

Recovery of Metal Values from Useless Printed Circuit Boards

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Abstract

This study provides a hydrometallurgical method to recover copper, lead, tin and gold from useless printed circuit boards. Metals in the board were leached with different mineral acids. Gold, if present, was first recovered by filtering from the acid solution, washed and polished. Metal salts went into the acidic leachant were separately recovered, washed and dried. These were thermally reduced using carbon to obtain reduced metals. The polymeric base material was found safe for feasible for reuse in the manufacture of new printed circuit boards. Parameters affecting the recovery factor were studied. Results obtained showed that nitric acid was more effective compared to sulfuric or hydrochloric acid. The extent of metals dissolution increases with increase in acid molarity, stoichiometric ratio, temperature and time of leaching. With sulfuric acid, copper dissolved in > 6 M solution at > 75°C whereas lead and tin did not. With nitric acid, all metals dissolved on hot conditions whereby tin deposited upon cooling as basic oxide. Lead was separated from copper as chloride. Copper was separated as solid sulfide. The recovered compounds were reduced with hydrogen gas or by carbon at temperatures up to 1000°C. A separation factor of 98.4-96.2% was achieved.

Introduction

The printed circuit boards found poor or failed to meet the technical specifications are wasted. As an alternative to off-site disposal, printed circuit boards can be handled and processed to recover the metal value used to re-manufacture the boards. Old electronic equipment may be disassembled and the usable parts salvaged.

Lidia B. S., *et al.*, [1] dissolved Cu–Co–Fe alloys in ammoniacal solution. No iron was found in the solution and the residual slimes contained iron and cobalt. Mecucci, M. and Scott, K. [2] recovered copper, lead and tin from scrap printed circuit boards (PCBs) using a combination of leaching and electrodeposition. A simple aqueous 1-6 mol/dm³ nitric acid demonstrated the potential for selective extraction of copper and lead from the PCBs. Precipitation of tin as H₂SnO₃ (metastannic acid) occurred at acid concentration above 4 M/dm³. Chi, Jung Oh *et al.*,

[3] and Oh, C.J., *et al.*, [4] studied the recovery of valuable metals from the printed circuit boards (PCBs) of waste computers. Samples were crushed to smaller than 1 mm grains by a shredder. Grains were separated into 30% conducting material by an electrostatic separator followed by magnetic separation. Leaching of the nonmagnetic component using 2 M H₂SO₄ acid and 0.2 M H₂O₂ at 85°C for 12 hrs extracted > 95% extraction of Cu, Fe, Zn, Ni, and Al. Gold and silver were extracted at 40°C using a leaching solution of 0.2 M (NH₄)₂S₂O₃, 0.02 M CuSO₄ and 0.4 M NH₄OH. The extent of recovery amounts to > 95% with gold 100% with silver. The residue was next reacted with 2 M NaCl solution to leach out lead within 2 hrs at room temperature. Rajko Vraar *et al.*, [5] leached copper from finely grained samples of copper (I) sulfide by H₂SO₄/NaNO₃ solution. It was found that the leaching rate was chemically controlled. The leaching reaction was first order with respect to the concentration of NaNO₃ and second order with respect to the concentration of sulfuric acid.

Zhao, Y., *et al.* [6] recovered copper from waste printed circuit boards by hummer mill, pneumatic

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separator and an electrostatic separator. Around 90% copper recovery was achieved using a combination of electrostatic separation and pneumatic separation. Mubarak, A.A., *et al.* [7] studied the rate of copper removal from waste solutions by cementation technique using a perforated reciprocating zinc disc. Abdel Basir, S. [8] suggested the mechanism for recovering of cupric chloride salts from spent etching solution used in printing circuits industry. Maximum extent of extraction amounted to 99%. Man-Seung Lee [9] recovered valuable metals from spent nitric etching solutions of printed circuit boards, by solvent extraction, stripping, electro-winning, precipitation and cementation experiments. Bingol, D., [10] studied the kinetic of sulfuric acid leaching of oxidized copper ore, and primarily malachite. The effects of leaching time, stirring speed, acid-concentration, solid to liquid ratio, reaction temperature, and particle size of the ore were investigated. The copper recovery was nearly 94% at 25°C and 99% at 80°C after 18 min leaching. Microbial recovery of copper from printed circuit boards of waste computer was also studied by Choi *et al.* [11] using *Acidithiobacillus* bacterium. The extent of recovery increased with addition of ferrous ions and a complexing agent such as citric acid.

Kékesi, *et al.*, [12] claimed a hydrometallurgical method to extract tin from tinned plates served for preparing steel scrap and producing secondary tin. The mechanism of the process was investigated to compare the efficiency of chemical and electrochemical removal of tin coatings. Increasing sodium hydroxide concentration (< 0.1 M) had a negative effect on tin dissolution because of the reduced oxygen diffusivity.

Barakat, M. A., [13] found that lead, tin and indium were successfully recovered from alloy wire scrap containing these metals by acid/alkali leaching. The scrap material was leached with hot HCl-HNO₃ acid solution. Upon cooling down to 10°C, 71.8% of lead initially present separated as lead chloride PbCl₂. Tin was recovered from the acidic solution as hydrated tin oxide by using Na(OH) solution. Lead & tin having purities of $> 99\%$, 99.7% were obtained. The recovery processes were favored at a temperature of $\leq 45^\circ\text{C}$ for maximum duration of 8 hrs at a pH ≤ 2.4 . M. The recovery extent of these metals was found to be 94.7 and 99.5% respectively.

Kinoshita, T. [14] found that nitric acid showed a great possibility of recovering gold flakes. The acid leaching performance was evaluated in terms of the

acid concentration, temperature, time and solid:liquid ratio. Gold flakes were detached spontaneously from the boards and recovered easily in high yield with excellent purity. Rabah, M.A., [15] reported that recovery of copper and lead from secondary resources was favored with concentrated acid and at high temperatures.

The objectives of this work are to recover valuable metals and some valuable salts from spent printed circuit boards without deforming the base material. Parameters affecting the extent of recovery, total efficiency of the suggested method were investigated. These include molarity of the acidic leachant, acid stoichiometric ratio, temperature, time.

Experimental

Materials

The spent printed circuit board sample was obtained from Banha Co. for electronic industries (KATRON), Banha, Egypt. The sample was structured from polymeric substrate plated with copper laminate boards having different thickness. Some boards were plated with lead, tin and in some cases with gold strips. The sample was de-dusted by compressed air and stored in clean polyethylene bags.

Chemicals and Water

The chemicals used for analysis were of technical pure grade. Sulfuric, hydrochloric and nitric acids were used for leaching the metals of concern. Hydrogen sulfide was used to precipitate copper. Ammonia solution, sodium hydroxide was used for pH control. Active charcoal was used for thermal reduction of the metal oxides. Doubly distilled water was used for chemical analysis. Mono-distilled water was used for the leaching experiments. Washing of glassware was performed using chromic acid, mono-distilled water, ethylated doubly distilled water and finally with ethyl alcohol. Tap water was used for other purposes.

Measurements of the Physico-chemical Properties

Analysis of copper, tin, lead, gold and intermediate compounds were carried out by atomic absorption spectrophotometer type Unicam 1000 SP and with the help of an emission spectrophotometer type 3460-880 ARL, Seuces.

Determination of the recovery extent (Σ) was calculated from the relation: $\Sigma = (wt_{rec}/wt_{sm}) \times 100$. Where wt_{rec} and wt_{sm} are the weight of the metal and alloy recovered or in the input material respectively.

Determination of the recovery efficiency (ξ_{rec}) was calculated from the relation: $\xi_{rec} = (wt_{ex}/wt_{rec} + wt_{sl}) \times 100$. Where wt_{ex} , wt_{rec} and wt_{sl} are the weight of the metal concerned in the extract, recovered and in the slag respectively.

Description of the Suggested Method

Figure 1 shows the process flow sheet of the suggested method. The PCB types (≈ 50 kg) were collectively washed with tap water, dried in the ambient conditions for 2 days. The following experimental steps were then executed:

- Visual inspection to get rid of foreign contaminants.
- Classification of the printed circuits scrap into:
 - PCBs containing copper only.
 - PCBs s containing copper, tin and lead.
 - PCBs containing copper and Gold.

Part of the washed sample was fired at temperatures up to 850°C in normal atmosphere to achieve complete burning off of the polymeric material. The

ash was dissolved in mineral acids to recover the respective metals.

Other part of the un-burnt PCBs was leached in hot solution of the respective acid having different molarity and filtered. The hot filtrate was cooled to $\approx 15^\circ\text{C}$ to help deposition of meta-stannic acid (basic tin oxide). Lead and copper ions were separately recovered on cold by chemical precipitation as chloride and sulfide respectively.

Gold strips in the PCBs sample remained un-dissolved. It was filtered, fluxed with boiling sodium persulfate in concentrated sulfuric acid for polishing. Polished gold strips were then washed with water and ethyl alcohol.

Table 1 shows the conditions applied throughout the experimental work.

The Leaching Experiments

Leaching experiments were carried out using a glass reactor. The equipment is 0.5 L round-bottom flask having three openings serving for a separating funnel, a condenser assembly and a mechanical stirrer. Heating was performed using thermo-stated heating mantel fitted with an automatic heat relay.

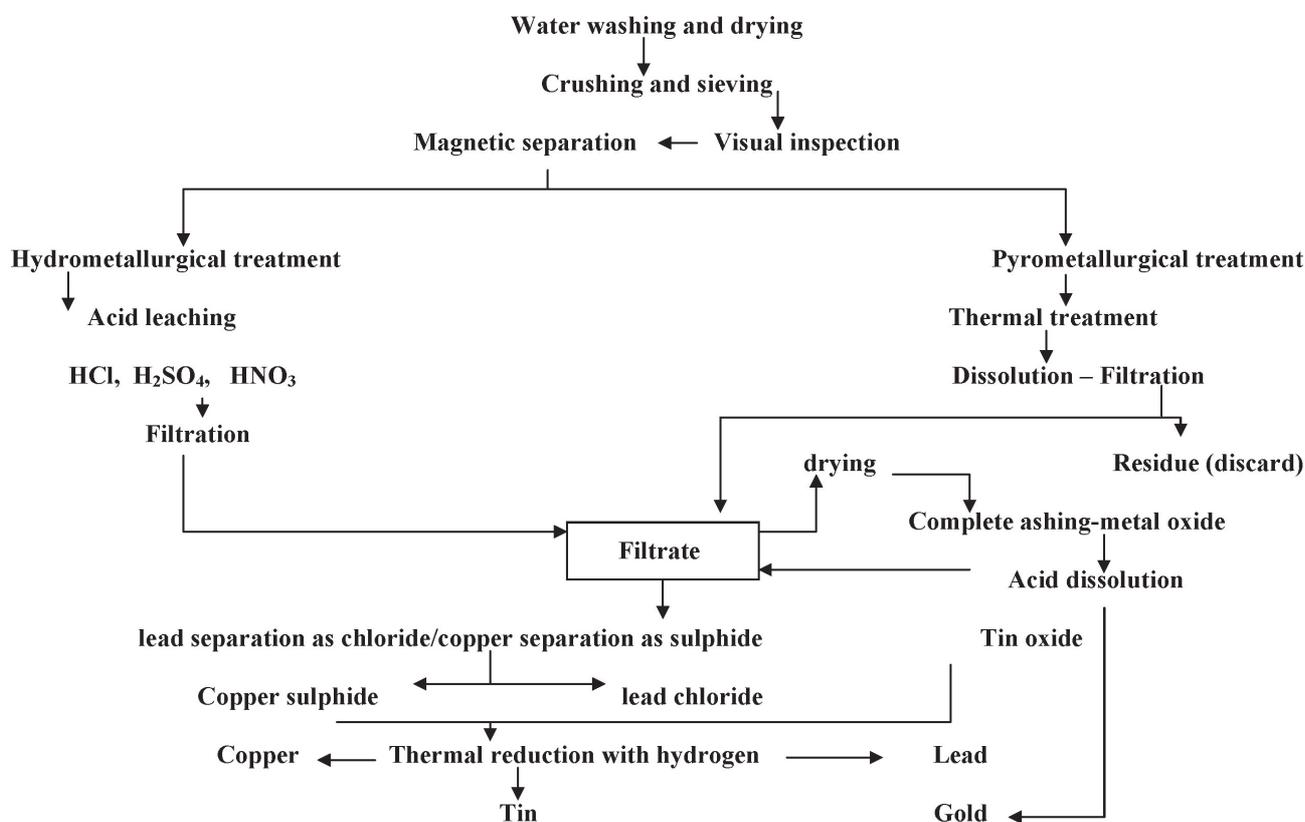


Fig. 1. A conceptual flow sheet for the recovery of metals and some valuable salts from spent printed circuit boards.

Table 1
Details of the experimental conditions

Experiments	Applied parameters conditions				
	Temperature		Duration time, min	Conc. M	Stirring
	Min	Max			
Metals dissolution (Mineral acids)	25	100	5-180	1-10	+
Gold separation	50	75	30	4	+
Refining	boiling		30	Conc.	-
Pyrometallurgy	750°C for firing		240		
	1000°C for reduction		30	-	-

Pyro-metallurgical Treatment

PCB samples were heated at different temperatures up to 850°C for different periods up to 3 hours in a porcelain crucible. Product of firing (ash and metal oxides) was dissolved in nitric acid and analyzed. The separated metal salts were then washed and dried. Free metals were obtained by thermal reduction using active carbon powder in a tube furnace maintained at the required temperature.

Results

Plates 1, 2a and 2b show photographs of some spent printed board samples used in this study. Table 2 shows the composition of these boards. It can be seen that three types were available. The common metal is copper. Tin and lead constitute the soldering alloy. The third type contains gold strips. Table 3 shows the composition of typical PCBs. The mass percentage of copper ranged from 15% for one-sided boards and increased to 25% for double sided type.

Tin and lead constitute 2-3% by weight each. Gold mass was 0.5-1.5%.

The Pyro-hydrometallurgical Treatment

Effect of Temperature

Figure 2 shows the effect of heating temperature on the weight loss of the spent printed circuit board sample. It can be seen that during the early period of the heating process, the sample exhibits a non-significant weight loss (about 5% at 300°C). With further increase in heating temperature up to 600°C, the extent of weight loss drastically increases to 60%. Within the temperature range 600-900°C a slight increase in weight loss takes place and a constant value amounting to 65% was reached at > 850°C.

Ash Dissolution in Sulfuric Acid

Figure 3 shows the extent of dissolution of the ash (left behind burning) in sulfuric acid having different molarity at room temperature. It is seen that

Table 2
The composition of the spent PCBs

PCB designation type	Color of the sample		Metals in the PCBs				
	Base plate	Coating	Base layer	Plated layer			
				Cu	Sn	Pb	Ag
Raw board	Conventional	Always green	Cu	+	+	+	
a	Dark, brown		Cu	+	+	+	
b	Yellow plate		Cu		+	+	
c	White plate		Cu		+	+	+

Table 3
Metal composition of typical PCBs

Metal	Percent mass	
	Single side PCB	Double side PCB
Cooper	15	25
Lead	2	3
Tin	2	3
Gold*	0.5	1.5
Base material	80.3	67.5

*In type b

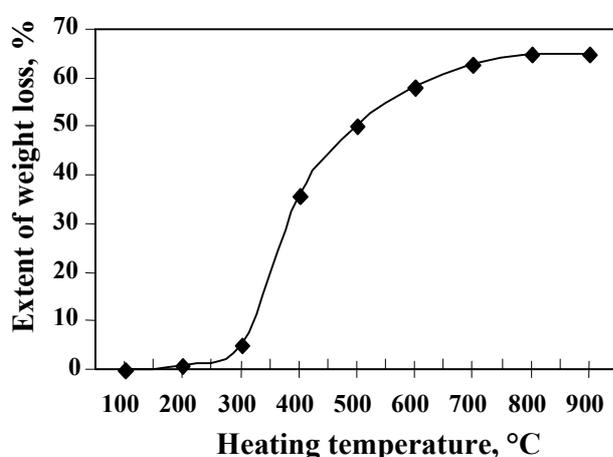


Fig. 2. The effect of heating temperature in air on the extent of weight loss % of printed circuit boards samples.

dissolution of the ash increases gradually with increase in time approaching a constant value after 50 minutes. Dissolution takes place more readily with concentrated sulfuric acid (> 3 M) as compared to the diluted acid solution (< 3 M). Maximum dissolved weight percentage amounted to 14.33% with 3 M sulfuric acid at room temperature. Figure 4 shows the extent of acid leaching of the ash using hot sulfuric acid (4 M) at 100°C as affected by the dissolution period up to 60 minutes. It can be seen that the dissolution extent increases with increase in time. Complete dissolution of tin and copper takes place at ≥ 50 minutes. It is also seen that lead showed a lower dissolution extent amounting to 4%.

Ash Dissolution in Nitric Acid

Figure 5 shows the effect of nitric acid concentration on the extent of dissolution of copper, tin and lead present in the PCB-ash at 100°C. It is seen that the dissolution extent gradually increases with the

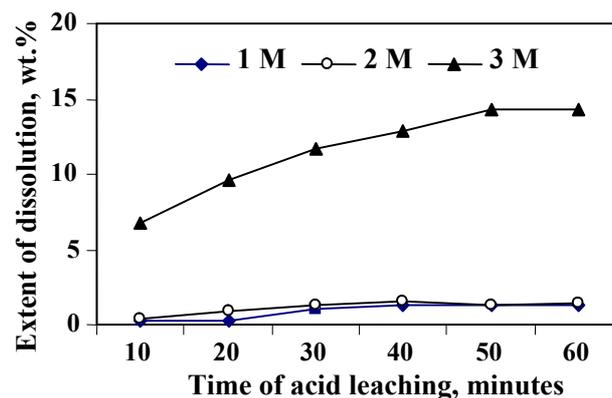


Fig. 3. Effect of time on extent of ash dissolution in sulfuric acid at room temperature.

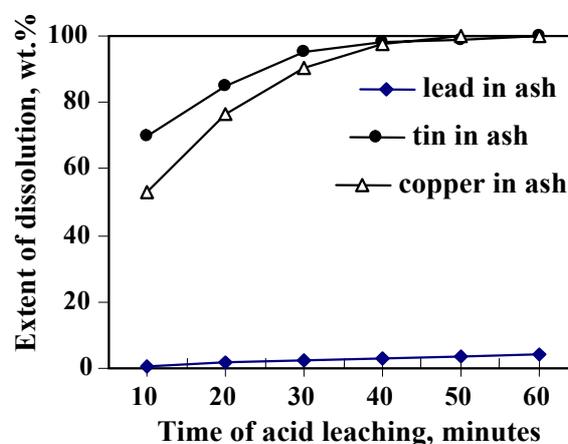


Fig. 4. Effect of time on the extent of ash dissolution in hot 4 M sulfuric acid at 100°C.

corresponding increase in time approaching complete dissolution after 40 minutes with copper, 50 minutes with tin and 60 minutes with lead. It is worthy to note that after cooling the solution to room temperature, tin nitrate so obtained precipitates as meta-stannic acid (basic tin oxide). Copper nitrate and lead nitrate are kept dissolved in the cold solution.

Hydrometallurgical Treatment without Thermal Pretreatment

Dissolution of Lead and Tin in 2 M Nitric Acid

Figure 6 shows that about 50% of lead dissolved in 2 M nitric acid at 20°C and after 60 minutes. The metal dissolved more readily at higher temperature (100°C) whereby complete dissolution takes place after ≥ 50 minutes. Figure 7 illustrates the extent of tin dissolution as a function of nitric acid concentration and for temperatures up to 100°C. It can be seen

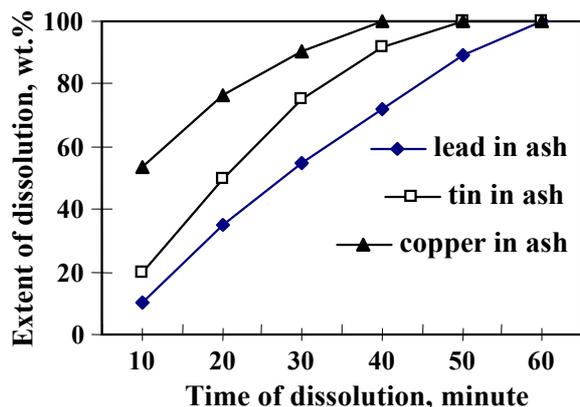


Fig. 5. Effect of time on the extent of dissolution of PCB ash in 4 M nitric acid at 100°C.

that tin dissolution increases with increase in nitric acid concentration. The acid attack becomes very pronounced at 100°C and becomes less aggressive at lower temperatures.

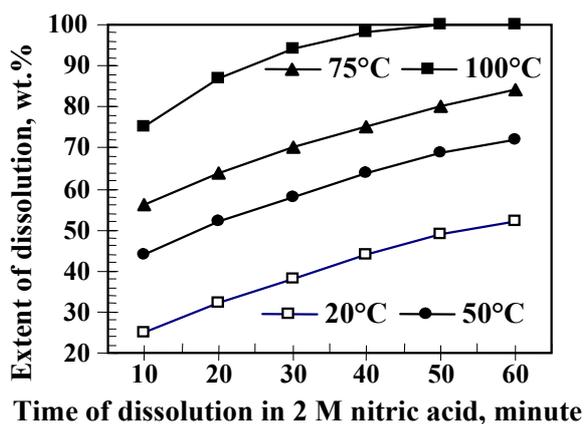


Fig. 6. The effect of time and temperature on the dissolution extent of lead in 2 M nitric acid.

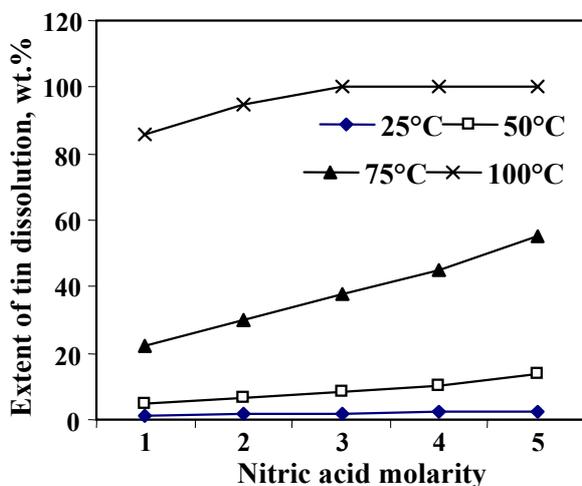


Fig. 7. Effect of nitric acid molarity on the extent of tin dissolution at temperatures up to 100°C.

Dissolution of Lead and Tin in Nitric Acid Having Different Concentrations

Figure 8 shows the effect of temperature on the extent of tin dissolution in nitric acid having different molarities up to 5 M and for 60 minutes. It can be seen that the extent of dissolution of tin increases slowly with increase in both temperature up to 50°C and acid molarity. However, tin dissolution increases drastically with the corresponding increase in temperature up to 100°C attaining complete dissolution extent at 100°C with nitric acid having ≥ 2 M concentration. Figure 9 shows the effect of cooling the temperature of the hot leachant on the extent of tin oxide deposition. It can be seen that the critical temperature for tin oxide separation was $< 50^\circ\text{C}$.

Dissolution of Copper in Nitric Acid

Figure 10 shows the extent of copper dissolution in 2 M nitric acid. Experiments were carried out at

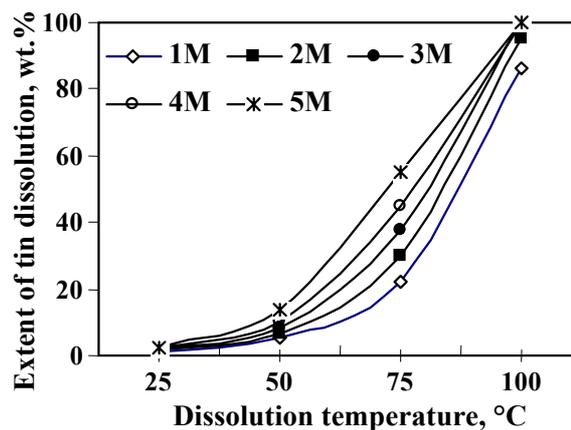


Fig. 8. Effect of temperature on the extent of tin recovery in nitric acid.

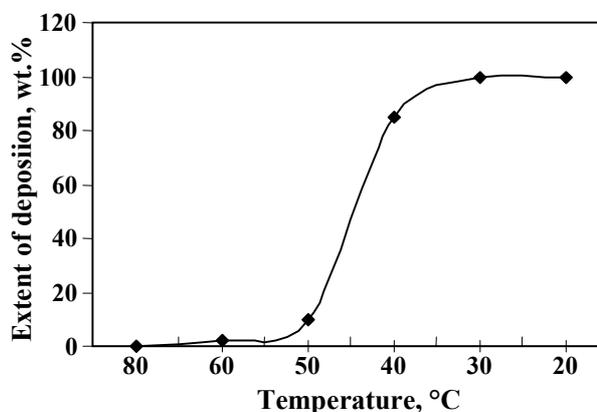


Fig. 9. Effect of temperature on the extent of deposition of tin oxide.

temperatures up to 75°C and for periods up to 100 minutes. It is seen that, for one and the same time, copper dissolved more readily with increase in temperature. Complete dissolution of copper takes place after 60 minutes when leaching process was conducted at 75°C. The same extent of dissolution was matched after 90 minutes when such process was carried out at lower temperature ($\leq 50^\circ\text{C}$).

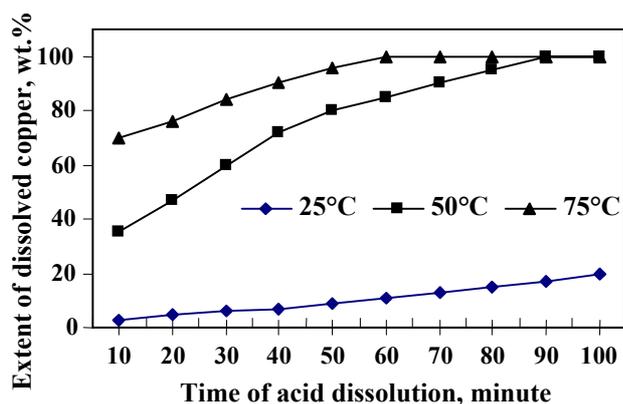


Fig. 10. Effect of time on the extent of copper dissolution in 2 M nitric acid at temperatures up to 75°C.

Thermal Reduction of Copper Oxide

Figure 11 shows the effect of temperature on the extent of reducing copper oxide using carbon in inert atmosphere. It is seen that the reduction extent begins at $\geq 600^\circ\text{C}$ (15% reducibility) and increases gradually with temperature rise. Complete reduction (100% reducibility corresponding to 33% weight loss) was matched at 1000°C. Figure 12 shows the Arrhenius plot for the reduction process. The calculated ΔE value amounts to 51.500 kJ/mol.

Discussion

Printed circuit board (PCB) is made of a base plate made of acrylic polymer plated with copper, solder alloy and may be fitted with gold strips. Boards failed to meet the technical specifications are wasted as scrap. Recycle of the useless PCBs would help to conserve the national resources and to benefit the metal values of this waste. The method applied in this study includes two routes. The first way was the pyrometallurgical technique that involves burning the PCBs to complete burn off. The ash left behind this step contains the oxides of all the metals available. The oxides are leached in acid solution to yield the respective salts.

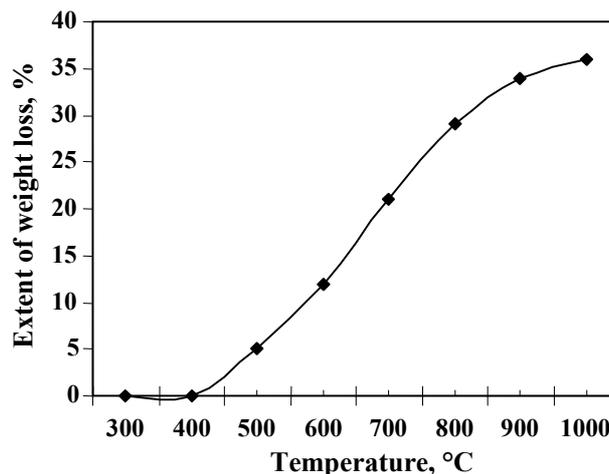


Fig. 11. Effect of temperature on the extent of reducing copper oxide using carbon in inert atmosphere.

Results given in Figure 2 show a slight weight loss taking place during burning the PCB at low temperature ($\leq 300^\circ\text{C}$). This criterion can be ascribed to volatilization of organic gases having low boiling point that generated during the thermal decomposition process of the acrylic polymer. At higher temperatures, complete decomposition of the polymer is gradually approached. Gaseous products altogether with carbon particles expelled during this phase. At $> 600^\circ\text{C}$, carbon is burnt out in presence of atmospheric oxygen to carbon dioxide. The horizontal plateau of the curve explains complete burning off of the polymer associating oxidation of the metals. However, pyrometallurgical technique has many disadvantages in the premise that thermal decomposition products of the polymer are highly polluting and carcinogenic. Dense carbon fumes also purged out.

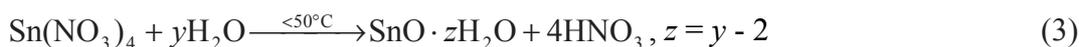
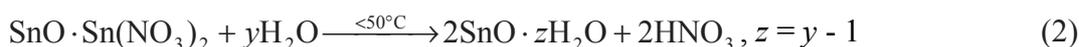
The other way to recover the PCBs was the hydrometallurgical route that involves leaching the metals in mineral acids. Sulfuric acid was tested and was found aggressive to the base material when high concentration $> 6\text{ M}$ was used. Concentrated sulfuric acid solution $> 6\text{ M}$ attacks the base material. The dissolved polymer inhibits the filtration efficiency and rate of the metal ions went into the solution. Sulfuric acid reacts with the solder alloy to produce water-insoluble lead sulfate. The later compound establishes a barrier that masks the reacting species and the leaching process stops. Sulfuric acid is therefore not recommended to leach metal values from the PCB. Tin sulfate is very soluble in cold water and decomposes in hot conditions to basic oxide. Hydrochloric acid was found similar to sulfuric acid as the formed lead chloride is also insoluble in cold

water. Nitric acid on the other hand was found most suitable to leach the metal values from the spent PCBs for the following reasons.

1. It does not affect the polymer base material in cold or hot conditions.

2. It reacts with all the metals except gold to form nitrate salts especially in moderate hot conditions.

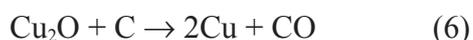
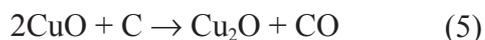
3. Upon cooling, only tin nitrate: $\text{Sn}(\text{NO}_3)_2 \cdot 20\text{H}_2\text{O}$ or $\text{Sn}(\text{NO}_3)_4$ decomposes to insoluble meta-stannic acid or basic tin oxide according to:



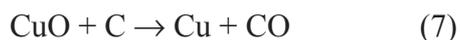
and the overall reaction may proceed as:



Results given in Figure 9 illustrates that tin nitrate starts decomposing at temperatures $< 50^\circ\text{C}$ and such decomposition seems to be time independent. Results given in Figures 3 through 8 are in agreement with Law of mass action. Increasing the acid concentration enhances the acid/metal reaction to the forward direction to produce the respective salt. Increasing the temperature also favors acid attack via supplying the system with the energy sufficient to accomplish the reactions in a shorter time. This model also supports the results obtained for leaching copper from the PCB as shown in Fig. 10. Reduction of copper oxide using carbon as graphically represented by the curve in Fig. 11 shows that the reduction process may proceed in a multi-step sequence. Copper oxide (CuO) is partially reduced to cuprous oxide Cu_2O and finally to copper metal.



The overall reaction is:



The activation energy of the overall reaction was calculated from the Arrhenius plot (Fig. 12). The ΔE value amounts to 51.500 kJ/mol. This value confirms carbon monoxide formation according to eq. 7 rather than formation of carbon dioxide. Results are in a good agreement with the computed value for from the heat of formation tables, 51.581 kJ/mol given by

Weast, R., *et al.*, [16]. It is worthy to note that the separation factor (recovery extent) of the overall steps of the tested method amounts to 98.4 with copper and 96.2 with tin. Gold was separated at a separation factor as high as 100%. Other salts of value can be prepared from the nitrate salts so obtained after leaching with nitric acid by the following options: chemical precipitation to hydroxide using ammonia solution, thermal decomposition to oxide, addition of other salt solution. The product of any of these options can be regarded as a starting compound to prepare the required chemicals. Organic salts of oxalate, acetate and stearate of copper and lead were successfully prepared from their respective hydroxide. The conditions, preparation cost and quality of these compounds will be published elsewhere.

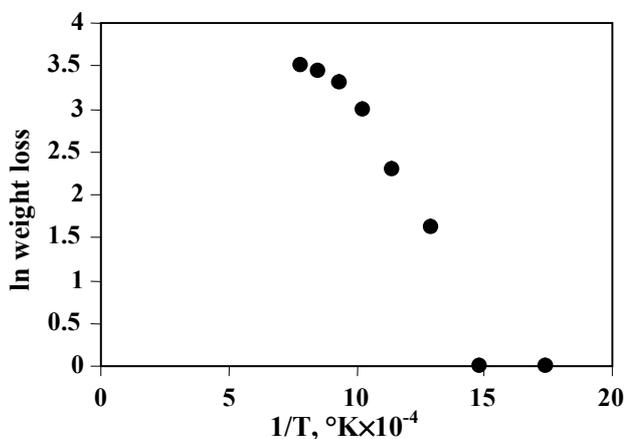


Fig. 12. The Arrhenius plot of the reduction process of copper oxide using carbon.

Conclusions

The output conclusion of this work highly recommends the hydrometallurgical treatment of the use-less printed circuit boards based on the following reasons. The method is simple, safe, friendly and non polluting. It also conserves the mineral resources, alleviates waste materials and saves money. The extent of recovery is high and the products are technically pure. The products are pure. The base boards after removal of metals were found clean, smooth surface and can be re-used for the manufacture of new circuit boards.

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Received 13 February 2007.