Recovery of copper and gold from waste mobile phones' printed circuit boards using the delamination pre-processing and a simple hydrometallurgical route

S. Fashu[1], A. Mukuya[2], and M. Mkhize[1]

[1]University of KwaZulu Natal, South Africa
[2]Harare Institute of Technology, Harare

In this paper we developed a simple and environmentally-friendly method to recover copper and gold from end of life mobile phones' printed circuit boards (PCBs) through PCBs' delamination, leaching of separated metallic layers (using a weak acid), purification and cementation rather than conventional comminution processes commonly employed in recycling. Dismantling of electronic components was first performed with a weak acid of 0.8 M H_2SO_4 at room temperature to prevent leaching of copper from the PCBs. Then dimethylacetamide organic solvent was used to delaminate small pieces of circuit boards into metallic layers before leaching copper for 1 h using 0.4 M $CuSO_4$ + 4 M NaCl + 0.5 M H_2SO_4 as an environmentally-friendly weak acid. Gold from the remaining solid residue was then leached using 3 M H_2SO_4 + 3 M NaBr at 70°C. Copper was first purified from impurities by cementation using zinc powder before recovering pure copper from the solution by cementation using iron powder. Gold solution was purified from the gold solution using solvent extraction before recovering pure gold by cementation with copper powder. The results show that full liberation of the metallic layers from the PCB structure occurred at 16°C and 135 min. The concentration of copper and gold content in delaminated metallic layers is 95.8 wt%Cu and 0.052 wtAu compared to 44% wtCu and 0.0011 wt%Au in comminuted ore. Thus, the delamination approach using an organic solvent produces higher recoveries compared to comminution of the whole circuit board. Complete dissolution of copper and gold and effective separation from impurities was achieved using leaching, solvent extraction and cementation.

INTRODUCTION

The generation of e-waste in South Africa continues to increase, fuelled by the improvements in technological advances and high demand. There are environmental and health issues associated with disposal of e-waste such that efficient management of urban and industrial waste is required. The world is generating about 62 million tonnes of e-waste annually (Balde *et al.*, 2021, Xia and Ghahreman, 2024) (Figure 2) and from this amount about 45 0000 tonnes is contributed by South Africa (Ichikowitz and Hattingh, 2020; Asante *et al.*, 2020). Printed circuit boards (PCBs) contain more metals compared to virgin ores; for example the grade of copper in e-waste is approximately 20 wt% compared to about 0.5 wt% from mining ores (Pietrelli *et al.*, 2019). This calls for sustainable recycling approaches to recover valuable metals in an environmentally-friendly manner.

It has been demonstrated that recovery of metals from e-waste through the hydrometallurgical route is favourable compared to using pyrometallurgy (Hao *et al.*, 2020; Kinoshita *et al.*, 2003). This is because of low capital costs, low energy consumption, absence of toxic gases, operational selectivity (high recovery and purity), simplicity and suitability in small-scale plants.

However, drawbacks of using comminution to crush and grind the ore include the loss of critical metals to the waste, high energy consumption, noise pollution, and generation of dust harmful to the environment (Kinoshita *et al*., 2003). PCBs' structure consists of interwoven metallic and non-metallic layers bonded with halogenated epoxy resin (HER). Dissolution of the HER polymer structure using organic solvents can dismantle the complex reinforced structure of the PCB to liberate metallic layers (Rao *et al*., 2021a; Rao *et al.,* 2021b). Early separation of metallic from non-metallic layers avoids complications associated with the presence of glasses, ceramics and resins in the downstream processes.

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In this work, delamination of downsized PCBs was performed to separate metallic layers from non-metallics using the dimethylacetamide (DMA) organic solvent. The optimum time and temperature for full liberation of the metallic layers through swelling of the structure was optimised. Then copper and gold from the liberated metallic layers were recovered from metallic fractions using the two-stage leaching to recover copper base metal and gold using a weak environmentally-friendly acid. Copper was recovered first before gold was leached from the solid residue because high copper concentrations affect the dissolution of gold by consuming excess acid solution (Rao *et al*., 2021a). This approach enhances gold concentration in the remaining solid residue to improve recovery, lower consumption of leaching acids and reduces residence time. Copper solution was purified mainly from lead and nickel impurities by cementation while gold solution was purified from tin and copper impurities by solvent extraction. Finally, copper and gold were recovered from pure solutions by cementation.

Experimental

The chemicals used were purchased from Sigma-Aldrich, South Africa and the waste mobile phones were obtained from a local cellphone repair shop.

PCBs Pre-Treatment

The PCBs were first dismantled manually from the main components and batteries before dipping them in 0.8 M H_2SO_4 at room temperature overnight to remove electronic components. The use of dilute sulfuric acid minimises leaching of copper into the solution. The separated PCBs were cleaned in acetone, hot water and dried before cutting them into sizes of approximately 2 cm× 2 cm.

The PCBs were pre-treated in DMA solvent (5:10 solid to liquid ratio) at different times and temperatures to optimise conditions for liberation using the design of experiments' conditions shown in Table I. Liberated metallic layers were then filtered, manually separated and washed for recovery of valuable metals. The metal concentration of the liberated metallic sheets was determined by dissolution of the metals at 50°C in freshly prepared aqua regia before analysing by inductively coupled plasma–optical emission spectroscopy (ICP-OES). The experimental steps followed from preparation of PCBs to final recovery of metals are depicted in the schematic shown in Figure 1.

Table I. Selected combinations of delamination temperatures and times and the extent of delamination observed

Experiment	Time (min)	Temperature (℃)	Extent of Delamination
1	150	155	Complete
2	120	155	Complete
3	150	130	Incomplete
4	120	130	Incomplete
5	135	142	Partial
6	113	142	Incomplete
7	135	124	Incomplete
8	156	142	Partial
9	135	160	Complete

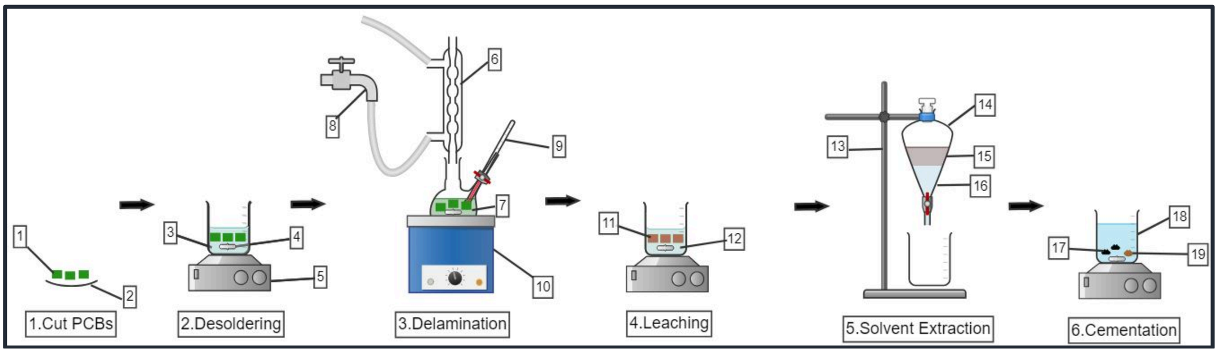

Figure 1. The schematic of the steps used from cutting to recovery of gold and copper.

Processing by Comminution
For comparison, some PCBs were shredded and pulverised in ball mill and the fine powder was dissolved in aqua regia at 50°C. The non-metallic portion was filtered and weighed while the filtrate was diluted and analysed by ICP-OES for chemical composition. The results in Table II show that PCBs contain about 65.39% Cu and 0.0011% gold.

Table II. The chemical analysis of pulverised PCB powder

Element	Cu	Ni	Au	Ag	Fe	Sn	Pb
Content (wt. %)	65.39	0.4	0.0011	0.03	0.23	21.48	12.29

Two-Step Leaching of Metallic Sheets

The flowsheet used for the two-stage leaching of copper and gold is shown in Figure 2.

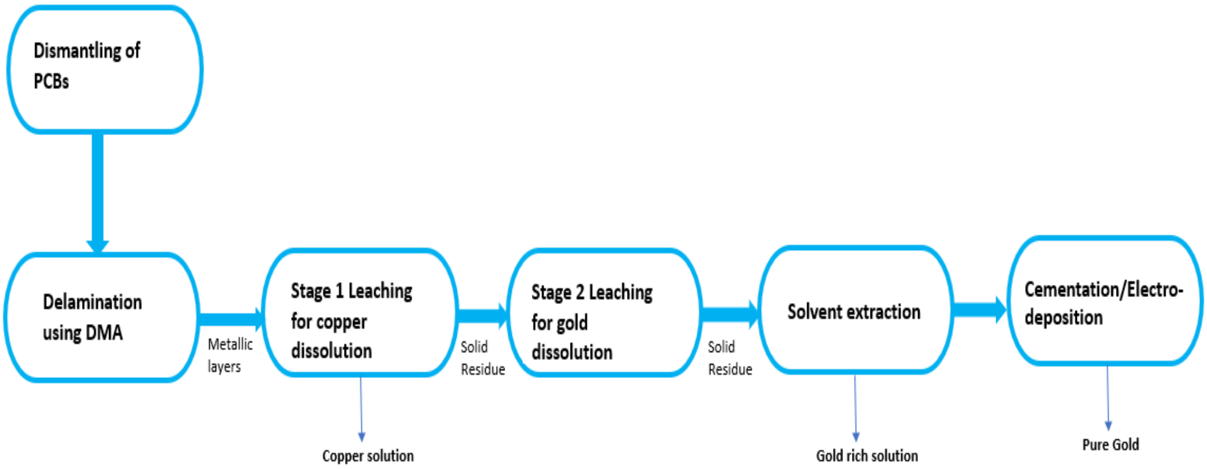

Figure 2. Flowsheet of the two-step copper and gold leaching process.

Copper Leaching

We examined the use of an environmentally-friendly weak acid (H_2SO_4) compared to traditional strong acids like nitric acid. The use of strong HNO_3 releases toxic NO_x gases into the environment. Samples of metallic layers from the delamination were treated with different concentrations of $CuSO_4$ + NaCl + H_2SO_4 under a range of temperature and time conditions to optimise for complete leaching of copper without gold dissolution under oxidising conditions. Optimum conditions include leaching liberated metallic sheets (15 g) in a 100 ml flask for 1 h using 50 ml of 0.4 M $CuSO_4$ + 4 M NaCl + 0.5 M H_2SO_4 solution at room temperature and stirring speed of 500 rpm. After leaching for 1 h, a sample was collected, diluted with distilled water and analysed using the ICP-OES technique. Chemical analysis showed that most of the copper was leached at this stage.

Gold Leaching

The residue remaining from copper leaching was filtered, weighed and subjected to the second leaching step. The remaining solid residue weighed about 0.17 g. Dissolution of gold was achieved by immersing a solid residue in 40 ml of 3 M H_2SO_4 + 3 M NaBr at 70°C, with mixing at 500 rpm for 1 h. The optimum leaching conditions were adapted from work by Rao *et al.*, (Rao *et al.*, 2021a). The use of bromine minimises the emissions of halide gases. The experimental set up is shown in Figure 1. The leachate was collected, diluted in distilled water and analysed by the ICP-OES method.

Metal Extraction from Leachates

Recovery of copper by cementation

The copper leachate was first adjusted to a known volume using distilled water. Copper solution was purified by adding a stoichiometric amount of zinc powder mainly to remove Ni and Pb impurities before filtering. Then solid copper powder was recovered by adding fine iron powder into the solution, before filtering, washing and drying. Room temperature, 1 h agitation time and a total volume of 20 ml were employed in all experiments.

Recovery of gold by solvent extraction

The separation of gold from the leachate was achieved by solvent extraction where 2 ethyl-hexanol in toluene was used as the extractant. These optimum conditions were obtained after testing with different volume rations and concentrations of sodium hydroxide stripping agent. The experiment was performed at room temperature followed by stripping with 1.0 M sodium hydroxide. The ratio of organic to aqueous phases was maintained as 1:1 in both extraction and stripping experiments. Pure gold from the gold solution was obtained by cementation using copper powder.

Results and Discussion

Figure 3. Photos of the PCBs collected from mobile phones.

Pre-treatment

We examined the effect of temperature and time on delamination of the PCBs of fixed sizes of 2 cm× 2 cm. Table 3 reveals that delaminating the waste PCBs (WPCBs) to separate the metallic fractions from the plastic and ceramic components enhances the concentration of copper and gold to 95.8 wt% and 0.052 wt%, respectively compared to pulverised powder containing 65.39% Cu and 0.0011% gold. This shows that the metallic sheets are already very rich in copper and the use of the delamination method completely removed iron as an impurity. The delamination times and temperatures demonstrate that complete delamination was achieved at a high temperature of 160℃ and time of 135 min (Figure 4). Delamination by dissolution is advantageous because the solvent can be easily recycled with a minimum loss.

Table III. The chemical analysis of delaminated metallic layers

Element	Cu	Ni	Au	Ag	Fe	Sn	Pb
Content (wt. %)	95.8	2.67	0.052	0.03	0	0.51	0.11

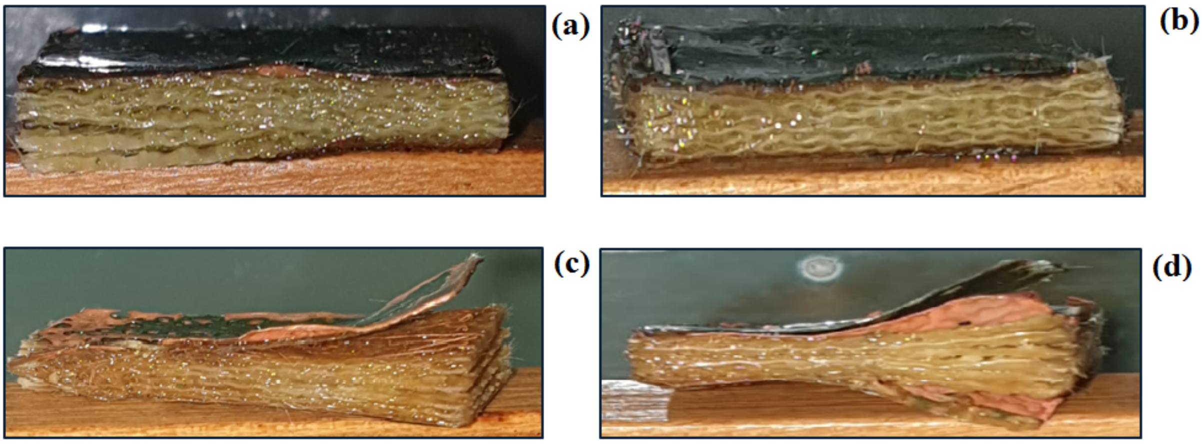

Figure 4. Photos of delaminated PCBs obtained in dimethylacetamide solvent for (a) 120 min and 130°C, (b) 113 min and 142°C, (c) 150 min and 15°C, and (d) 135 min and 160°C.

Leaching

Sulfuric acid leaching

Chemical analysis of the leachate revealed that almost all copper is dissolved (>95%) along with other elements such as nickel and lead, and to a lesser extent, tin (Figure 5); importantly, gold and silver remained in the residue. High amounts of Sn and Pb observed are likely to be due to the use of a weak H_2SO_4 in desoldering such that the solder components remained. The leached copper solution is shown in Figure 6 and the dark blue colour demonstrates the presence of copper in high concentrations.

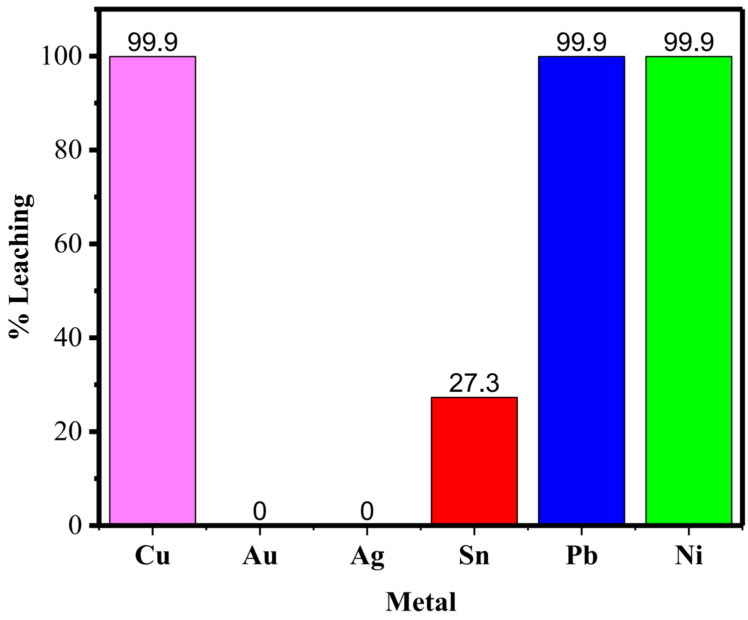

Figure 5. Leaching efficiency of various metals in stage-1 leaching using 0.4M$CuSO_4$+4MNaCl+0.5MH_2SO_4 solution, room temperature and stirring speed of 500 rpm.

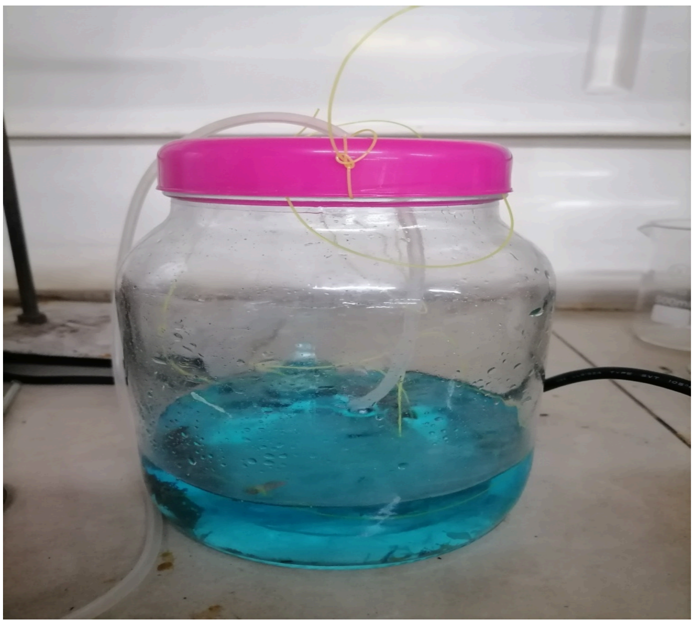

Figure 6. Copper leach solution obtained in stage 1 leaching of metallic sheets using 0.4M$CuSO_4$+4MNaCl+0.5MH_2SO_4 solution, room temperature and stirring speed of 500 rpm.

Gold leaching

The conditions selected for effective leaching of gold (95%) was 3 M sulfuric acid with 3 M NaBr, for 1-h residence time, at 70°C and 500 rpm stirring speed (Rao *et al.*, 2021a). The leached gold solution from the solid residue is shown in Figure 7. The concentrations of obtained leachates stage-1 and stage-2 leach are compared in Table 3. It is apparent that the effectiveness of the two-stage method was good. The results show that leaching from a solid residue selectively dissolved gold, silver and tin. The presence of impurities in both solutions, for example tin and silver in gold solution means further purification is required. Calculations using concentrations in Table 2 and 3 show that the leaching solution managed to extract about 90% of gold from the solid residue.

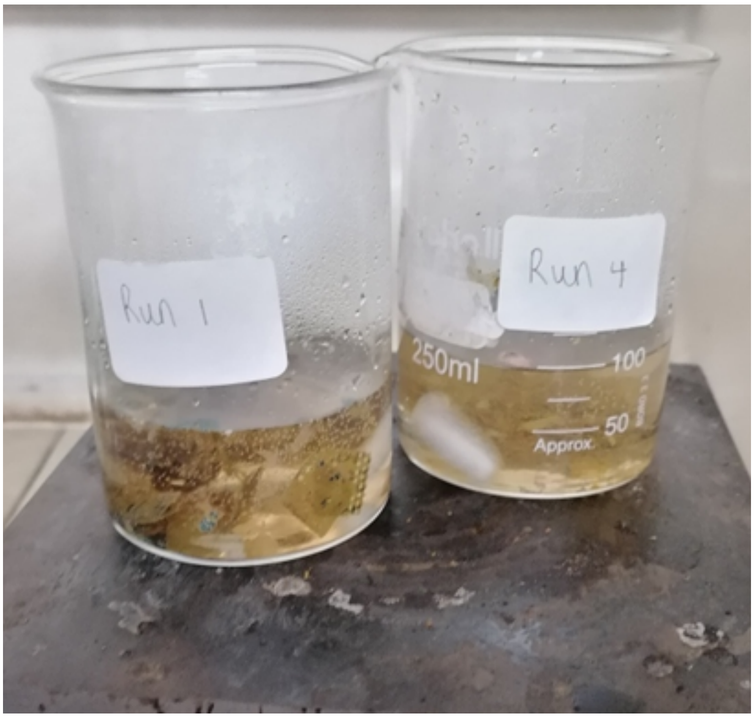

Figure 7. Solution obtained in stage 2 leaching of gold using 3 M H_2SO_4 and 3 M NaBr solution for 1 h at 70°C and 500 rpm stirring speed.

Table III The concentration of metals in stage-1 and stage-2 leach solutions obtained using delaminated metallic sheets obtained from WPCBs.

Element	**Stage 1 Leaching (Wt%)**	**Stage 2 Leaching (Wt%)**
Cu	98.2	0.25
Ni	0.85	0.0
Au	0.0	5.46
Ag	0.0	2.52
Sn	0.39	92.3
Pb	0.22	0.0

Separation of gold by solvent extraction
Solvent extraction of gold from tin and silver was achieved using 2 ethyl-hexanol as a carrier agent in toluene, followed by stripping with 1.0 M sodium hydroxide in the experimental set-up shown in Figure 8. The novel solvent used in solvent extraction recovered about 70% of the gold from the leach solution and proved to be an effective solvent. Further purification of gold from tin can be achieved through extraction and strip cycles. A small amount of copper powder was added to cement a few gold particles.

Figure 8. Solvent extraction of gold using 2 ethyl-hexanol in toluene before stripping in 1.0 M NaOH.

CONCLUSIONS

This research studied the potential of using environmentally-friendly hydrometallurgical conditions and delamination using a novel organic solvent to enhance recovery of copper and gold from mobile phones' PCBs. It was observed that by using the DMA solvent, the metallic PCB components were fully separated from the non-metallic sheets at 160℃ and 135 min. A two-stage leaching was used to obtain copper- and gold-rich solutions. This was followed by purification and recovery of copper using cementation. Gold was recovered by solvent extraction and cementation. This approach minimises contamination of the solution with iron and minimises losses of valuable metal to waste to improve recovery. This approach is also sustainable for up-scaling to recover critical metals from e-waste. Research into more environmentally-friendly and effective solvents, reagents recycling and pH adjustments should be investigated further for economic feasibility.

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Simbarashe Fashu

Senior Lecturer
University of Kwazulu Natal

Dr Simbarashe Fashu is working as a senior lecturer in the department of Chemical Engineering at Kwazulu Natal University, Durban. His main research interests include recovering of critical metals from secondary resources and development of high performance alloys. He received his PhD degree in Materials Science and Engineering at Zhejiang University, China in July 2015. From 2016-2017, he was a Post-Doctoral Researcher in the Department of Advanced Materials at the University of Western Cape, South Africa. Then from November 2019-September 2021, he joined Guangdong Technion Israel Institute of Technology, China as a Post-Doctorate. He worked in several industries including metal casting, refractory ceramic manufacturing and steel making.