ISSN Print: 2394-7500
ISSN Online: 2394-5869
Impact Factor: 5.2
IJAR 2017; 3(3): 634-637
www.allresearchjournal.com
Received: 09-01-2017
Accepted: 10-02-2017

Ashok K Sharma
Professor Department of Chemical Engineering College, M.TECH Chemical Engg

Sarita Sharma
Professor Department of Chemical Engineering College, M.TECH Chemical Engg

Usha Bagdi
M.TECH Chemical Engineering, Ujjain Engineering College, Ujjain, Madhya Pradesh, India

Priya Gautam
M.TECH Chemical Engineering, Ujjain Engineering College, Ujjain, Madhya Pradesh, India

Correspondence
Ashok K Sharma
Professor Department of Chemical Engineering College, M.TECH Chemical Engg

Copper extraction from the discarded printed circuit board by leaching

Ashok K Sharma, Sarita Sharma, Usha Bagdi and Priya Gautam

Abstract
Printed circuit boards (PCBs) are currently dumped in landfills or incinerated which is causing a serious environmental harm in the form of toxic gases or leached hazardous compounds. PCBs contain large amounts of precious metals; about 20 wt% copper, 0.04 wt% gold, 0.15 wt% silver, and 0.01 wt% palladium. The extraction of these metals from PCBs is both profitable and environmentally worthwhile. Leaching copper from shredded particles of waste printed circuit boards (PCBs) was carried out in sulphuric acid solution using hydrogen peroxide as an oxidant at room temperature. The influence of system variables by leaching on copper recovery was investigated, such as sulphuric concentration, amount of hydrogen peroxide addition, waste PBCs particle size, presence of cupric ion, temperature and time.

Keywords: Electronic waste management, copper, extraction, printed circuit board (PCB), recovery

1. Introduction

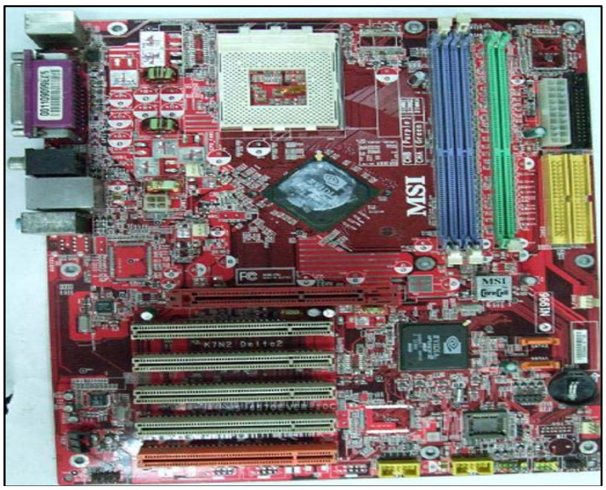
Printed circuit boards (PCBs) are the base of the electronic industry as it is an essential part of almost all the electric and electronic equipment (EEE). Both technological innovation and market expansion accelerate the replacement of EEE, which leads to a significant increase of waste PCBs [1]. Waste PCBs has been attracting the public attention by its environmentally harmful materials and abundant valuable non-ferrous metals. If the waste PCBs are improperly disposed, hazardous materials could cause serious environmental problems and numerous valuable metals would be lost. Therefore, recovery of valuable metals from waste PCBs is one of hot topics in industrial waste reclamation [2]. It can be noted from review of the literatures that, the processes for recovering metals from waste PCBs include mechanical [3–6], pyrometallurgical [7, 8] and hydrometallurgical [9–11] methods. The mechanical process is usually used as a pre-treatment process before pyrometallurgy and/or hydrometallurgy, such as shredding the boards into fine particles for improving valuable metal recovery and processing operations. Pyrometallurgical process can efficiently recover copper and precious metals, which need further refined. However, this high-temperature process easily causes serious environmental problems, especially air pollution. Pyrometallurgical methods currently are seldom used in recovery of waste PCBs for their shortcomings. Hydrometallurgy may be more exact, more predictable and more easily controlled comparing with pyrometallurgical process [12]. So far, hydrometallurgical processes have been widely applied in recovering metal components from waste PCBs using mechanical as pre-treatment process. However, most of previous researches focused on recovering precious metals for its higher value [13] With the development and innovation of manufacturing of PCBs, the content of precious metals is lower and lower. Thus, recovery of main metals from waste PCBs becomes more and more evident. The previously related studies were mainly focused on the recovery of main metals such as copper, tin and lead simultaneously [14–16]. Therefore the composition of leaching solution was complicated which resulted in difficultly to separate the metals. Additionally few experiments were reported on investigating the effect of the size of mechanically shredded particles on the metal recovery by leaching with hydrometallurgical process.

In this regard, a green process for leaching copper from shredded particles of waste PCBs at room temperature was investigated in the present research. The objective of the research is to recover valuable metal copper by leaching process with solutions of sulfuric acid and hydrogen peroxide. The effect of the waste PCBs particle size on the leaching behavior of copper will be discussed as well.

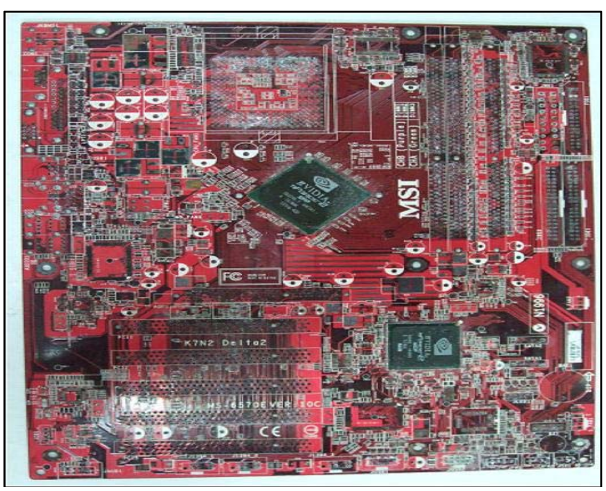
2. Materials and Experimental Procedures

2.1 Preparation of the PCBs

Pieces of different kinds of waste computer mainboards with different sizes were immersed in dilute nitric acid solution, in which welding jointed components were removed, as presented in Fig. 1. About 4 kg of waste PCBs was selected from 10 kg waste mainboards. Waste PCBs were firstly cut into small pieces of about 3 cm×3 cm by pliers. Then the pieces were pre-treated by liquid nitrogen to increase the crushability of waste PCBs and shredded by cutting mill (Retsch SM2000) with 8mm final fineness. Then the samples obtained were mixed uniformly for later experiment.



(a) Before pre-treatment of nitric acid solution



(b) After pre-treatment of nitric acid solution.

Fig 1: Photos of printed circuit board obtained from waste mainboards

The schematic of specimen preparation and leaching processes presented in Fig. 2. Soldering tin reacts with nitric acid to make insoluble stannic acid and soluble lead nitrate. By this method tin is separated from lead. Then tin was recovered as the form of stannic acid. The lead ion in leaching solution was precipitated as PbSO4 with adding sulfuric acid. Copper exists in boards at middle layer and it does not expose in nitric acid solution at the beginning reaction stage. Copper in the middle layer just reacts with nitric acid solution when the soldering-tin completely reacts with nitric acid solution. Therefore, copper almost did not leach out by controlling the immersed time and the concentration of nitric acid. The concentration of the nitric acid used for preparation of waste PCBs is about 2mol/L and the PCBs were immersed for about 3 h at room temperature. The waste mainboards mainly contained metal copper after the pre-treatment. The current research just focuses on the characterization of copper leaching in dilute sulfuric acid solution using hydrogen peroxide as oxidant

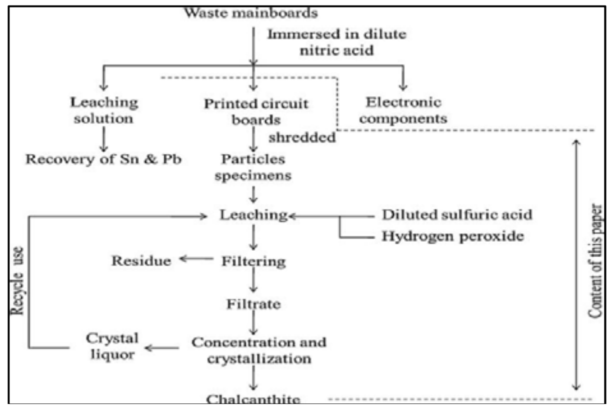


Fig 2: Process of leaching copper from particles of PCBs.

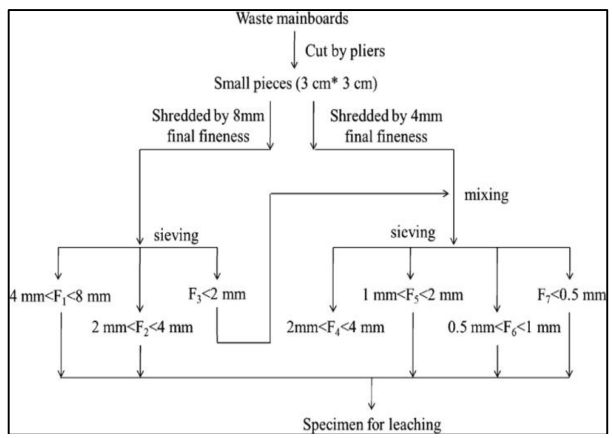


Fig 3: Preparation of the shredded specimen of different sizes for leaching experiment.

2.2 Material Characteristics of Waste PCBs Specimen

Aqua regia and perchloric acid was used to fully leach the metals from the specimen. The metal concentrations of the digestion solution were tested by Atomic Absorption Spectrophotometer (Hitachi, Z2000). The digestion results are showed in Table 1.

X-ray diffraction pattern was investigated on grounded waste PCBs powders by X-ray diffractometer (XRD) (PANalytical B.V. company, X' Pert PRO), and the result indicates that the copper in the PCBs exists as metal copper.

2.3 Leaching Procedures of Waste PCBs Specimen

Specimen sampled from particles shredded by 8mm final fineness by coning and quartering method were shredded gradually to pass the 1mm final fineness for leaching experiment. Analytical grade commercial concentrated sulfuric acid, hydrogen peroxide (30%) and chalcanthite were used as received in experiments. Leaching experiments were carried out in a 200mL conical flask under magnetically stirring at room temperature (~23 ºC). Initial concentration of copper ion was adjusted by adding chalcanthite.

2.4 Shredding and Size Separation of Waste PCBs Specimen

Samples were sieved into different fraction by sieve shaker (Retsch, AS200) using a series standard sieve with a pore size of 8mm, 4mm, 2mm, 1mm, and 0.5mm. Specimen sampled from particles shredded by 8mmfinal fineness by coning and quartering method was separated into three different fractions by sieve shaker (amplitude = 1.0 mm/g, interval = 30 s, interval on, time=5min), i.e. fraction 4 mm< F1 <8mm, 2 mm<F2 < 4mm and F3 <2mm. The sample shredded by 4mm final fineness and fraction F3 were mixed and sieved into four different fractions: 2 mm< F4 <4mm, 1mm<F5 <2mm, 0.5mm<F6 < 1mm and F7 < 0.5mm. The shredding process is showed in Fig. 3. The sample F1, F2, F5, F6 and F7 were utilized to study effects of particle sizes on copper recovery. Copper content in sections F1, F2, F5, F6 and F7 is showed in Table 2. The results show that individual shredded fractions with different particle sizes have different copper content. The particles of leaching residues of sections F1, F2 and F5 were too large to be digested completely. Therefore all those residues were separately collected and then calcined in muffle furnace at 600 ºC for 2 h. The residues calcined were then digested to determine the copper content in residues. Leaching residues of sections F6 and F7 with fine particle sizes were digested directly. Specimens of shredded waste PCBs are not homogenous, especially for sampling specimen of large particles. Therefore, material balance method was used to deduce the total amount of copper in shredded waste PCBs specimens, expressed as copper extracted into leaching solution + copper in residues. The amount of recovered copper was expressed as the amount of copper extracted into leaching solution from original specimen, deduced as copper in final leaching solution – copper in initial leaching solution. Therefore, copper recovery could be expressed as the percentage of copper extracted into leaching solution from original specimen, which was calculated as the following formula:

$$\text{Copper recovery} = \frac{\text{Copper extracted into leaching solution}}{\text{Total copper in shredded specimens}} \times 100\%$$

3. Related Work

3.1 Effect of Different Leaching Conditions on Copper Leaching

Oishi *et al*. [17] and Alam *et al*. [18] carried out numerous experiments on recovery of copper from waste PCBs. The leaching system they used was ammoniacal sulfate or chloride solutions for its high leaching selectivity of copper. For there was a high impurity content (Sn 4.9%, Fe 3.4%, Pb 3.2%, etc.) in original materials. The leaching solution was purified with solvent extraction by LIX 26. The purified solution was then electrowon to obtain high purity metal copper. The samples used for there experiment contains about 25.3 (wt%) of copper and other heavy metals are pretty low (below 0.35%). The solvent extraction is not necessary to purify the leaching solution since other impurities of metals are much low, i.e. Sn, Fe, and Pb, etc. Therefore, sulfate acid leaching system could be suitable for waste PCBs samples used in this study to obtain cupric sulfate directly. Oxidants commonly used in sulphuric acid system for leaching copper from waste PCBs are air or hydrogen peroxide. Air is a promising oxidant for the consideration of economy. Hydrogen peroxide is not regenerable and its price is higher, however, the condition of experiment is easily controlled, and the leaching reaction is more effective comparing to other oxidant, i.e. air.

In the leaching system of sulfuric acid and hydrogen peroxide, the overall reaction for copper dissolution can be expressed by reaction follows Eq. (1): $Cu + H_2O_2 + H_2SO_4 = CuSO_4 + 2H_2O$ (1)

10 g of waste PCBs sample contains about 2.53 g metal copper. The copper theoretically needs 3.98 g concentrated sulphuric acid and 3.1mL hydrogen peroxide (30 wt%) to fully dissolve into aqueous phase according to Eq. (1). However, as the processes are designed, the raffinate from crystallization of cupric sulfate would be reused for copper leaching. In this regard, the influence of copper ion concentration on copper leaching kinetics was investigated. Copper recovery from waste PCBs specimen was carried out at room temperature (~23 ºC). There are many factors influencing the leaching rate or copper recovery such as sulfuric acid concentration, amount of hydrogen peroxide added, copper ion concentration, solid– liquid ratio, leaching temperature and time.

3.2 Effect of particle sizes on copper recovery

Some research works were done to recover metal from waste PCBs. Nevertheless, few studies were carried out on the effect of shredded particle size on copper leaching behavior. Yang *et al*. [19] performed experiments on bioleaching copper from waste PCBs and the particle size of the specimen was less than 0.5mm. Xiu and Zhang [14] recovered copper from waste PCBs by supercritical water oxidation combining with electrokinetic process and the materials used in his research was the fraction less than 0.1mm.

The size of the specimen Mecucci and Scott [15] used to recover copper, tin and lead by nitric acid was about 2.5mm2. The samples Oishi *et al*. [17] and Alam *et al*. [18] used for copper leaching were the fraction of 0.5– 3mm. Shredding waste PCBs was a high-energy consumption process and it was extremely hard to shred all the waste PCBs samples smaller than 0.5mm in practice.

In the present research, the influence of shredded particle size on copper leaching behavior was examined. Fig. 5 presents the copper recovery by leaching versus reaction time with different sample particle sizes. The copper recovery increases with the decrease in particle size. The accumulated copper recoveries for samples F1, F2 and F5 increase with the increase of leaching time, and copper recovery reaches 55.35%, 69.69% and 87.38% after 5 h, respectively. There is no difference on leaching recovery between sample F6 and F7. The leaching recovery for both samples reaches over 96% after 5 h.

The temperature was recorded by thermometer when leached samples with different particle sizes. The curve of temperature versus time is showed as Fig. 6. The results presented in Fig. 6 indicate that the leaching is an exothermic reaction. Wu *et al*. [20] carried out experiment of thermal decomposition of hydrogen per- oxide in the

presence of sulfuric acid. The T0 of hydrogen peroxide (20%) in 1N sulfuric acid is about 100 ºC corresponding value with pure water about 67 ºC. Although the max temperature occurs at 42 ºC in our experiment as shown in Fig. 6, it is possible that the max temperature exceed 67 ºC at a situation of more reactant. Hydrogen peroxide is more stable in diluted sulfuric acid, which makes the use of hydrogen peroxide more effective. The temperature change is evident during the leaching experiments. The maximum temperatures are observed at 140 min, 65 min, 52.5 min, 32.5 min, and 22.5 min for the samples of F1, F2, F5, F6 and F7, respectively. Copper exists in the middle layer of the PCBs. The small particle size is, the
more copper exposes in leaching solution, and the less mass transfer resistance in the middle layer for a certain amount of PCBs samples, the quicker the reaction occurs, and the more energy releases. The results are consistent with those shown in Fig. 5.

3.3 A reasonable shredding processes

A reasonable shredding process should be considered since it can extract copper efficiently when the particle size of waste PCBs is smaller than 1mm. 422.8 sample of about 3 cm×3 cm pieces of waste PCBs was shredded with cutting mill by 8mm final fineness. The crushed sample was separated into different fractions by sieve shaker and the weight of each fraction was measured. Then all the sections were collected and shredded by 4mmfinal fineness. Crushed sample was separated and the weight of each section was measured. The sample was shredded by 1mm and 0.5mm final fineness at the same way step by step.

4. Conclusion

1. The copper in powder of waste PCBs was recovered by leaching process in sulfuric acid using hydrogen peroxide as an oxidant. The optimum leaching condition for 10 g of waste PCBs at room temperature (~23 ºC) is proposed as following: 100mL of 15 (wt%) sulfuric acid, 10mL hydrogen peroxide addition, solid–liquid ratio of 1/10, initial concentration of copper ion 10 g/L and a leaching time of 3 h.
2. Copper was extracted efficiently by the leaching process when the pieces of waste PCBs were shredded smaller than 1mm. When particle sizes of waste PCBs decrease smaller than 0.5mm it did not increase the copper recovery by leaching. However, grinding of the PCBs smaller than 0.5mm significantly increased the energy consumption. Therefore, a suitable shredding pre-treatment process was proposed.
3. The leaching solution was concentrated to produce $CuSO_4 \cdot 5H_2O$. The mother liquor from crystallization was recycled to leach copper from waste PCBs powders. The leaching recovery reached 96% for 5 cycles.

5. References

1. Cui J, Forssberg E. Mechanical recycling of waste electric and electronic equipment: a review, J Hazard. Mater. 2003; 99:243-263.
2. Niu X, Li Y. Treatment of waste printed wire circuit boards in electronic waste for safe disposal, J Hazard. Mater. 2007; 145:410-416.
3. Shigeki K, Hitoshi O, Shigehisa E, Hiroyuki I, Pavel D. Recovering copper from electric cable wastes using a particle shape separation technique, Adv. Powder Technol. 1997; 8:103-111.
4. Zhang S, Forssberg E. Optimization of electrodynamic separation for metals recovery from electronic scrap, Conserv. Genet. Resour. 1998; 22:143-162.
5. Veit HM, Bernardes AM, Ferreira JZ, Tenório JAS, deF C. Malfatti, Recovery of copper from printed circuit boards scraps by mechanical processing and electrometallurgy, J Hazard. Mater. 2006; 137:1704-1709.
6. Veit HM, de Pereira CC, Bernardes AM. Using mechanical processing in recycling printed wiring boards, JOM 2007; 54:45-47.
7. Hennie V, Bob S. Mining discarded electronics, UNEP Ind. Environ. 1994; 17:7-11.
8. Chiang HL, Lin KH, Lai MH, Chen TC, Ma SY. Pyrolysis characteristics of integrated circuit boards at various particle sizes and temperatures, J. Hazard. Mater. 2007; 149:151-159.
9. Baba H. An efficient recovery of gold and other noble metals from electronic and other scraps, Conserv. Recycl. 1987; 10:247-252.
10. Macaskie LE, Creamer NJ, Essa AMM, Brown NL. A new approach for the recovery of precious metals from solution and from leachates derived from electronic scrap, Biotechnol. Bioeng. 2006; 96:631-639.
11. Vegliò F, Quaresima R, Fornari P, Ubaldini S. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning, Waste Manag. 2003; 23:245-252.
12. Andrews D, Raychaudhuri A, Frias C. Environmentally sound technologies for recycling secondary lead, J. Power Sources. 2000; 81:124-129.
13. Cui J, Zhang L. Metallurgical recovery of metals from electronic waste: a review, J Hazard. Mater. 2008; 158: 228-256.
14. Xiu FR, Zhang FS. Recovery of copper and lead from waste printed circuit boards by supercritical water oxidation combined with electrokinetic process, J. Hazard. Mater. 2009; 165:1002-1007.
15. Mecucci A, Scott K. Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards, J. Chem. Technol. Biotechnol. 2002; 77: 449-457.
16. Scott K, Chen X, Atkinson JW, Todd M, Armstrong RD. Electrochemical recycling of tin, lead and copper from stripping solution in the manufacture of circuit boards, Resour. Conserv. Recycl. 1997; 20:43-55.
17. Oishi T, Koyama K, Alam S, Tanaka M, Lee JC. Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions, Hydrometallurgy 2007; 89:82-88.
18. Alam MS, Tanaka M, Koyama K, Oishi T, Lee JC. Electrolyte purification in energy-saving monovalent copper electrowinning processes, Hydrometallurgy. 2007; 87:36-44.
19. Yang T, Xu Z, Wen JK, Yang LM. Factors influencing bioleaching copper from waste printed circuit boards by Acidithiobacillus ferrooxidans, Hydrometallurgy. 2009; 97:29-32.
20. Wu LK, Chen KY, Cheng SY, Lee BS, Shu CM. Thermal decomposition of hydrogen peroxide in the present of sulfuric acid, J Therm. Anal. Calorim. 2008; 93:115-120.