

## Selective leaching of valuable metals (Au, Ag etc.) from waste printed circuit boards (PCB)

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This study was carried out to recover gold, silver and other valuable metals from the printed circuit boards (PCB) of waste computers. PCB samples were crushed to under 1mm by a shredder and initially separated into 30% conducting and 70% non-conducting materials by an electrostatic separator. The conducting materials, which contained the valuable metals, were then used as the feed material for magnetic separation where it was found that 42% was magnetic and 58% non-magnetic. The non-magnetic materials contained 0.227mg/g Au and 0.697mg/g Ag. Further leaching of the non-magnetic component using 2.0M sulfuric acid and 0.2M hydrogen peroxide at 85°C extracted more than 95% copper, iron, zinc, nickel and aluminium. Au and Ag were not extracted in this solution, however, more than 95% of Au and 100% of Ag were selectively leached with a mixed solvent (0.2M ammonium thiosulfate, 0.02M copper sulfate, 0.4M ammonium hydroxide). Finally, the residues were reacted with a NaCl solution to leach out Pb while sulfuric acid was used to leach out Sn. Recoveries reached 95% and 98% in solution, respectively.

Keywords: printed circuit boards (PCB), Selective leaching, electrostatic separation, magnetic separation.

### Introduction

The development of the electronics industry has not only led to an increase in the production of new goods but also in the scrap generated and volume of waste materials after its lifetime. In particular, the rapid growth in information and telecommunications technology has seen an improvement in the capacity of computers but simultaneously, a decrease in the product's lifetime such that the volume of waste generated is increasing by 10% annually. Thus, the volume of waste computers, presently about 1.2 million, is predicted to increase by almost 100% to reach 2.2 million by the year 2005. Thus the appropriate treatment and disposal of these waste products poses a serious challenge [1,2].

As well as the many valuable metals contained in waste computers and other electronic scraps, there are toxic heavy metals which pose a serious environmental threat unless proper treatment of these wastes is carried out. Additionally, disposal means a depletion of raw materials. Thus, there has been much research to date on the possibility and practicability of recovering valuable metals from electronic scraps and in particular, from PCB of waste computers. Presently, the wet and dry methods of recovering metals are either being used, or in trial, in industry. In the case of the dry method, chlorine reaction, plasma, electric arc furnace etc. are being used for dissolution, and by chemical treatment, to recover metals. The advantage of this method is that all forms of scrap can be treated as the material properties pose no limit, however, it does add to atmospheric pollution, and the increase in slag results in a lower recovery of valuable metals. In particular, the recovery of Zn, Al, Pb and Sn is not possible with this method [3,4]. On the other hand, the leaching methods used to treat and recover valuable metals include cyanide, chlorine and NaOH leaching and more recently, the use of thiosulfate is being investigated [5-7]. Although the wet method produces less pollution and

greater recovery of the main components in scrap, this method cannot treat more complicated scrap materials and thus pre-treatment is necessary. Furthermore, the volume of the leaching solution is large and corrosion and toxicity is a problem. Thus, in recent years, electrochemical and biochemical recovery methods have also been investigated, however, to date, none have been economically feasible.

The aim of the present study was to develop a process for recovering valuable metals by a physical pre-treatment followed by chemical treatments to extract gold, silver and other valuable metals. In particular, the present process should overcome the problems encountered when recovering valuable metals from complex scrap materials and acidic and alkaline solutions. The recovery procedure should be simple such that application in industry is feasible.

### Experimental

#### Materials and Methods

The samples used in the experiment were printed circuit boards (PCB) weighed to a specified mass, sourced from various waste computers regardless of brand. Component analysis of the PCB used in this experiment found the metal component to be 30% by weight and this consisted of common metals (Cu 10.91%, Fe 7.7%, Ni 2.5%, Sn 3.9%, Pb 1.5%, Al 1.7% and Zn 1.1%) and precious metals (Au 0.00498% and Ag 0.00813%). Plastic materials were 30% by weight and consisted of more than 25% C-H-O polymers which include polyesters and phenolformaldehyde, less than 5% halogenated polymers (mainly PVC, traces of PTFE and polybromo compounds) and less than 1% nitrogen containing polymers, including nylon and polyurethanes. Also, metal oxides were 40% by weight and included 15% silica, 6% alkaline & alkaline earth oxides, 6% alumina and 13% other oxides [1].

In order to extract valuable metals, Cu, Fe, Zn, Ni and Sn were dissolved using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98% EP grade) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35% EP grade). Ammonium thiosulfate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 75% EP grade), copper sulfate (CuSO<sub>4</sub>, 99.5% EP grade) and ammonium hydroxide (NH<sub>2</sub>OH, 28% EP grade) were used in combination to selectively extract Au and Ag.

### Experimental set up and analysis procedure

Figure 1 shows a flow sheet for the recovery of valuable metals from PCB. The PCB were crushed by a specialised industrial shredder (Shredder, Sambo Milling) and sorted by size using a screen whereby only pieces less than 1mm passed through. Pieces greater than 1mm were crushed again to suitably smaller sized pieces. The crushed materials then passed through an air separator so as to separate and discard any plastic pieces [8]. It was then passed through an electrostatic separator (Dings Magnetic Group Co.) to separate the conducting and non-conducting components [9]. The conducting materials then passed through a magnetic separator (Dings Magnetic Group Co.) to be separated into magnetic and non-magnetic components. The non-magnetic materials were used as the source from which to extract valuable metals. The leaching reactions were carried out in three 1L flasks and pH and temperature controlled. Component analysis was carried out using AAS (Atomic Absorption Spectrometer – Spectra220, Varian, Australia) and ICP (Inductively Coupled Plasma-Atomic Emission Spectrometer- JY 38Plus, Jobin Yvon, France).

### Results and Discussion

#### Electrostatic separation of conducting and non-conducting materials

The crushed materials (average diameter of 0.85mm) were fed through the electrostatic separator which separated them into conducting and non-conducting components. A feed rate of 300g/hr and power supply between 500-3000W were the experimental conditions for electrostatic separation. Table 1 shows the separation of conducting and non-conducting materials at different power supply. Results showed that the efficiency of separation was greatest at 1500W. The yield of conducting material was 12% and included mainly metals. Non-conducting materials included plastics and the yield at 1500W was 72%. The yield of semi-conducting materials was 16%. Conducting and semi-conducting materials were then fed through a magnetic separator to divide into magnetic and non-magnetic components, while plastic materials remained with the non-conducting materials.

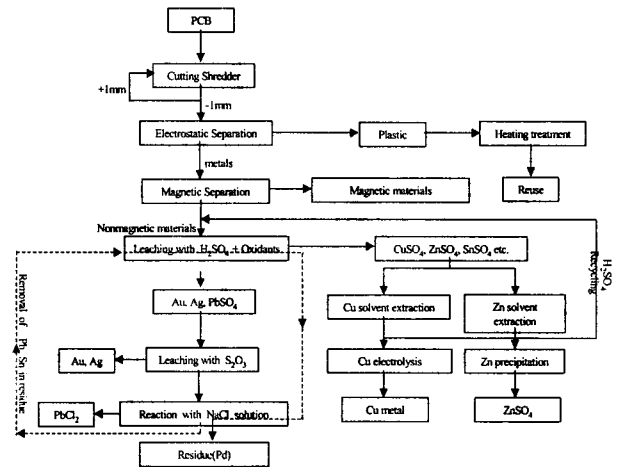


Figure 1. Flow sheet for the recovery of valuable metals from PCB

Table 1. Separation of conducting and non-conducting materials

	Electrostatic power (W)				
	500	1000	1500	2000	3000
Conductive materials (wt.%)	5.66	9.45	12.00	13.35	13.68
Middling (wt.%)	13.82	13.50	16.23	15.15	15.00
Non-Conductive materials (wt.%)	80.52	77.05	72.77	71.50	71.32

[Non-conductive materials]



[Conductive materials]



Figure 2. Conducting and non-conducting materials separated by an electrostatic separator

Table 2. Separation of magnetic and non-magnetic materials by a magnetic separator

Magnetic Power(gauss)	Magnetic (wt.%)	Non-magnetic (wt.%)
3000	28.35	71.65
6000	36.50	63.00
8000	41.61	58.39
12000	42.05	57.95

Table 3. Chemical analysis of materials after magnetic separation at 8000 gauss

	Au	Ag	Cu	Ni	Fe	Zn	Pb	Al	Sn
Assay (mg/g)	0.23	0.7	489	1	3.3	10	15	26	31
%	0.02	0.07	48.9	0.1	0.3	1.0	1.5	2.6	3.1

### Magnetic separation of magnetic and non-magnetic components

The conducting and semi-conducting materials from the first separation based on electrostatics were fed into the magnetic separator to be divided into magnetic and non-magnetic components. The experimental conditions for magnetic separation used a dry magnetic separator, feed rate of 1000g/hr and field strength between 3000-12000 gauss. Table 2 shows the separation of magnetic and non-magnetic materials by the magnetic separator.

The results of magnetic separation showed that at 8000 gauss, nearly all of the magnetic components were separated with a maximum yield of 42% while the yield of the non-magnetic component which included most of the valuable metals was 58%. Table 3 shows the chemical analysis of the non-magnetic materials after its separation. The amount of Au and Ag was 0.227mg/g and 0.697mg/g respectively, which represents high yields thereby fulfilling the aim of the experiment. The separated non-magnetic materials were then used for the next extraction process.

### Leaching of metals with sulfuric acid

Sulfuric acid was used as the leaching solvent to extract precious metals with hydrogen peroxide as the oxidation catalyst. Hydrogen peroxide added to sulfuric acid solution was used to dissolve Cu, Fe, Zn and Ni from the PCB and each metal component of the leached solution was separately eliminated. The materials which were not leached were filtered and leached in the next phase. Leaching with sulfuric acid was carried out at 65, 75 and 85°C respectively, and the sulfuric acid concentration ranged from 0.25M to 2.0M, with the concentration of hydrogen peroxide ranging from 0.05M to 0.2M. The feed rate was 10g/L and this was mixed at a speed of 350rpm. The optimal conditions for sulfuric acid leaching were

2.0M sulfuric acid, 0.2M hydrogen peroxide, and a reaction temperature of 85°C at which point Cu and Zn achieved 100% recovery within 8 hours, while Fe, Ni, and Al were 95% recovered in 12 hours. Figure 3 shows the dissolution of metals with sulfuric acid at 85°C, while Figure 4 shows the effect of concentration on the rate of dissolution. The chemical process describing the dissolution experiment for Cu, Fe, Zn and Ni is given in the following equations 1 and 2.

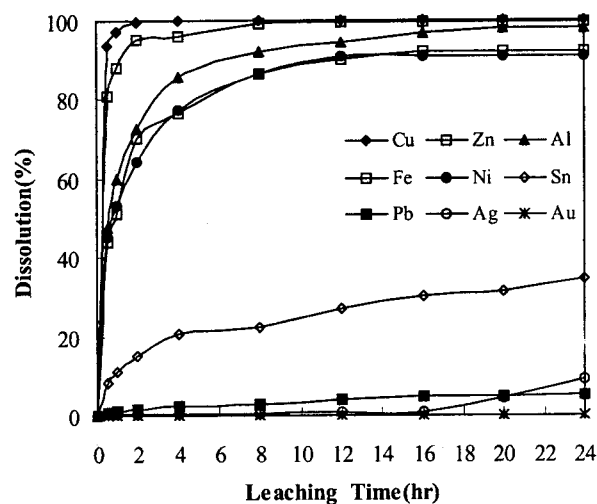
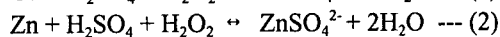
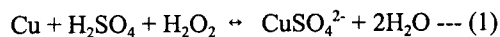


Figure 3. Dissolution of metals with sulfuric acid. (Temp. 85 °C, Sample:10g/L, 350rpm, H<sub>2</sub>SO<sub>4</sub>: 1.0M, H<sub>2</sub>O<sub>2</sub>: 0.2M)

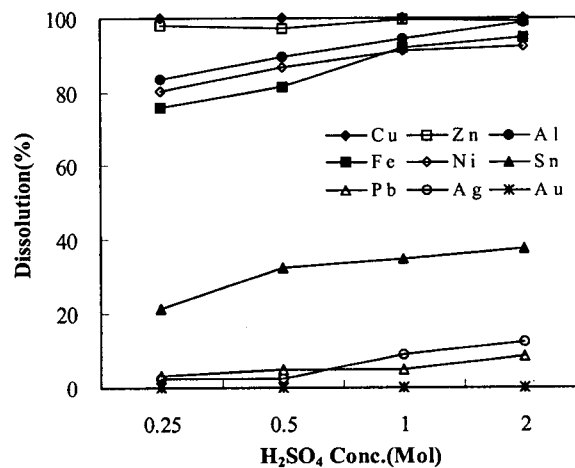


Figure 4. Dissolution of metals at different concentration of sulfuric acid. (Temp. 85 °C, Sample: 10g/L, H<sub>2</sub>O<sub>2</sub>: 0.2M, 350rpm, Reaction times: 24hr)

### Selective leaching of Au and Ag using a mixed solvent solution

After leaching using sulfuric acid, a mixed solvent of ammonium thiosulfate, copper sulfate and ammonium hydroxide was used to selectively leach Au and Ag. The concentrations being 0.2M, 0.02M and 0.4M respectively

at the reaction temperature of 40°C and feed rate of 5g/L. Figure 5 shows the extraction of Au and Ag at different solvent concentrations. Results show that Ag was fully extracted within 24 hours and 95% of Au extracted within 48 hours. Equations 3 and 4 describe the extraction reaction of Au and Ag, respectively, using a mixed solvent. The solution which contained a mixture of Au and Ag were then separated into its components.

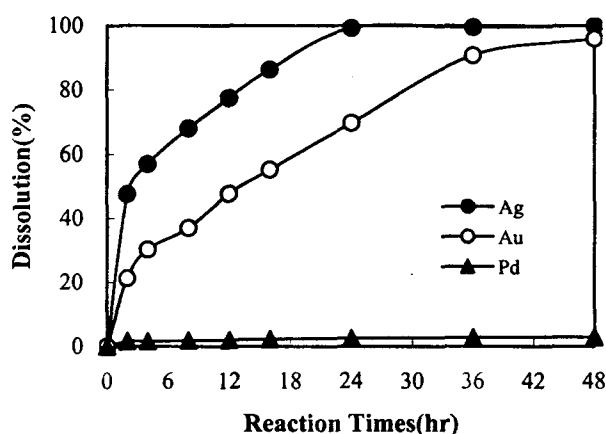
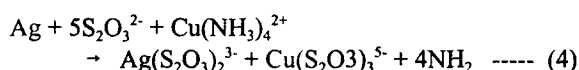
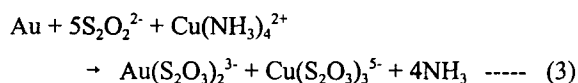


Figure 5. Dissolution of gold and silver by the mixed solvents. (Mixed solvents : 0.2M  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  + 0.02M  $\text{CuSO}_4$  + 0.4M  $\text{NH}_4\text{OH}$ , Temp. 40°C, pH 10, Sample 5g/L, 300rpm)

#### Selective leaching of Pb using NaCl solution

After leaching of Au and Ag using a mixed solvent, the remaining materials contained much Pb and Sn. Thus, in order to recover this efficiently, the solution properties of sodium chloride in an alkaline medium was investigated. The leaching conditions ranged from 0.5M-4M NaCl and the feed rate was 20g/L. When NaCl was used as the leaching solvent, the Pb in the remaining leached materials followed the chemical reaction shown in Equation 5 and the reaction proceeded rapidly. At the highest concentration of NaCl (2.0M) the reaction proceeded quite rapidly such that 95% reacted within 120 minutes. After the first leaching using NaCl, the remaining Pb was recycled back so as to achieve complete leaching (as shown in Fig 1) and the resulting  $\text{PbCl}_2$  solution was separated. On the other hand, the reactivity of Sn with NaCl was so low that sulfuric acid had to be added, which resulted in 98% extraction using 2.0M sulfuric acid at a reaction temperature of 85°C and a feed rate of 20g/L. Figure 6 shows the leaching characteristics of Pb and Sn with NaCl solution and Figure 7 shows the leaching of Pb and Sn with sulfuric acid.

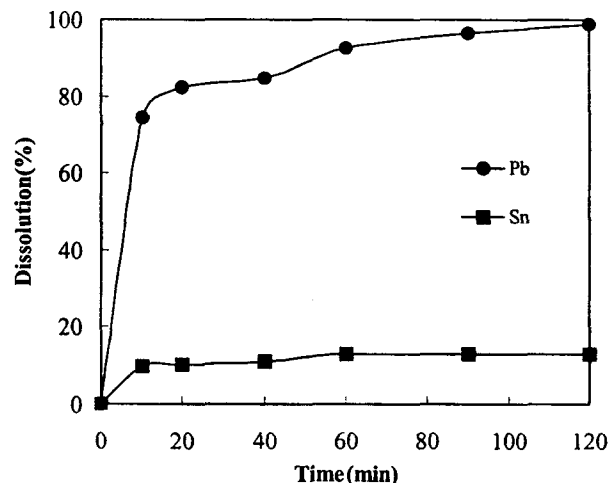


Figure 6. The dissolution of Pb and Sn by NaCl. (NaCl: 2.0M, Temp. 27°C, Sample: 20g/L)

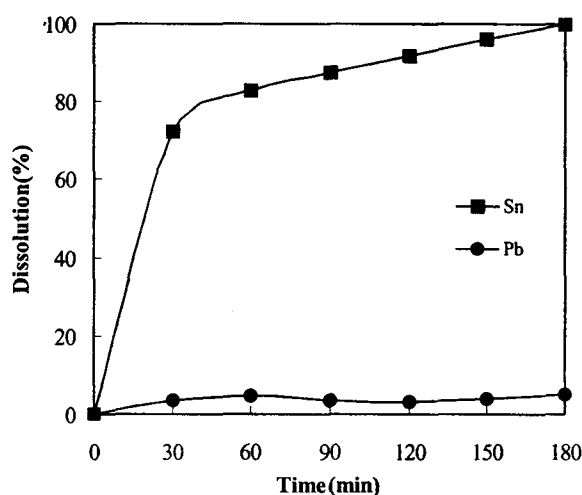


Fig. 7. The dissolution of Sn and Pb by  $\text{H}_2\text{SO}_4$ . ( $\text{H}_2\text{SO}_4$ : 2.0M, Temp. 85°C, Sample: 20g/L)

#### Conclusion

The present study developed a leaching procedure for the recovery of valuable metals from PCB via physical pretreatment and chemical treatment, and the results at each stage are as follows.

1. Electrostatic separation of conducting and non-conducting materials was most efficient at 1500W. The yield of metals included in the conducting component was 12%, while the non-conducting component containing mostly plastic materials was 72%, with the remaining semi-conducting component being 16%.

2. The results of the magnetic separation showed that optimal separation occurred at 8000 gauss where magnetic component was 42% and the non-magnetic component, containing most of the valuable metals, was 58%. Of the recovered non-magnetic component after magnetic separation, the yield of Au and Ag was quite high at 0.227mg/g and 0.697mg/g respectively.

3. In the leaching reaction using 2.0M sulfuric acid and 0.2M hydrogen peroxide, at 85°C, 100% of Cu and Zn were leached out within 8 hours and 95% of Fe, Ni and Al within 12 hours.

4. In the case of leaching with the mixed solvent solution of 0.2M ammonium sulfate, 0.02M copper sulfate and 0.4M ammonium hydroxide, at a reaction temperature of 40°C, pH 10, and feed rate of 5g/L, 100% Ag was leached out within 24 hours while 95% of Au was leached out in 48 hours.

5. When Pb and Sn compounds were reacted with 2.0M NaCl, over 95% of Pb was recovered and the remaining Pb was recovered as shown in Fig 1 by repeat treatments to completely leach out the metal, while over 98% of Sn was leached out using 2.0M sulfuric acid at 85°C with a feed rate of 20g/L.

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