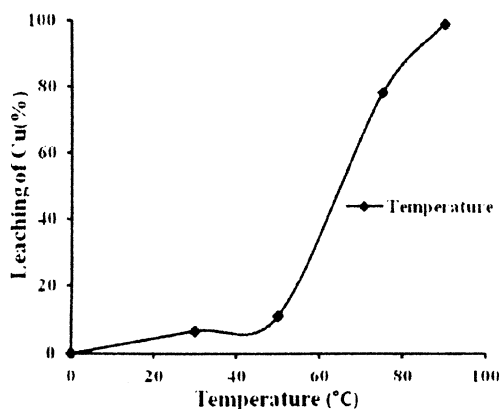


Fig. 4. Leaching of copper from crushed small electronic devices of PCBs at different temperature in nitric acid [Experimental conditions : Acid = 5 M HNO<sub>3</sub>, Pulp density = 15 g/L, Time = 60 min, Stirring speed = 300 rpm].

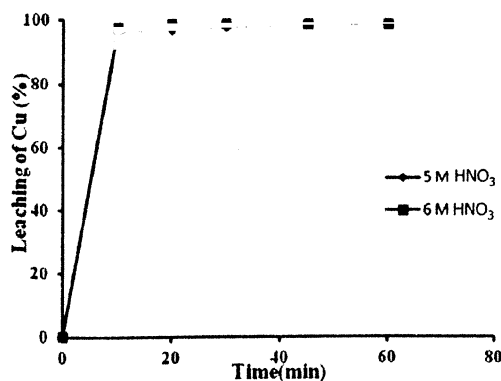


Fig. 2. Leaching of copper from crushed small electronic devices of PCBs at different concentration of nitric acid [Experimental conditions : Temperature = 90 °C, Pulp density = 15 g/L, Time = 60 min, Stirring speed = 300 rpm].

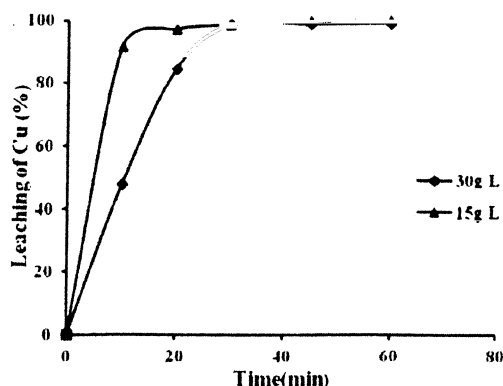


Fig. 3. Leaching of copper from crushed small electronic devices of PCBs at different pulp densities in nitric acid [Experimental conditions : Acid = 5 M HNO<sub>3</sub>, Temperature = 90 °C, Time = 60 min, Stirring speed = 300 rpm].

#### Characterization studies :

The characterization of the original crushed small electronic devices and dry leached residues after leaching in nitric acid by X-ray diffraction using Bruker AXS D8 instrument running at 0.2 s/step shows various diffraction peaks. XRD of the original sample shows the various peaks such as copper, lead etc. in Fig. 5. XRD of the dry leached residues shows the various peaks such as CuO, Pb(NO<sub>3</sub>)<sub>2</sub>, Si<sub>2</sub>N<sub>2</sub>O in Fig. 6. From Fig. 7 showed that EPMA/EDS studied of original sample and dry leached residues using electron probe micro analyzer for micro-structure and EDS shows the peaks of copper, lead, iron etc. are present in sample and presence of CuO, other metals in the leached residue. Process flow-sheet for recovery of copper from crushed small electronic devices of PCBs samples as shown in Fig. 8.

#### Conclusions

Based on the above leaching studies, the following conclusions could be drawn as mentioned below :

- Nitric acid is the best leachant for the recovery of copper. This may be due to the hindrance provided by formation of precipitates in case of sulphuric and hydrochloric acid.
- 99% copper recovered from crushed small electronic devices of PCBs using 5 M HNO<sub>3</sub>.
- Leaching of copper increases with increase in temperature and time.

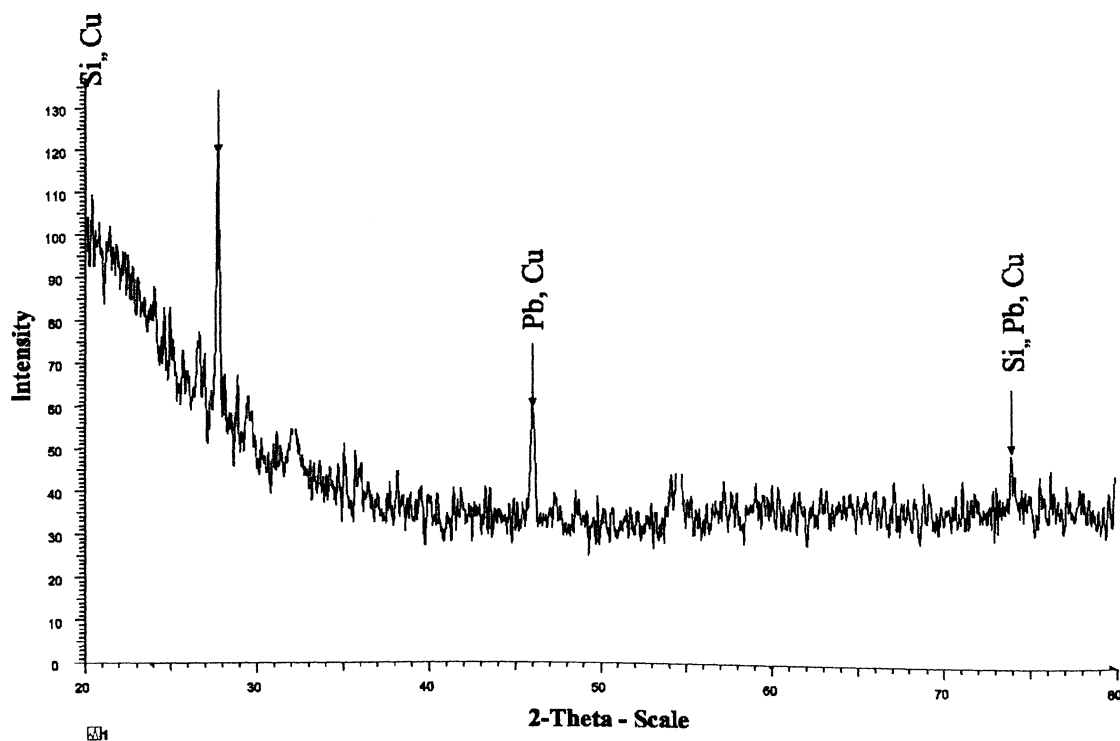


Fig. 5. XRD of crushed small electronic devices of PCBs.

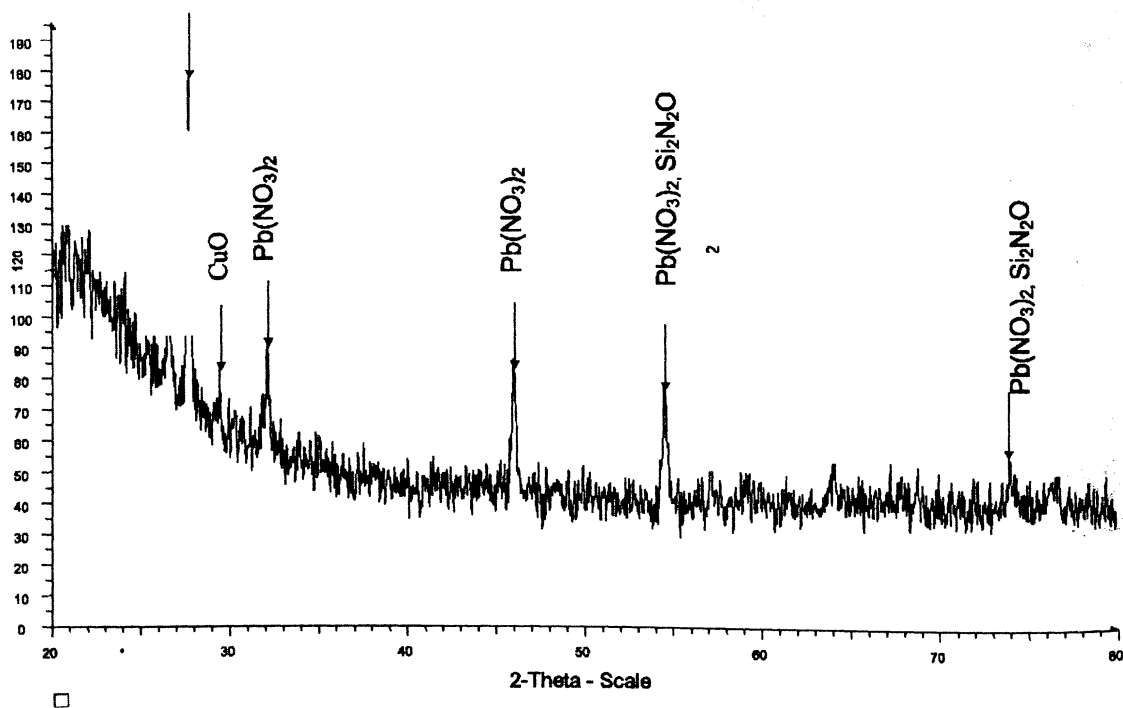


Fig. 6. XRD of dry leached residue which is left after leaching in Nitric acid.

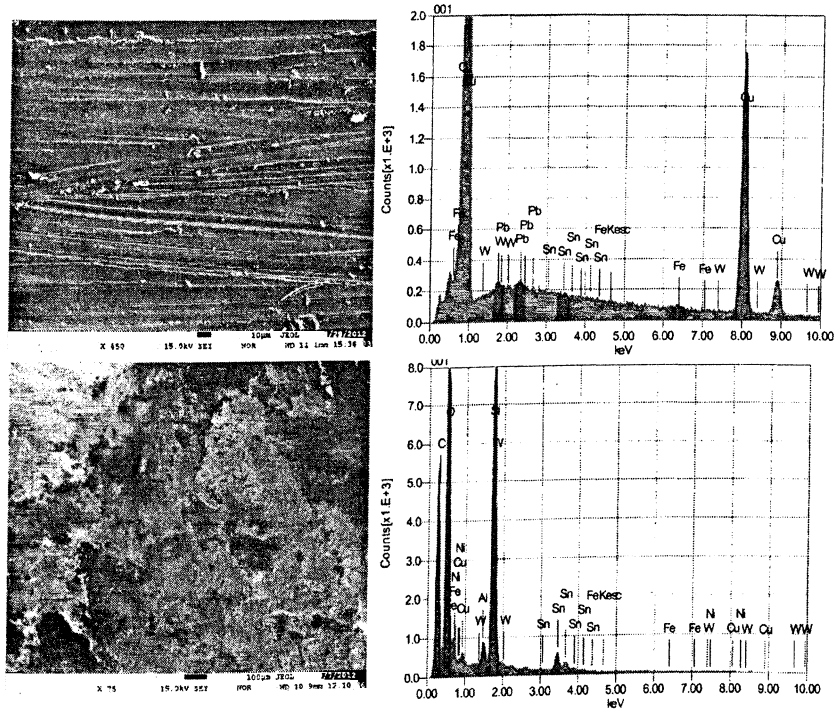


Fig. 7. Electron Probe Microanalysis (EPMA) and EDS of crushed small electronic devices of PCBs before and after leaching.

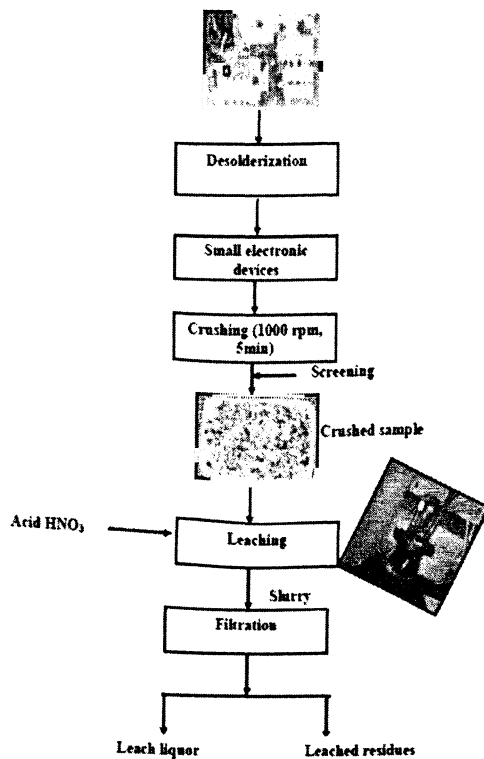


Fig. 8. Process flow-sheet for recovery of copper from crushed small electronic devices of PCBs samples.

- With decrease in pulp density with time the leaching of copper increases. This is because of increase in the surface area available for reaction.
- Maximum copper were dissolved in nitric acid and very less amount of copper contain in leached residues noticed by characterization studies such as XRD, EPMA-EDS.

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