Evaluation of solvent swelling pre-treatment for copper recovery from waste printed circuit boards

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Electronic waste has emerged as a valuable, rapidly-growing waste stream, expected to exceed 82 million tonnes by 2030. This has made the recycling of this waste stream of interest, with particular emphasis on the recovery of metals from waste printed circuit boards (PCBs) as they contain a high content of copper as well as a significant quantity of precious metals such as gold, silver, and palladium. In the South African context, there exists potential to increase the proportion of e-waste recycled through the development of accessible beneficiation techniques that can be implemented by small scale industries. Copper is found on the surface of PC boards, in through-holes that connect copper layers as well as within the internal copper layers that are tightly laminated between non-conductive epoxy resin sheets thus rendering them inaccessible to lixiviant. This paper explores solvent swelling pretreatment for liberation of the encapsulated inner layer copper. The solvents explored are N- methyl-2-pyrrolidone and an N- methyl-2-pyrrolidone-based proprietary solvent used in the desmear process used in PCB manufacturing. The degree of metal liberation by the chemical pretreatment method employed was determined by diagnostic column leaching using primarily samples of waste ammoniacal etchant from a local printed circuit board manufacturing factory, as well as synthetic etchant modelled after a typical waste etchant stream. Solvent swelling yielded promising copper recoveries as high as 93.4%. A combination of both physical and chemical pretreatment by combining 6-pass grab shredding with solvent swelling yielded lower copper recoveries, assumed to be the consequence of preg-robbing. The waste etchant from printed circuit board manufacturing was found to leach copper at a rapid rate with the only limitation being copper saturation. This limitation can be managed by integrating the leach circuit with a downstream copper recovery unit as is common in the manufacturing process.

Keywords: PCBs, Pretreatment, NMP, Etchant, Ammonia, Leaching

INTRODUCTION

The Global E-Waste Monitor Report of 2024 (Baldé *et al.*, 2024) highlights electronic waste (e- waste) as one of the fastest-growing waste streams, growing at a rate of 2 million tons per annum. The potential value from the beneficiation of e-waste for metal recovery has made this a stream of economic interest with particular emphasis being on the recovery of metals from waste printed circuit boards (PCBs) which contain one of the highest contents of copper in addition to precious metals such as gold, silver, and palladium compared to the contents of these metals in their natural ores. The highest monetary value can be attributed to the precious metals content. However, this paper focuses on copper which is the most abundant metal in waste PCBs with a significant monetary value (Golev, Corder & Rhamdhani, 2019; Forti *et al.*, 2020).

Typically, smelting in integrated pyro-hydrometallurgical operations such as the one at Umicore in Belgium is carried out to bring target metals into solution followed by electro refining for the recovery of copper and precious metals (Cui & Zhang, 2008). This is done on a large scale together with co-processing, with additional metal-rich streams for economic viability. This method is reasonably viable in developed nations where established e-waste collection systems are present and relatively large volumes of e-waste are generated from higher consumption of electronics (Ilankoon *et al.*, 2018). However, within the South African context as well as that in other developing economies, challenges such as poor e-waste collection, high energy costs and poor supportive legislative frameworks make the relatively costly and energy intensive large-scale pyrometallurgical operations uneconomical and inaccessible. In contrast, hydrometallurgical processing routes, such as solvent swelling for metal liberation and oxidative ammonia leaching, have proven to be promising for minimising cost, environmental impact and maximising recoveries for small-scale applications (Tuncuk *et al.*, 2012). This is of particular interest within the South African context where the e-waste recycling and collection sector is small scale, with an estimated 12% of e-waste generated being collected in 2016 (GreenCape, 2018).

PCBs can be classified as single-sided, double-sided, or multi-layered, based on the number of copper conductive layers present as illustrated in Figure 1.

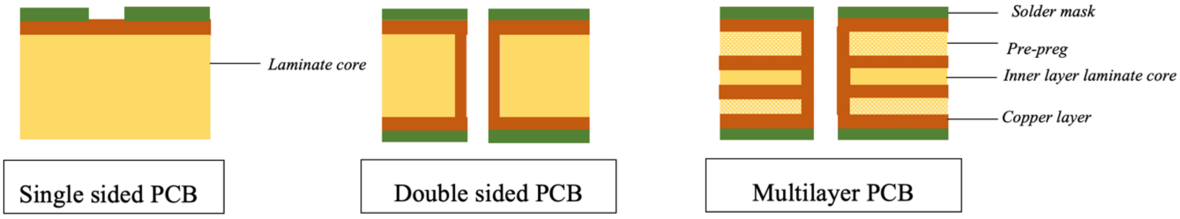

Figure 1. Classification of PCBs by conducting layers.

The most basic PCB design is single-sided, comprising of one layer of copper on the non-conductive laminate core, with the most complex design being a multilayer PCB which can have as many as 20 conductive layers pressed together with semi-cured pre impregnated resin 'pre-preg' which acts as the glue between the copper layers to yield a tightly laminated composite as illustrated in Figure 2.

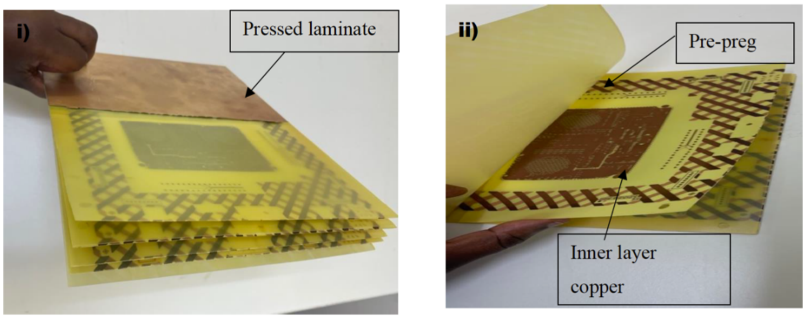

Figure 2. Deconstructed illustration of a 10-layer multilayer PCB sample supplied by ICAPE Trax i) Top surface copper layer and first pre-preg layer ii) Inner layer copper.

In hydrometallurgical beneficiation of PCBs for copper extraction, the process is reliant upon the lixiviant's ability to access the metal, most of which is located within the inner layers of the PCBs, tightly laminated between the non-metallic phases. These typically comprise of thermally cured epoxy resin, brominated flame retardants, curing agents, fillers and accelerators (Monteiro *et al.*, 2021; Sanapala, 2018). Therefore, pre-treatment of the PCBs for metal liberation is an essential precursor to subsequent hydrometallurgical extraction of copper by lixiviants. This can be achieved by compromising the structural integrity of the PCB to render lixiviant-metal contact with the inner layer copper possible.

Various methods have been employed to achieve this, in particular physical size reduction and delamination methods such as grinding, shredding and pulverising (Cui & Anderson, 2016; Sethurajan *et al.*, 2019). Prestele (2020) detailed the optimisation of various size-reduction methods such as the use of an industrial grab shredder with reported maximum copper recoveries of 57.8% from 6 pass shredding alone. It was noted that size reduction contributed to partial delamination thus aiding in copper liberation. The introduction of a chemical pre-treatment, for example soaking in sodium hydroxide combined with 6 pass shredding increased the copper recovery by a further 10% (Prestele, 2020). To achieve high copper recoveries with mechanical methods alone, finer particle sizes are required which increases the energy consumption. Thus, the exclusively mechanical methods have a higher capital investment input and operating cost in addition to having an environmental impact from the generation of dust.

Due to these challenges, solvent swelling has been explored as an alternative, less energy intensive and hence more economical method. In addition, the solvents utilised are not consumed and can be regenerated and recovered (Zhu *et al.*, 2013). These solvents dissolve the non-metallic fractions such as bromine epoxy resin (BER), the main constituent of epoxy resin found in PCB laminates, without attacking the metal, thus preventing metal losses (Wath *et al.*, 2015). The dissolution of BER leads to delamination of the non-metallic and metal layers, thus availing the metal for contact with lixiviants. Some of the solvents of interest explored in literature include N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), di-methyl formamide (DMF) and dimethyl acetamide (DMAc).

Similar to solvent swelling in PCB recycling, the PCB manufacturing process employs a solvent swelling process for the removal of resin smear in drill holes in a process known as 'desmearing' prior to copper plating of the through-holes as detailed in European Patent 2287357A2 (Li *et al.*, 2011). The key steps include drilling of copper clad laminate to facilitate electrical connections between the copper layers, followed by the desmear process where resin smear and debris generated from the drilling process are removed from the holes using solvents as detailed by US Patent No. 5,985,040 (Carano, Polakovic & LaFayette, 1999). In addition to cleaning the holes, the desmear process generates microcavities in the laminate material by etching a small amount of the epoxy resin in the hole walls, thus creating a roughened surface which facilitates good epoxy/copper adhesion during the subsequent copper electroplating process (Ge, Turunen & Kivilahti, 2003).

After copper plating, the desired circuitry is created by using a chemical etching process utilising ferric chloride, cupric chloride and ammonia/ammonium chloride etchants to develop the final circuit pattern visible on the surface by leaching the excess amount of copper from the laminate (Shah, Gupta & Sengupta, 2018; Patil, 2014). This etching process in PCB manufacturing uses similar lixiviants to those that can be used in the hydrometallurgical beneficiation of waste PCBs for copper dissolution through oxidative leaching. An example is ammonia/ammonium chloride which is the lixiviant in use at ICAPE Trax, the PCB manufacturer considered in this study. This same oxidative ammonia leaching process employed in PCB manufacturing has been explored by various studies in literature as a viable hydrometallurgical process for the selective recovery of copper from waste PCBs (Oishi *et al.*, 2007; Koyama, Tanaka & Lee, 2006). Equation 1 shows a summary of how copper metal is reacted and dissolves in solution. (Chemcut Corporation, 2002; Koyama, Tanaka & Lee, 2006).

$$Cu + \frac{1}{2}O_2 + 2NH_3 + 2NH_4Cl \rightarrow Cu(NH_3)_4Cl_2 + H_2O \qquad [1]$$

The etching process in PCB manufacturing often generates excess amounts of copper-bearing waste etchant as is observed at ICAPE Trax. The cupric ion present in this waste etchant acts as an oxidising agent to dissolve metallic copper (Radmehr *et al.*, 2013) through the redox reaction illustrated by Equation 2 (Habashi, 1963).

$$Cu + Cu(NH_3)_4{}^{2+} \rightleftharpoons Cu(NH_3)_2{}^{+} \qquad [2]$$

In PCB etching, the pH of the etchant is maintained between 8-8.5 (Chemcut Corporation, 2002) since both the cupric Cu(II) and cuprous Cu(I) ions are insoluble ionic species in neutral and alkaline solutions without the presence of sufficient complexing agents such as ammonia (Koyama, Tanaka & Lee, 2006). Similarly, in waste PCB leaching studies the pH is maintained between 8-10 within the stable region of the copper ammonia complex (Koyama, Tanaka & Lee, 2006).

Solvent swelling presents as a viable pre-treatment method for complete metal liberation through delamination as detailed in literature. However, most of the research presented in the literature focuses on the dissolution of the BER as a measure of the degree of separation of the copper layers and hence the degree of metal liberation. The enhanced copper recovery in subsequent leaching processes after solvent swelling has not been explored, yet this is the critical aspect of any viable industrial copper recovery process. The aim of this study therefore is to evaluate the effectiveness of solvent swelling with NMP-based solvent used in the desmear process in liberating copper from waste PCBs. The degree of metal extraction as an indicator of metal liberation can be determined through ammonia leaching with waste etchant from PCB manufacturing where the lixiviant contains reagents in excess, such that the extent of copper dissolution is not limited.

Materials and methods

Printed Circuit Boards

The PCBs used throughout the experiments were unpopulated, solder-free four-layer boards manufactured by ICAPE Trax. Figure 3 illustrates the top surface layer of the PCB and Figure 4 illustrates the bottom surface layer of the 142 x 102 x 1,55mm PCB.

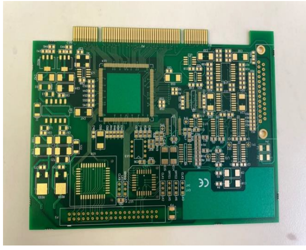

Figure 3. Custom-made PCB top surface layer (Layer 1).

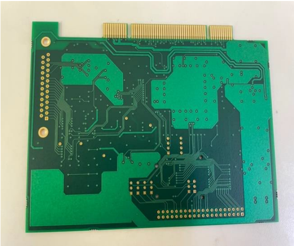

Figure 4. Custom-made PCB bottom surface layer (Layer 4).

The copper content of the PCB was determined by measuring the thickness of each of the four copper layers on the PCB (see Figure 5).

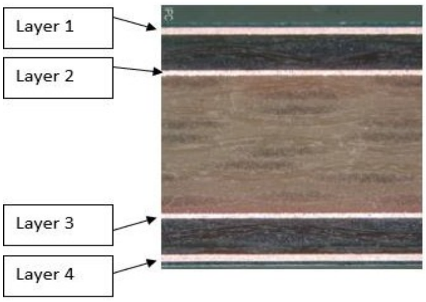

Figure 5. Coupon B X50 magnification view of copper layer.

A total of 5 PCB samples were analysed and the resulting copper thickness of each layer measured using a metallographic microscope. Once the copper thickness of each layer was established by microsection analysis, the corresponding copper area of each layer was extracted from the manufacturing blueprint provided by the PCB manufacturer. The blueprint provided a detailed breakdown of the manufacturing design of the board including the copper area for each layer of the board and the copper surface area of the drilled holes. From this information the copper volume was determined by multiplying the copper thickness by the copper area per layer, thereafter converting this to mass using a copper density of 8.93 g/cm3 (Perry, Green & Maloney, 1997). Using this method, the copper content of each custom-made

PCB was found to be 10.82±0.45g. This was reasonably in line with the theoretical copper mass determined by the PCB manufacturer from the design blueprint and copper area with a 6% difference attributed to the allowable process tolerance. In addition, the copper mass distribution as determined by the microsection analysis was as illustrated in Figure 6.

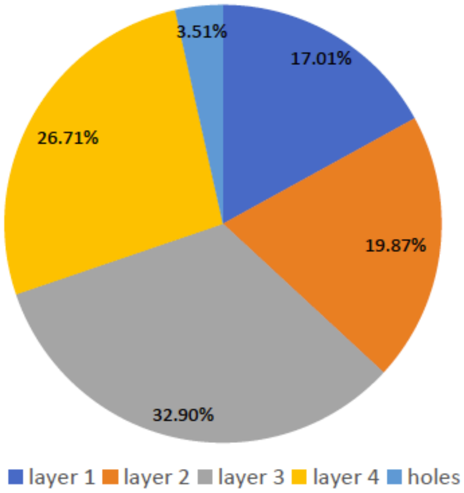

Figure 6. Copper mass distribution through the layers as determined from cross-sectional analysis.

Pre-treatment methods

Two types of solvent swelling pre-treatment configurations were evaluated and reported in this study, namely determining the effect of solvent swelling with NMP vs the NMP based proprietary solvent used in the desmear process and evaluating the effect of combining solvent swelling with mechanical pre-treatment.

All solvent swelling tests were conducted on PCBs that had been cut into 2x1.5 cm pieces for the purposed of fitting into the reactor. The PCBs were reacted in solvent for 90 minutes at a temperature of 150^{0}C. After solvent swelling pre-treatment, the PCBs were washed, dried and leached in a diagnostic leaching column to determine the extent of copper liberation.

Solvent swelling NMP vs NMP based proprietary solvent (Solvent B)

The laminate material used to manufacture the custom-made PCBs was FR-4 with a glass transition temperature (Tg) of 150^{0}C. The Tg is the temperature at which the rigid laminate material begins to soften (Pacáková & Virt, 2005), hence the solvent swelling temperature used was 150^{0}C for maximum delamination. The performance of NMP (experiment 1) vs solvent B (experiment 2) was evaluated at this elevated temperature to establish the degree of copper liberation from the PCBs after pre-treatment with the respective solvents alone. The boiling point of both NMP and solvent B is 202°C allowing for its use at higher temperatures that enhance delamination without being released to the environment. In order to evaluate the performance of these solvents, the pre-treated PCBs were leached in a synthetically prepared etchant modelled after typical ammonia/ammonium chloride PCB manufacturing etchant. Synthetic etchant was utilised to eliminate the effects of any background contaminants found in waste etchant.

Solvent swelling combined with shredding.

Mechanical pre-treatment for metal liberation and further size reduction to smaller particle sizes was carried out by shredding the cut PCBs through 6 passes as the maximum number of cycles as determined by Prestele (2020). This was done prior to solvent swelling for experiment 3 and after solvent swelling for experiment 4. The shredded PCBs were treated with solvent B using the same parameters as the cut PCBs.

Diagnostic copper leaching.

Diagnostic leaching was carried out as an indicator of the extent of copper liberation from the preceding solvent pre-treatment processes. This was carried out in two column reactors 0.5 m in height and 0.09 m in diameter. Solution was fed into the column through a closed loop system using a peristaltic pump at a flowrate between 6 L/day. The pregnant leach solution flowed through an outlet at the bottom of the column as illustrated in Figure 7 and continuously circulated through the column.

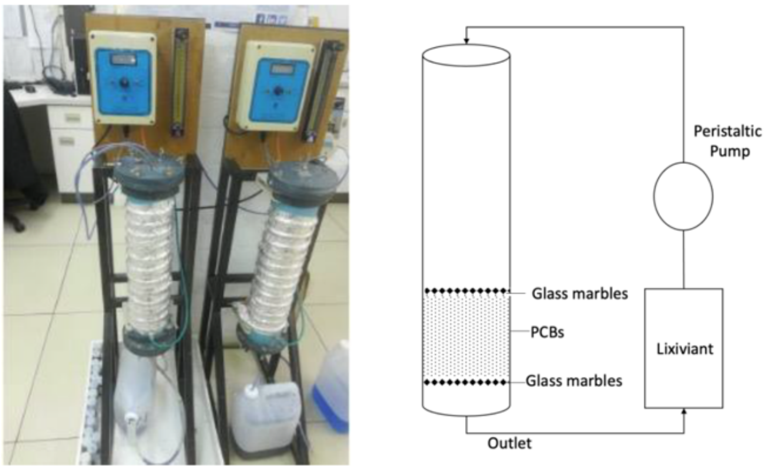

Figure 7. Leaching column configuration.

Two lixiviants were utilised, namely waste etchant collected from ICAPE Trax with 150g/ L copper content and synthetic etchant prepared as detailed in Table I .

Table I. Preparation methods for lixiviants utilised

Lixiviant	Preparation method
Waste etchant	A sample was collected from the waste stream at ICAPE Trax. The copper content was analysed by complexometric titration with EDTA and determined to be 150g/L.
Synthetic Etchant	50g/L synthetic etchant was made up by dissolving 100 g of pure copper foil in a solution with 200 g NH4Cl dissolved in 500 ml de-ionised water and 500 ml NH4OH. Upon dissolution of the copper foil, the solution was made up to a final volume of 2 L with DI water. The final pH was adjusted to 10 by adding ammonia. 10g/L synthetic etchant was made up by dissolving 20 g of pure copper foil in a solution with 40 g NH4Cl dissolved in 500 ml de-ionised water and 150 ml NH4OH. Upon dissolution of the copper foil, the solution was made up to a final volume of 2 L with DI water. The final pH was adjusted to 10 by adding ammonia.

The procedure utilised for diagnostic leaching was as detailed below.

1. Pre-treated PCBs were added to the reactor column.
2. 2 L of lixiviant were continuously circulated at a flowrate of 6 L/day
3. Leaching was carried out for a minimum of 72 hours. Samples were collected at various time intervals for copper analysis using atomic absorption spectroscopy to track the leaching progress.

No air was pumped into the column which was run at room temperature. The PCBs were loaded into the column as illustrated in Figure 7. Given the excess amount of copper present in the lixiviant, sufficient oxidant was present in the form of cupric ion to oxidise the copper on the PCBs, therefore the build-up of cuprous ions was not considered a hinderance. Further, the lixiviant was exposed to air in the receiving vessel thus allowing for oxidation of any accumulated cuprous ion during circulation.

Evaluating diagnostic leaching lixiviants

Experiment 5 was carried out as a baseline study where cut PCB pieces that had not undergone any pre-treatment to liberate the inner layer copper were leached, hence these were considered as 'untreated' PCBs. The goal of this was to exclude the effects of background contaminants while determining the leaching characteristics of synthetic etchant without factoring in the degree of liberation of the inner layer copper of interest to this study. For the purposes of evaluating the performance of waste etchant, experiment 6 was carried out using the same parameters as in experiment 5, however waste etchant was the lixiviant used for diagnostic leaching. This allowed for the evaluation of the performance of waste etchant against synthetic etchant without the influence of any pre-treatment that would render access to the inner layer copper.

Prior to cutting, the PCBs in both experiments 5 and 6 were soaked in sodium hydroxide for the removal of solder mask to expose top and bottom surface copper layers as shown in Figure 8. Thereafter the cut pieces were charged to the leaching column.

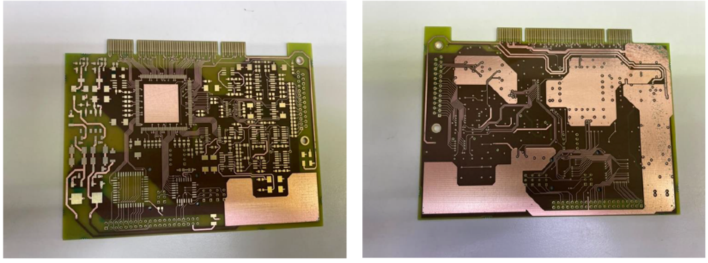

Figure 8. PCB after sodium hydroxide soak for solder mask removal.

The synthetic etchant lixiviant was prepared with a copper to ammonium chloride mass concentration ratio of 1:4 and ammonia was added to maintain the pH between 8-10 throughout the leaching process. The lower copper content synthetic etchant was utilised for leaching the mechanically shredded PCBs as illustrated in Table II. The waste etchant collected from ICAPE Trax was utilised in experiments 6 and 7.

Table II. Pre-treatment methods and lixiviants used for diagnostic leaching

	Solvent Swelling Pre-Treatment conditions			
Experiment	**Organic Solvent**	**Temperature**	**Time**	**Lixiviant**
1	NMP	150°C	90 minutes	Synthetic etchant-50g/L
2	Solvent B	150°C	90 minutes	Synthetic etchant-50g/L
3	Solvent B	150°C	90 minutes	Synthetic etchant-10g/L
4	Solvent B	150°C	90 minutes	Synthetic etchant-10g/L
5	Untreated	-	-	Synthetic etchant-50g/L
6	Untreated	-	-	Waste etchant
7	Solvent B	150°C	90 minutes	Waste etchant

Results and Discussion

***Evaluating of solvents** NMP **and** Solvent B*

Figure 9 illustrates the leaching profile of the pre-treatment comparison tests between NMP and solvent B.

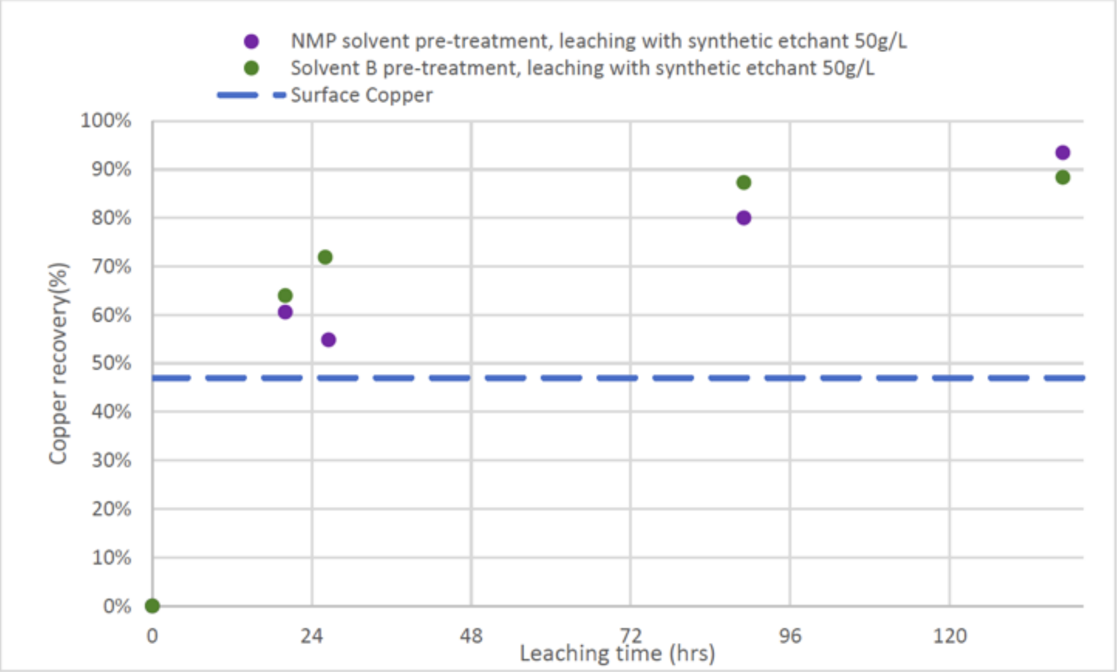

Figure 9. Comparison in performance of swelling with NMP in experiment 1 and solvent B in experiment 2 at 150°C.

The copper recovery from PCBs treated with NMP was 5% higher compared to solvent B after 120 hours of leaching. Significant lifting of the surface copper foil as well as partial delamination was observed in both experiments upon visual observation of the PCBs after solvent swelling (see Figure 10). This indicated that the swelling of the laminate material had progressed and there were no noticeable visual differences in the degree of delamination between experiments 1 and 2; partial delamination was observed in both instances.

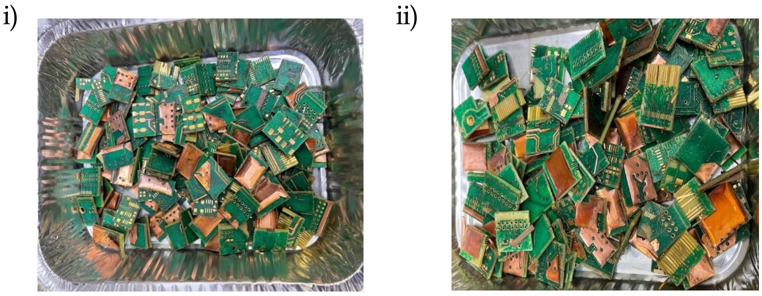

Figure 10. i) Experiment 1 -Cut PCBs after swelling with NMP ii) Experiment 8 - Cut PCBs after swelling with solvent B.

It was concluded from the leaching results that there were no added benefits with regards to copper recovery when using Solvent B compared to NMP given the marginally lower copper recovery as well as the increased cost from using a proprietary solvent. In addition, for an industrial process separate from PCB manufacturing, NMP would be the more feasible solvent to use due to its ease of access and lower cost of USD 6.25/kg (ECHEMI, n.d.) which is around half the price of proprietary solvents used in the desmear process.

A proprietary solvent such as Solvent B is often formulated with multiple solvent combinations that are designed to optimize swelling of various types of laminates other than FR4 in the desmear process and may thus be beneficial to PCB recycling where various PCB laminate materials are present in the feed (Carano, Polakovic & LaFayette, 1999). Moreover, in considering integrating a PCB recycling plant with a PCB manufacturing process, this presents the opportunity to utilize the waste solvent from the desmear process. Despite the lower recovery obtained with the proprietary solvent, significant copper liberation was achieved. Figure 11 illustrates residual pieces of PCBs after copper leaching. Some remaining inner layer copper was present as seen through the yellow laminate material.

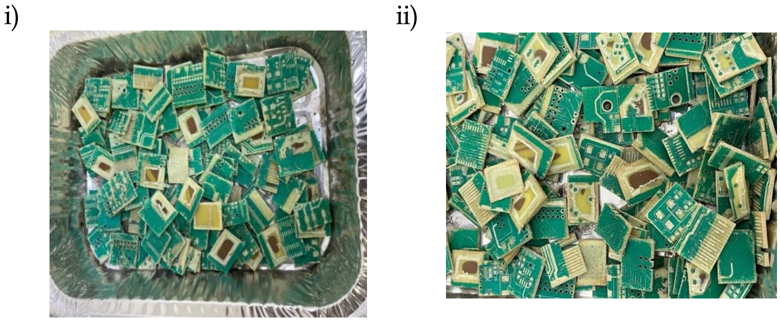

Figure 11. i) Experiment 1-NMP swelled PCBs leached with synthetic etchant ii) Experiment 2-Solvent B swelled PCBs leached with synthetic etchant.

On visual observation, there is no copper remaining on the outer surface layer as illustrated by a close up of one PCB piece from experiment 1 in Figure 12. The laminate layers were separated by peeling the layers apart with minimal force, highlighting that delamination may have progressed over time during leaching long after solvent swelling.

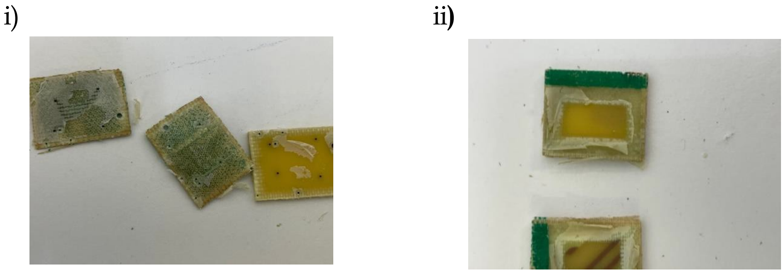

Figure 12. i) Swelled PCBs with layers separated ii) residual copper trapped under pre-preg.

Overall, NMP was found to outperform solvent B with a 5% increase in copper extraction. Hence NMP was found to be the better performing solvent in exposing copper for extraction.

Evaluation of combining mechanical shredding with solvent swelling

Upon visual analysis of the residual PCB pieces post leaching in the solvent swelling pre-treatment methods carried out, it was observed that the remaining amount of copper was encapsulated underneath the epoxy resin that had not been completely dissolved by solvent swelling – see Figure 12ii). It was postulated that combining solvent swelling with mechanical shredding would aid in further delamination. Hence experiments 3 and 4 were conducted in which the PCB size was reduced, thus increasing the surface area for subsequent solvent swelling.

Figure 13 outlines the leaching results obtained over a leaching period of 283 hours. The copper concentration of the synthetic etchant was reduced to 10 g/L to minimise the risk of precipitation as previously observed with etchant concentrations of 50 g/L and above. This however extended the leaching time given that the cupric ion was the oxidant.

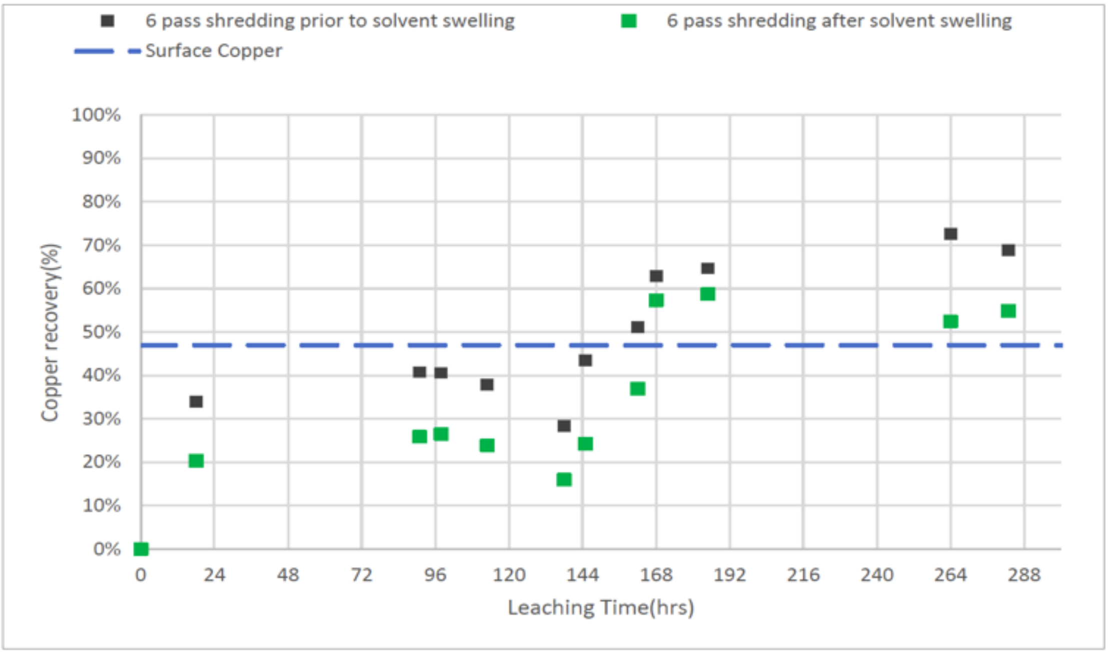

Figure 13. Copper extraction curves for solvent swelled PCBs leached with synthetic etchant prior to solvent swelling in experiment 3 and after solvent swelling in experiment 4.

It was established that the minimum time required to surpass the 47% surface copper content for both experiments was 162 hours. The leaching was allowed to progress until after the rate of recovery peaked at 264 hours. It was observed that the copper recovery dropped after a leaching time of 96 hours until

144 hours. From this it was concluded that the leaching progression was continuously hindered within this time period, thus highlighting the possibility of preg-robbing. The mechanism for this action in regard to copper is unknown; however similar occurrences have been extensively detailed in the gold ore leaching literature (Goodall, Leatham & Scales, 2005; Ng, Wang & Chen, 2022). Preg-robbing occurs when constituents of the ore, in this case the waste PCBs, adsorb the metal complex from solution. Further studies are recommended to explore this phenomenon for copper recovery from waste PCBs. Despite the reduction in the leaching progression, it can be concluded that solvent swelling aided copper liberation in both instances since the copper recovery exceeded the 47% related to the outer surface. The results validate the conclusion made by Prestele (2020), noting the encapsulation of copper by the BER and hence a need for combining mechanical shredding with another pre-treatment method. The solvent swelling aided shredding by dissolving some of the BER thus resulting in a maximum recovery of 72.6% compared to Prestele's 57.8%.

Evaluation of diagnostic leaching

The performance of the lixiviant was measured by the leaching time required to completely extract the surface copper. Figure 14 illustrates the leaching progress for experiments 5 and 6; it was established that the waste etchant had a faster leaching rate and achieved 100% recovery of the surface copper (47% of total copper) within the first hour of leaching compared to synthetic etchant which got close after 100 hours with full recovery of the surface copper firmly reached only after 244 hours.

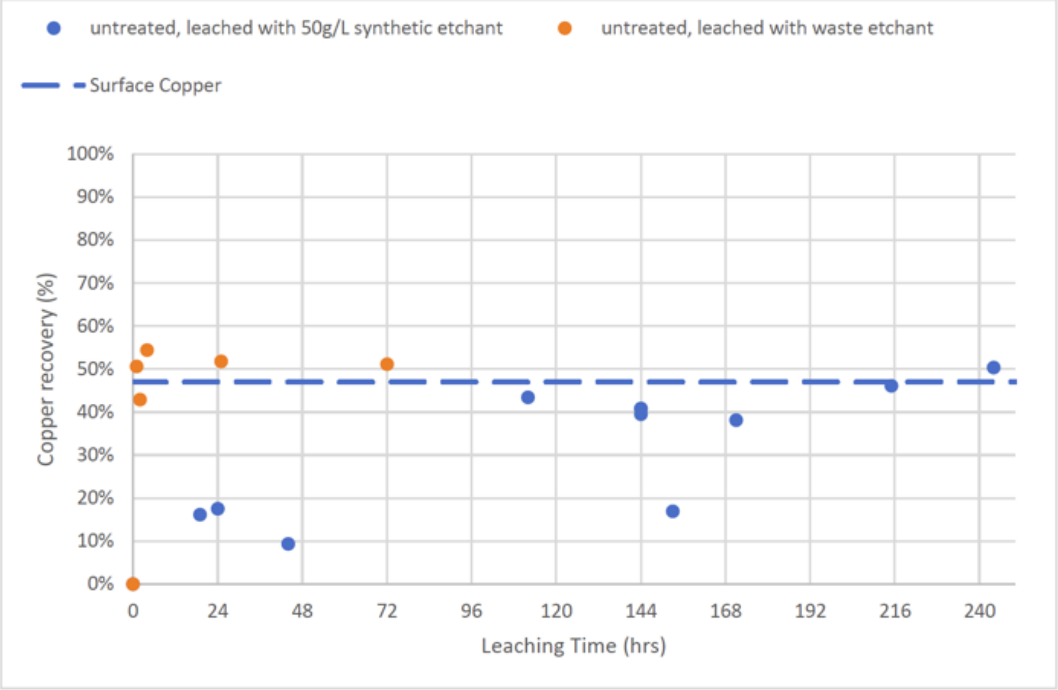

Figure 14. Copper extraction curves for untreated PCBs leached with synthetic etchant (experiment 5) and waste etchant (experiment 6)

Analysis of the leaching curve for the waste etchant highlights an initial drop in copper recovery from 50.6% after one hour to 42.9% after two hours, indicating possible precipitation in the leaching system within the first few hours. The synthetic etchant exhibited a similar trend of periodic drops in the copper recovery as well with an initial drop of 18% after 24 hours to 9% after 44 hours of leaching. The pH in all experiments was maintained between 8-10 to retain the stability of the cupric ammonia complex, and oxygen limitations were not considered a factor due to the excess supply of cupric ions which acts as the oxidant for the leaching reaction; in addition the solution was exposed to air during intermediate storage in the receiving vessel at the bottom of the columns. The reduction in copper recovery was attributed to precipitation of copper in the column due to the copper saturation level in the waste etchant increasing to the point where further leaching resulted in precipitation. In addition, one of the disadvantages of the percolation method utilised in column leaching is the difficulty in managing liquid channelling and the possible formation of pH gradients which may also lead to copper precipitation in the column (Ghorbani, Franzidis & Petersen, 2016)

Figure 15 shows the PCBs after leaching with waste etchant; it was noted that some of the residual PCBs showed a light blue precipitated copper residue after leaching, thus indicating that precipitation did indeed take place within the column.

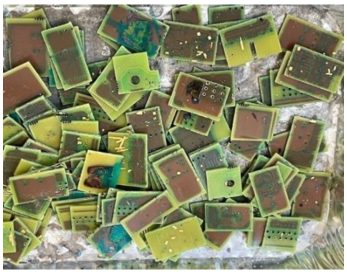

Figure 15. Untreated PCBs in experiment 6 after leaching with waste etchant.

The motivation for using column leaching in this study was to simulate heap leaching in a preliminary bench scale experimental method for scale up to a potential low capital cost industrial pilot phase setup. The benefit of heap leaching in this instance was that the copper recovery could be allowed to progress over a long period of time at ambient conditions with minimal input.

It was concluded that waste etchant has the advantage of a faster leaching rate, however the system was more prone to precipitation compared to synthetic etchant due to the higher copper content of waste etchant. Based on this observation it is recommended that the leaching process be coupled with a lixiviant recycling unit which extracts copper from the lixiviant to maintain chemical stability through the continuous recycling of copper loaded lixiviant as is the case with the PCB etching process at ICAPE Trax. This will aid in minimising precipitation by maintaining the copper concentration of the lixiviant within a determined range.

CONCLUSIONS

In this study, a series of solvent swelling pre-treatment experiments were undertaken as a method of liberating copper from multilayer PCBs for subsequent ammonia leaching. A key aspect was exploring the use of the chemistry utilised in PCB manufacturing, specifically waste etchant in the hydrometallurgical recovery of copper from waste PCBs. This required firstly the creation and characterisation of a standard PCB due to the difficulties associated with characterising a generic PCB waste stream as a result of the varying copper content. In addition, determining the copper distribution was key in establishing the success of the pre-treatment process in liberating copper from the inner layers.

It was determined from the characterisation that 47.2% of the copper on the PCB was located on the surface thus the success of the pre-treatment in liberating copper was measured against the degree to which the leaching was able to attain a copper recovery above 47.2%.

The lixiviants utilised in this study were ammonia/ammonium chloride-based waste etchant from ICAPE Trax and synthetic etchant modelled after a typical waste etchant stream. Of these lixiviants, synthetic etchant with a copper content of 50g/L had the greatest degree of stability and achieved good copper recovery and thus was the optimum lixiviant. Waste etchant was also found to be a suitable lixiviant, however it was found to be limited in that the copper saturation level in the waste etchant was so high that any additional copper leaching would rapidly increase the copper concentration to the point of precipitation. It is recommended that the waste etchant be diluted with fresh ammonium chloride lixiviant to reach similar conditions as the synthetic etchant. In addition, for an industrial process, the leaching system can be integrated with a copper recovery unit to reduce the copper content in the lixiviant as is the case with the etching process at ICAPE Trax.

A maximum copper recovery of 93.4% was obtained from PCBs swelled with NMP at 150°C for 90 minutes after 120 hours of column leaching. Pure NMP was found to outperform the proprietary NMP-based on cost and slightly better copper recovery under the same leaching conditions. Lastly, it was concluded that combining solvent swelling with mechanical pre-treatment aided in unlocking encapsulated copper; however significant copper losses were encountered through preg-robbing. Further investigations into the copper losses associated with adsorption on the BER are recommended.

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