Co-processing of PCB leach solutions with effluent streams from PCB manufacturing

Technical report

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EXECUTIVE SUMMARY

Electronic waste (e-waste) makes up a significant proportion of solid waste streams globally, and its volumes will continue to increase in the future. In South Africa, about 12% of these materials are recycled and there is potential to increase this recycled portion through the growth of small-scale industries already common in the South African e-waste recycling sector. Printed Circuit Boards (PCBs) are a key component of e-waste, containing valuable metals such as gold and copper. Although various technologies for the beneficiation of PCBs exist, limited availability of and access to these is the key hindrances to the growth of the sector in South Africa.

This project has built and expanded on research towards the development of a novel hydrometallurgical process based on alkali ammonia leaching of metals from suitably size-reduced PCBs, which uses the same process chemistry as the standard manufacturing process of PCBs. The project was executed in collaboration with a PCB manufacturer (Trax Interconnect (Pty) Ltd.) located in Cape Town with a view to initially integrating waste etchant solutions and cut-off and reject boards within the ongoing manufacturing process and eventually expanding to processing waste PCBs collected from external sources.

The work completed under this project encompasses 7 separate studies around the size reduction and delamination of PCBs, Cu leaching in Cu-NH_3 etchant solutions and its recovery by direct electrowinning, Au leaching in thiosulphate solutions and its recovery using ion exchange resins, and de-soldering of PCBs using various acid leaching techniques. The studies were conducted initially on custom-made unpopulated PCBs to represent typical reject boards produced by the industrial partner, but later expanded to populated waste PCBs which would constitute the primary feed to the envisaged process. In an 8th study, thus, the knowledge developed from research around these process stages was drawn together into a preliminary process design, supported by a detailed mass balance and consideration of internal re-utilisation of the process products.

The outcomes of the 8 studies are summarised below:

- <u>Study 1 – Comparison of PCB comminution methods:</u> The comminution behaviour of unpopulated PCBs using ball mill, ring mill, liquid nitrogen freezing and a 8mm grab shredder was evaluated in terms of energy consumption and degree of Cu liberation during subsequent ammonia leaching using a standard diagnostic procedure. Final grind size strongly correlates with the degree of Cu leaching achieved in the diagnostic tests. It was also found that energy consumption by the grab shredder is substantially lower than in any of the other methods investigated, but that size reduction is limited by the gap size of the shredder. Repeated passes of material through the shredder only marginally improve size reduction but contribute to the increased delamination of the boards and thus to improved leach performance in the diagnostic leach tests. I was also found that mode of agitation during leaching (tumbling vs overhead stirring) contributes to faster extraction from coarsely cut boards.

- <u>Study 2 – Investigation of organic solvents for the delamination of shredded PCB material and subsequent ammonia leaching in column reactors</u>: In combination with cutting and shredding, delamination of PCB pieces was investigated using various organic solvents. The most successful delamination was tested further in small percolation column reactors allowing for

the slow dissolution to proceed in an unagitated system. N-Methyl-2-pyrrolidone (NMP) was found to be effective in delaminating the shredded PCBs to a significant degree during thermal pre-treatment. The pretreated boards were leached in packed column reactors with industrial etchant solution (10 & 50 g/L Cu) trickled through them over an extended period of time (up to 14 days). Very high Cu extractions (>90%) could be achieved from leaching with shredded boards pre-treated with NMP after 5 days of percolation with 50g/L Cu etchant solution. Using the 150 g/L Cu waste etchant was less efficient due to oversaturation and the 10g/L etchant solution was not strong enough, resulting in only 70% extraction after 14 days.

- Study 3 – Development of thiosulphate leaching for Au recovery from PCBs: As an alternative to the commonplace cyanide leaching of gold, thiosulfate dissolution of Au from PCBs and gold powder was investigated in ammonia solution in agitated reactors against different background copper concentrations which is required as a catalyst but can become inhibitory at high concentrations. It was found that the leaching of both gold powder and gold form PCBs proceeds reasonably rapidly over a 6-hour period. A minimum copper concentration of 20 mM appears to be required to promote the reaction. Increased copper concentration had a significant effect on Au leaching from PCBs but less so on leaching of the gold powder. Leaching form PCBs appeared to become inhibited at initial gold concentrations exceeding 0.1M, as under the given experimental conditions significant amounts (up to 33%) of additional Cu are extracted from the PCBs which then inhibit Au dissolution due to surface precipitation and destruction of the thiosulphate compound.
- Study 4 – Investigation of process sequencing between Au and Cu leaching in an integrated process: Copper leaching using the ammonia system and Au leaching using the thiosulphate system were investigated in conjunction to identify the preferred sequencing of leach and size reduction stages. The standard diagnostic ammonia leach method and that developed in Study 3 for Au thiosulfate leaching were used under standard conditions. The dissolution of Ni, which is plated together with Ni to form the contacts on PCBs, was also investigated. Four different sequences, comprising of cut or shredded boards being subjected to the standard Au and Cu leaching procedures in the order of Au-Cu or Cu-Au. Confirming the results from Study 3 it was clearly shown that leaching the gold from coarsely cut boards first was the most effective in terms of Su recovery, but that leaching the Cu from shredded boards was the most effective sequence in terms of Cu recovery. Thus marginal cutting boards (to fit into the reactor) followed by Au thiosulphate leaching, followed by shredding followed by Cu leaching in Cu-NH3 etchant solution appears the most suitable sequence of process steps.
- Study 5 – Investigation of direct electrowinning of Cu from ammonia liquors: The direct electrowinning of Cu from a high concentration liquor obtained from the industrial operation was investigated in a batch cell and through a laboratory-scale flow-through cell apparatus, in each case investigating the quality of the Cu deposit and energy efficiency of the plating process. It was found that Cu can easily be plated from ammonia solutions even at low Cu concentrations, but current efficiencies and Cu product quality were low. Electroplating from a 15 g/L Cu etchant solution at a current density of 250 A/m^2 showed excellent cathode quality at a high current efficiency. Further test work is required to complete this work to judge whether direct electrowinning performs better overall to the industrially practiced SX/EW process where the Cu is extracted from alkali into acid solution and electrolysis proceeds in acid solution.

- Study 6 – Investigation of Au recovery from thiosulphate solutions using IX resins: Three ion exchange resins, strong base MTA5013 and medium base MTA5011 and AURIX 100, specifically targeted for anionic Au complexes were investigated through capacity, loading and elution tests using a synthetic leach liquor based on that produced in Study 3 under optimised conditions. The strong base MTA5013 was found to be the better performing resin. Overall, however, ion exchange tests showed very poor overall recoveries (<4% for Au) and selectivity to gold over the copper catalyst in the solutions, potentially due to limited residence times.
- Study 7 – Investigation of Pb-Zn solder leaching from waste PCB boards using HCl systems: Various lixiviants were investigated initially with solder wire of different Pb/Sn compositions and the most promising system – HCl with $SnCl_4$ – was then tested with real populated PCBs in a column leach apparatus for selective Sn removal. Solutions with citric and nitric acid were investigated for selective Pb removal. The experiments carried out with solder wire showed that Fe^{3+} and Sn^{4+} are strong oxidants affecting Sn dissolution. Even though the mix of Sn^{4+} + Fe^{3+} increased the leaching in 10% for some cases, it is not worth to have Fe as an impurity for the further purification process. It was concluded that, the stannic chloride is the best oxidant to use in hydrochloric acid, with 1-2M HCl and 5g/L Sn^{4+} showing the best results. Column experiments that submerged leaching with a slow recirculation of solution showed the best results and again a combination of strong HCl and 5g/L Sn^{4+} gave the best performance. However, the extraction rate was limited by the supply of oxygen (through air) into the reactor system. Pb extraction was limited under these conditions, with an opportunity for separate lead recovery through a follow-up HNO_3 leach.
- Study 8 – Considerations towards the development of an integrated process flowsheet for the complete processing of PCB boards: The results and insights obtained from the forgoing 7 studies were reviewed. A key insight was the need to sequence the leaching of coarsely cut, de-soldered PCBs before the thiosulphate leaching of Au before shredding and NMP delaminating and then leaching in strong Cu-NH_3 leaching. The solder removal can proceed in 2-stages achieving a high degree of selectivity towards Sn dissolution in the first stage. A revised process flowsheet was drawn up as the basis for further exploration of the process. A comprehensive mass balance around this flowsheet is under development for a 1000 kg/day PCB plant with a view to scaling the p. Potential uses for recovered Cu and Au from the proposed process, such as making Cu foil for application in battery systems or as anode material in the PCB electroplating process have also been discussed, indicating that targeting the product to specific markets influences the design of the recovery process.

Overall, the project has delivered substantial insights into the design of a hydrometallurgical process for the efficient recovery of metals from waste PCBs – to a degree based on the principles of the PCB manufacturing process. The challenge is now to develop this process further and evaluate it at the scale of a pilot process that integrates all the process steps and evaluating its techno-economic feasibility at different industrial scales. A follow-on project to tackle this is currently getting underway.

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1. Introduction

Waste Printed Circuit Boards (PCBs) are a value metals rich fraction of electronic waste (e-waste) streams and are often the focal stream of e-waste recyclers. In 2016, it is estimated that just over 350 000 tonnes of e-waste were generated in South Africa, only 12% of which were recycled (Lydall et al, 2017). PCBs are estimated to make up to 6% of the total weight of electronic waste (Judhav et al, 2016). South Africa exports at least 90% of the collected PCBs after initial dismantling of and separation from the e-waste that hosts them (Lydall et al, 2017). In so doing, the country loses access to valuable metals, as well as the opportunity to create jobs (CSIR, 2017). Considering that e-waste is one of the fastest growing waste streams in the world, the global shift towards sustainable management of resources and the continuous depletion of high grade virgin ore bodies, there is an increased need to explore recycling options for recovery of the metals found in PCBs, as well as to characterise and carry out safe disposal of the residue after recovering the desired metals in an integrated end-processing facility. Furthermore, it is worthwhile to evaluate the potential to use the recovered metal as a feed stream to local electronics and high-tech manufacturing. South Africa stands to benefit from recycling this valuable waste stream by contributing to the growth of a waste economy i.e. growing the e-waste recycling industry which has potential to create much needed jobs as well as divert waste from going to landfill sites or overseas for further processing.

Although various technologies that can be suitably applied for the beneficiation of some of the value fractions of PCBs exist, availability of and access to these technologies is one of the key hindrances to the growth of the e-waste industry in South Africa. As a result, locally the focus has remained on collection and preparation of PCBs for overseas processing, whereas local end-processing to recover metals is hampered by several challenges, among which are the availability of and access to suitable technologies and equipment, as well as availability of sufficient e-waste volumes for sustainable operation of large-scale smelter-based technologies currently applied by global leaders in the recycling business (Sadan, 2018, Moyo et al., 2022).

Generally, PCBs are composed of 40% metals, 30% plastics and 30% ceramics (Ogunniyi et al. 2009). and consists of three primary constituents – the “circuit board” (generally fibre-glass with copper circuitry and nickel-gold contacts and protective coating), electronic components (with a vast variety of ceramic and plastic components, but usually only traces of metal values) and soldered contacts which connect the electronic components with the circuitry on the board (with the solder being mostly lead-tin alloys, and the connectors being steel or various metal alloys).The “circuit board” is a complex composite structure comprising of a matrix phase, a reinforcement phase and a conductive phase. Tightly woven continuous glass fibres make up the reinforcing phase, which is embedded within the matrix phase, most commonly a type of thermoset epoxy resin (Coombs et al. 2001). The conductive phase (predominantly copper metal) allows for conductivity between the board and its attached components. During the PCB manufacturing process, the epoxy resin is heated and cured forming strong polar and direct bonds between with the glass fibres and the copper layers. This results in PCBs being incredibly difficult to delaminate or to break apart when one intends to liberate the metal layers embedded in these composite structures.

Globally, the end processing of e-waste operates in high-capacity integrated plants with sophisticated equipment using high-temperature smelting with sophisticated flue gas scrubbers as an initial step in processing. In such conditions metal is liberated and is further processed via hydrometallurgical processes, while the gas scrubbers ensure that toxic gases are not released into the atmosphere. On the other hand, numerous bench-scale hydrometallurgical processes for the PCBs are reported in literature (Koyama et al, 2006, Petter et al 2013, Tuncuk et al,2011, Luyim et al 2011, Xiu et al, 2019).

In these studies, shredding, milling and separation/classification are used for liberating and upgrading the metal content of PCBs prior to leaching. While this approach is akin to the traditional processing route for traditional minerals and thus an established technology, it cannot be applied economically within the current structures of the PCB recycling industry due to the energy intensive nature of size-reduction especially through the fact that the elastic nature of the boards makes the use of conventional mineral comminution techniques inefficient. Evaluation or use of other, more suitable size-reduction techniques have not yet been systematically investigated. Beyond metal liberation processes, leaching technologies are established for different chemistries and have been widely reported in literature (see for example summaries offered by Cui and Anderson, 2016, or Ilankoon et al., 2018, also Birloaga et al., 2013). The present project has built on earlier work at UCT, which aimed to develop and test a hydrometallurgical flow sheet for the recovery of metals from waste PCBs in alkaline solutions as represented in the preliminary flowsheet shown in Figure 1.

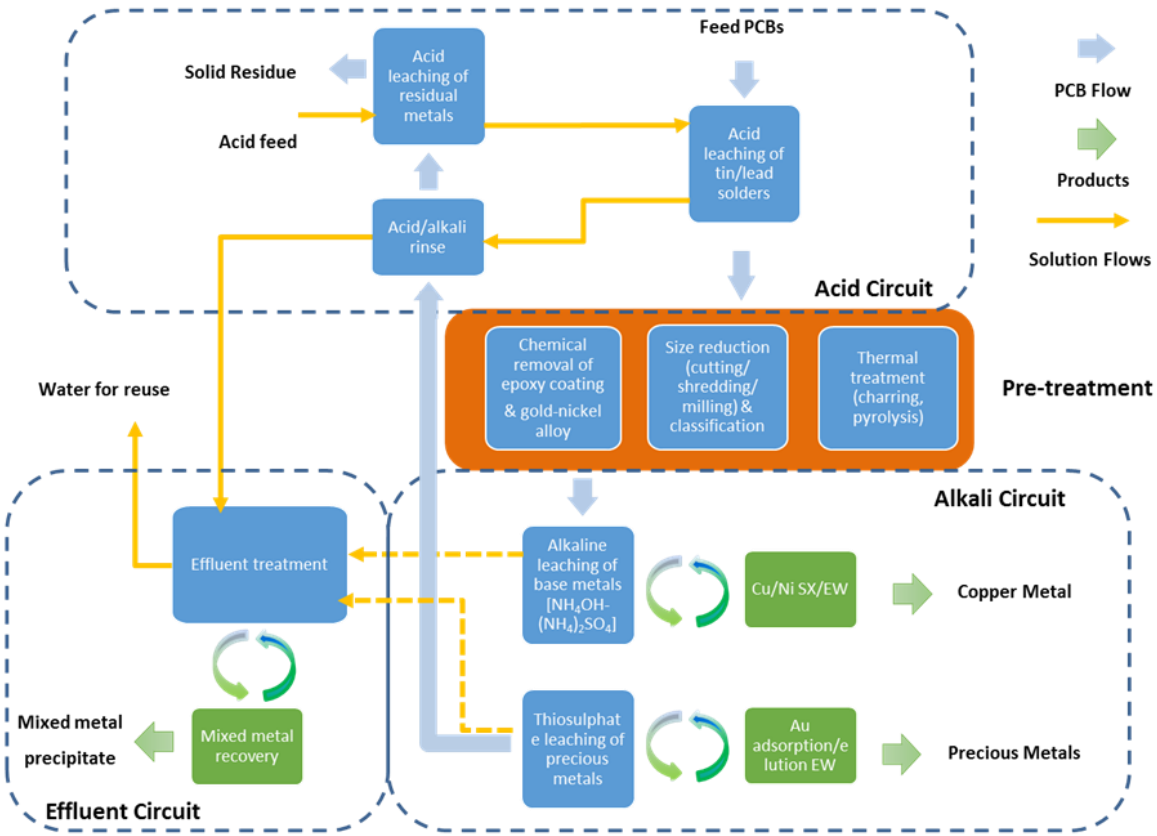


Figure 1. *Initially proposed hydrometallurgical flow sheet envisaged for the recycling of waste PCBs*

The recovery of copper in ammonia-ammonium carbonate solutions has already been validated (Chirume, 2019; Moyo et al., 2020). Electrowinning of the dissolved copper, leaching of solder using chloride systems and gold from the PCB contacts using the thiosulphate system and its recovery from leach solution using ion exchange technology form a part of the scope of the present work.

Collaboration with a local PCB manufacturer has allowed us to explore the potential to co-treat leach solutions of waste PCBs with their metal-rich effluent streams. Further, the study has offered an opportunity to explore the potential to integrate purified solutions and recovered copper back into the manufacturing process, reducing costs and the need to import raw materials.

2. Project Aims and Objectives

It was the aim of this project to explore the core process steps for the leaching and recovery of PCBs in the ammonia alkali system at both the laboratory, develop a revised flowsheet and test it at the pilot scale. The steps explored include the physical pre-processing of PCBs for size-reduction and metal liberation, optimisation of copper extraction using spent ammoniacal etching liquors, extraction of gold using ammoniacal thiosulphate chemistry and its recovery by resin ion exchange, as well as recovery of solders in the case waste PCBs are introduced into the process.

A pilot study was to focus on treating reject PCBs from the participating manufacturing plant using waste etching solutions and process technology available at the plant; however due to various factors this only partially materialised. From the insights at bench and pilot scale, further considerations can be given to an integrated waste recovery process for said PCB rejects as well as waste PCBs obtained from local waste collectors. In particular, the developed process should be a good fit for operation at the local scale with input of the local e-waste stream, i.e. it should not be capital and energy intensive, and be scalable and environmentally friendly.

The specific aims of the proposed project were to

- Investigate the leaching of the Pb/Zn solders hydrochloric acid to remove components on waste PCBs as part of the pre-treatment process According to the preliminary flowsheet in Figure 1.
- Compare the extent of liberation of metal from waste PCBs from shredding, ball milling, hammer milling and integration of the different physical pre-treatment methods with chemical pre-treatment methods. This includes determination of the optimal parameters of the pre-treatment i.e. size fraction, optimal cycles to allow for maximum delamination of the PCB layers, and of energy consumption.
- Test the application of thiosulphate leaching and ion exchange technology for gold recovery from PCB leach solutions by using selected resins and identify the best operating conditions.
- Evaluate the possibility of co-treating waste PCBs with treatment of effluent streams from PCB manufacturing and opportunities for integration of PCB recycling with manufacturing through the development of process flowsheets.
- Evaluate the possibility of re-integrating product streams such as electrolytic copper or gold solutions directly back into the manufacturing process.

3. Research Overview

Work prior to the commencement of this project has been conducted on a custom-made 'standard' PCB that has never been populated (and thus solder-free) of known composition, thereby allowing for effective comparison of data across different sets of experiments. In this sense the boards resemble the reject and off-cut material produced by PCB manufacturers, which constitute part of their solid waste stream. In order to minimise the waste generation from the manufacturing process, metal recovery from such material was under consideration by a local manufacturer (at the time called Trax Interconnect (Pty) Ltd.) and the principal chemistry to be employed was the same ammonia-based etching technique used in the manufacture of the boards, as that would potentially allow a close integration of the recycling with the manufacturing process. The foundation for this work were laid in the study by Chirume (2018, see also Moyo et al., 2020).

In line with the project objectives, the following dedicated studies were conducted expanded on the initial work by Chirume:

Pre-processing and leaching of unpopulated reject PCBs

- Study 1 – Comparison of PCB comminution methods (MSc Prestele, 2020): The comminution behaviour of unpopulated PCBs using ball mill ring mill and grab shredder was evaluated in terms of energy consumption and degree of Cu liberation during subsequent ammonia leaching using the standard procedure developed by Chirume (2019) – Section 4.
- Study 2 – Investigation of organic solvents for the delamination of shredded PCB material and subsequent ammonia leaching in column reactors (MSc Kondo, 2023): In combination with cutting and shredding, delamination of PCB pieces was investigated using various organic solvents. The most successful delamination was tested further in small percolation column reactors allowing for the slow dissolution to proceed in an unagitated system – Section 5.
- Study 3 – Development of thiosulphate leaching for Au recovery from PCBs (MSc Maharaj, 2022): As an alternative to the commonplace cyanide leaching of gold, thiosulfate dissolution of Au from PCBs and gold powder was investigated in agitated reactors against different background copper concentrations which is required as a catalyst but can become inhibitory at high concentrations – Section 6.
- Study 4 – Investigation of process sequencing between Au and Cu leaching in an integrated process (MSc Gonte, 2023): Copper leaching using the ammonia system and Au leaching using the thiosulphate system were investigated in conjunction to identify the preferred sequencing of leach and size reduction stages. The leach methods developed by Chirume (2019) for Cu ammonia leaching and that developed in Study 3 for Au thiosulfate leaching were used under standard conditions – Section 7.

Separation and recovery

- Study 5 – Investigation of direct electrowinning of Cu from ammonia liquors (Intern Mr Ortega): The direct electrowinning of Cu from the high concentration liquors obtained from the industrial operation was investigated in a batch cell and through a laboratory-scale flow-

through cell apparatus, in each case investigating the quality of the Cu deposit and energy efficiency of the plating process – Section 8.

- Study 6 – Investigation of Au recovery from thiosulphate solutions using IX resins (MSc Maharaj, 2022): Three ion exchange resins specifically targeted for anionic Au complexes were investigated through capacity, loading and elution tests using a synthetic leach liquor based on that produced in Study 3 under optimised conditions – Section 9.

Process development for populated waste PCBs

- Study 7 – Investigation of Pb-Zn solder leaching from waste PCB boards using HCl systems (Intern Mr Ortega): Various lixiviants were investigated initially with solder wire of different Pb/Sn compositions and the most promising system – HCl with $SnCl_4$ – was then tested with real populated PCBs in a column leach apparatus for selective Sn removal. Solutions with citric and nitric acid were investigated for selective Pb removal – Section 10.

- Study 8 – Considerations towards the development of an integrated process flowsheet for the complete processing of PCB boards (MSc de Wet, expected 2024; various contributors): The results and insights obtained from the forgoing 7 studies were reviewed and new, revised process flowsheet was drawn up, evolved from the initial flowsheet shown in Figure 1. A comprehensive mass balance around this flowsheet is underdevelopment for a 1000 kg/day PCB plant. Potential uses for recovered Cu and Au from the proposed process are discussed – Section 11.

Research within this project was conducted over the period January 2020 until 30 September 2023 under Prof Petersen as the Principal Investigator. The primary project leader was Dr Thandazile Moyo in her capacity as Research Officer (2020-2022), assisted by a laboratory manager (Dr Kathija Shaik), 4 full-time MSc students (Mr Mark Prestele 2018-20, Ms Dasmi Maharaj 2019-22, Ms Melissa Gonte 2021-23, Ms Ariana de Wet 2022-24) and 1 part-time MSc student (Ms Takunda Kondo 2020-22) working as an employee at the partnering PCB manufacturing plant (Trax Interconnect (Pty) Ltd., Diep River, Cape Town). Mr Fernando Ortega, as a research intern from Chile (2020-2022), worked on the solder leaching and Cu electrowinning. A postdoctoral fellow, Dr Emmanuel Ajiboye (July 2021-Jun 2023), contributed with method development and assisted in the supervision of the MSc students.

4. Study 1 – Assessment of a Grab-Shredder for Waste Printed Circuit Boards in Preparation for Ammonia-based Copper Leaching

4.1. Introduction

Metal extraction from the tightly laminated PCBs is a complicated as well as an energy-intensive process. One metal extraction route is hydrometallurgical processing which, unlike pyrometallurgical processing, requires pre-treatment of the boards for successful metal "liberation" (exposing it for contact with leach agents) through mechanical action. It is generally accepted that complete pulverization of the PCBs to ≤ 2 mm is required to achieve the complete liberation of the copper and other metals from the dielectric material (Prestele, 2020). Research has further shown that shearing or impact action forces are the most adequate forms of size reduction for e-waste (Ruan & Xu, 2016). Various milling actions, including ball, hammer, stamp, cutting and disc milling (Wang, Gu & Qi, 2005; Yoo et al., 2009; Yamane et al., 2011; Hanafi et al., 2012; Birloaga et al., 2013; Pietrelli et al., 2014) have also been considered.

Mechanical size reduction is therefore a vital stage for the recovery of precious as well as base metals. Zhou et al, 2016 reported power consumption and associated particle size distribution after cryogenic modification of PCBs; besides this, there are no other studies in literature that highlight the energy consumption and material losses associated with the individual mechanical size reduction process. Grinding of PCBs is usually the initial step of the recycling process. The generated particles from this process generally have a large particle range. Oliveira et al. (2010) investigated the liberation of precious and base metals from two types of grinders producing particles ranging in size between particle sizes of 3 and 0.2 mm. According to the authors, base metals tend to be liberated form the dielectric material in size fractions of ≤ 1.55 mm.

The objectives of this paper are to evaluate the effectiveness of the clawing mechanics of an industrial grab shredder in terms of liberating copper from the PCBs, to assess the energy consumption (at laboratory scale) of the industrial grab shredder and compare to that of methods such as the ball mill and to test the effectiveness of liberation through determining extractions in a subsequent diagnostic ammoniacal leach step.

4.2. Materials and Methodology

Custom-made printed circuit boards, 10 cm x 15 cm and 1,55 mm thickness, were supplied by Trax Interconnect (Pty) Ltd and used throughout this study. By ensuring that all the boards were of uniform material composition, design and quality; reproducibility and accurate comparison of the obtained experimental data can be achieved. Preliminary head-grade analysis conducted by Chirume (2019) on the custom-made PCBs concluded that the boards contain 22.5 % Cu which equates to a total of 11.77 g of copper per board.

Each individual PCB was size reduced at least once in a custom-made shredder Figure 2 supplied by Filamaker GmbH in Germany. The shredder has a length of 170 mm and a width of 140 mm, with 14 circular blades each of 8 mm thickness responsible for the shredding action.

Figure 2 *– Custom-made Industrial Grab Shredder*

In each test, PCBs were treated uniquely either by varying the number of passes of each board going through the shredder (referred to as shredding cycles) or by integrating the shredding with another process prior to or post treatment. A sodium hydroxide pre-treatment was carried out in 8 M NaOH solutions for 24 hrs at room temperature, removing the upper- and lower-most epoxy layers and the PCBs were subsequently shredded. In the nitrogen pre-treatment step, PCBs were dipped in liquid nitrogen, advertently freezing them and they too were subsequently shredded. Table 1 summarises the experimental conditions for the pre-treatment processes. Where milling constituted the overall pre-treatment process, milling times varied and were up to 120 min. in each case, the PCB samples were weighed before and after each size reduction method.

Table 1. *PCB treatment methods of experimental procedure*

Size Reduction Method	Shredding cycles	Milling times (min)	Material loss (g)
Method 1: Shredding only	1 – 6	-	± 0.5 g after 6 cycles
Method 2: Shredding + Planetary Ball Milling	2 4	60 & 120 60 & 120	± 0.5 g after 4 cycles
Method 3: NaOH pre-treatment + Shredding	1 – 6	-	± 0.5 g after 6 cycles
Method 4: Liq. N_2 + Shredding +	1	-	0.11 g after 1 cycle
Method 5: Shredding + Pulverization in Ring Mill	1	3	1.12 g after 1 cycle

The output material of each of the pre-treatment methods outlined in Table 1 were then screened into six size fractions in order to determine the particle size distribution (PSD). The samples, in their different size fractions were then pulverised, leached in aqua-regia and the leach solutions were analysed to determine the deportment of copper across the different size fractions.

In separate experiments, the output material from methods 1-5 were subsequently leached in ammonia-ammonium carbonate solutions (4 M NH_4OH +2 $(NH_4)_2CO_3$). Each leach test was run for over 72 hours in a jacketed stirred reactor (Figure 3a) maintained at 25 °C and pH 10, agitated at 100 rpm with an airflow of 0.1 l/min. Samples were taken every 20 min for the first hour and hourly for the next 7 hours. Thereafter, sampling occurred every 24 hours and samples were analysed for copper

content using ICP-AAS. Experiments were run in duplicates with some samples obtained in triplicate. Due to poor suspension of the PCB particles in the agitated reactors, selected tests were repeated in a bottle roller unit run at 30 rotations per minute under otherwise similar conditions (Figure 3b).

Individual power profiles of the different size reduction methods were measured and where multiple passes through the shredder were required, the power profiles were combined in succession to create a general power consumption profile.

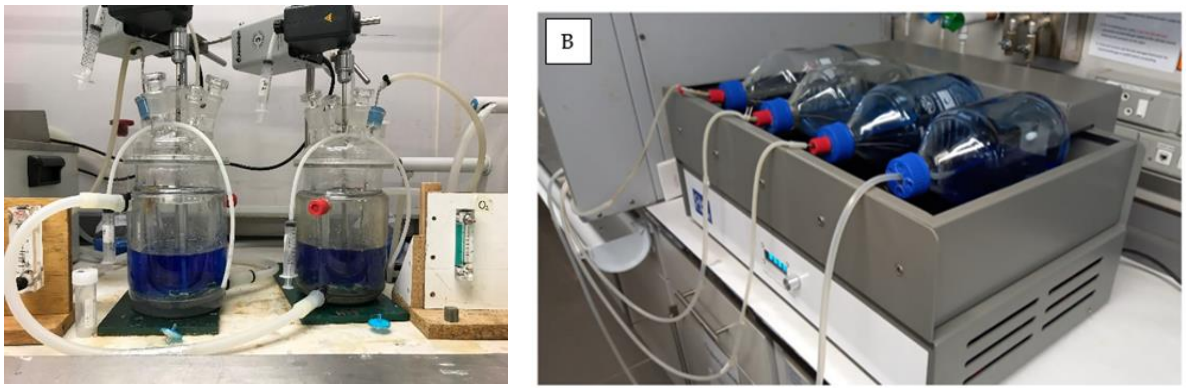


Figure 3. *(A) Overhead-stirred glass reactors (B) Bottle roller experiments (with air supply)*

4.3. Results and Discussion

Figure 4 shows a cross sectional view of the PCBs used in this study. It can be seen that there are four copper layers, two of which are just below the solder mask on the lower and upper faces of the PCB and the remaining 2 layers being closer to the FR-4 core. Figure 5 in A and C shows the upper and lower most faces of the sample PCB while B and D shows the same faces of the PCB after 24 hrs of sodium hydroxide pre-treatment. It can be seen that the sodium hydroxide pre-treatment effectively removed both the lowermost and uppermost soldier mask thereby “liberating” or exposing the copper for the subsequent leaching step. The copper closer to the FR-4 core as seen in Figure 4 remains locked away and inaccessible to leach agents and hence the need for size reduction or alternative ways to liberate it. What is not depicted in this schematic is that the precious metal is found on the upper most layers or in vias and is thus accessible without the need for size reduction (Moyo et al., 2020).

FIG

Figure 4. *Cross-sectional view of the custom-made PCB*

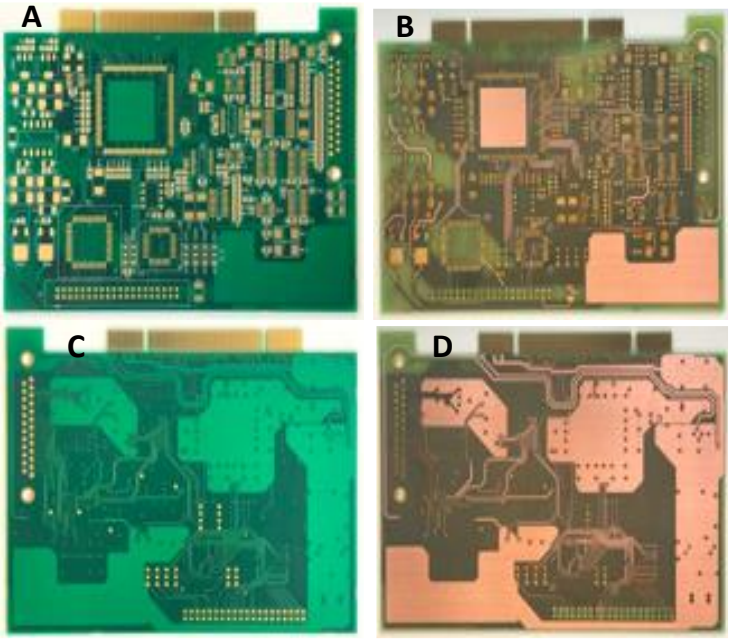


Figure 5. *Bottom and upper faces of a PCB sample prior to and after the sodium hydroxide pre-treatment*

Figure 6 shows images of a PCB after it has undergone a various number of passes through the shredder starting from a single pass in Figure 6.A up to 6 passes in Figure 6.E. Effort was made to sort the particles according to size and delamination, with the delaminated particles shown more to the right of each image. It should be mentioned that this delamination was observed to either be complete (Figure 7.B) or partial (Figure 7.A). And thus, it follows that both particle size and the extent of delamination influence the accessibility of copper found in the inner layers of the PCB.

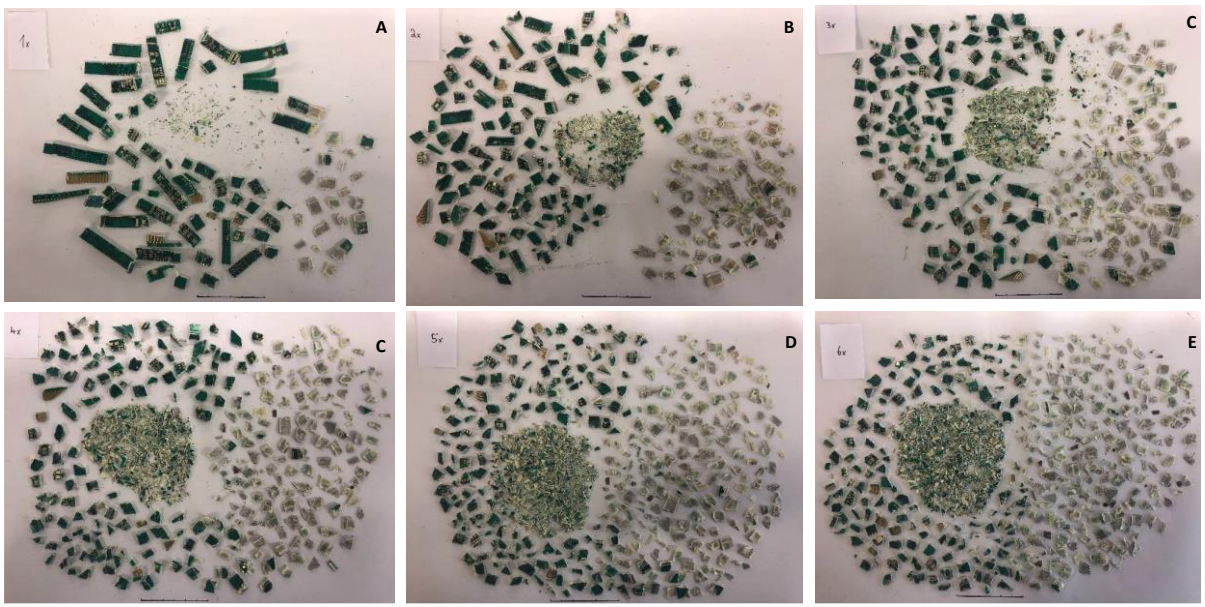


Figure 6. *Visuals of a PCB after each pass through the shredder, A being out put material after a single pass and E the output material after the sixth pass through the shredder.*

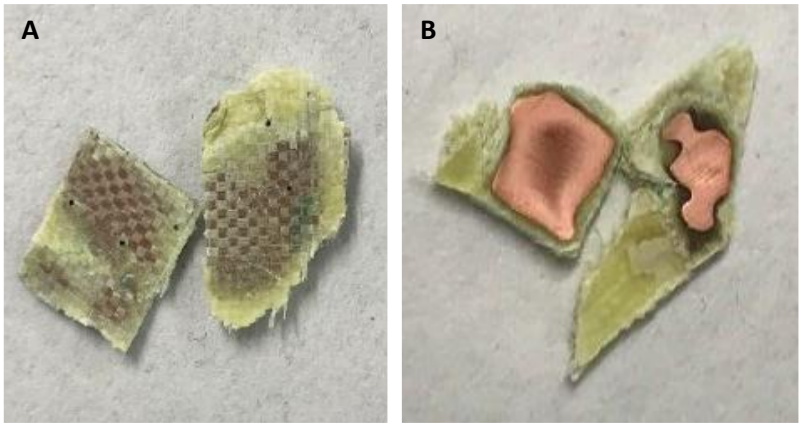


Figure 7. *Delaminated pieces of a PCB coming out of a shredder*

Particle size analysis of the PCB after the various methods of pre-treatment (Table 1) is shown in Figure 8, where 'Standard' refers to PCBs that underwent shredding only and 1st, 2nd etc indicates the number of passes i.e. 'Standard, 1st' refers to a PCB that underwent only one pass in the shredder. Under 'Liq. N_2 ' and 'Milling 1st and 2nd + 60 min' refer to a PCB that was dipped in liquid nitrogen then shredded once and a PCB that underwent two passes in the shredder then subsequently milled for 60 seconds, respectively. It is expected and evident from Figure 8 and Figure 6 that increasing the number of passes through the shredder resulted in the generation of particles passing 2000 µm. From Figure 8 it can be seen that after the 4th pass, there is no significant shift in the relative proportions of weight percentages of fractions of +6700 µm and below. However, there are still some changes in the weight fractions of particles larger than 8000 µm, but even this becomes relatively small between the 5th and 6th pass.

It was noted that dipping the PCBs in liquid nitrogen resulted in an even larger proportion of the output material reporting to +8000 µm. This was contrary to expectations. However, it was observed that the PCB treated using this method had more delaminated particles despite their large size. Unfortunately, this delamination was not complete, leaving the copper still covered in pre-preg material as illustrated in Figure 7. The results contradicted those of Zhou et al. (2016), who reported fine size reduction and good liberation when grinding particles that had undergone cryogenic pre-treatment. Notably, the feed size of PCBs used by these authors was significantly smaller than that used in the current study (4 cm^2 vs 150 cm^2).

An integration of shredding and milling showed a sharp drop in the +8000 µm particles but increasing the milling time did not result in any dramatic increases in the -2000 µm particles. Milling for 60 min after 4 passes in the shredder resulted in a significant decrease in the amount of material larger than 8000 µm.

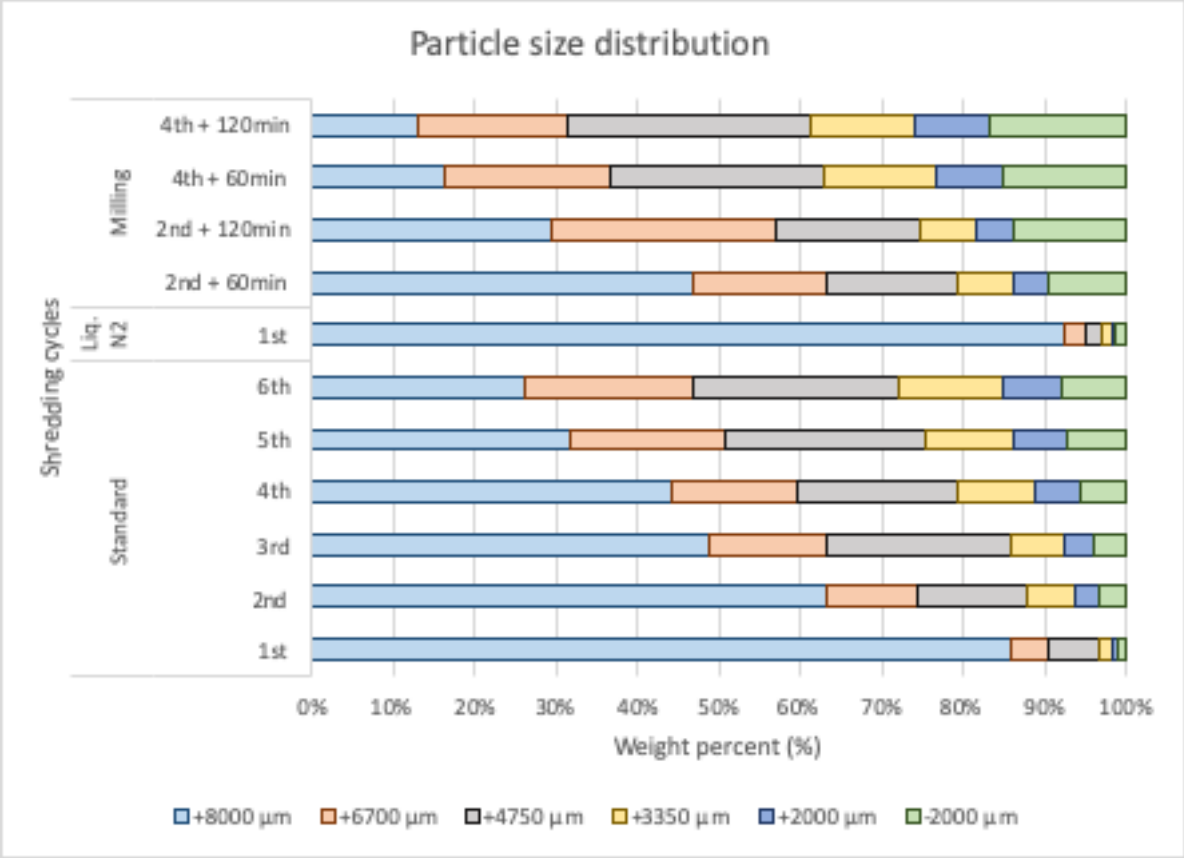


Figure 8. *Particle size distribution of the industrial grab shredder and planetary ball mill*

An analysis of copper distribution across the different size fractions and the migration of this copper with subsequent size reduction steps as per Figure 9 shows that the largest copper concentration was initially in the bigger size fractions, as expected. This was due to most copper still being trapped in the inner layers, so essentially each piece of material in this size fraction had in it a significant amount of copper. With each subsequent size reduction step, copper migrated to the more intermediate size fraction despite a notable increase in the percentage fraction of the finer material. A direct comparison cannot be made to studies reported in literature because most research has worked with more finely ground particles. There is also no consensus in literature on the ideal particle size or the particle size in which copper enrichment is highest. An observed trend across different sources (Verma et al, 2018, da Silva, et al 2019, Burat and Özer, 2018, Quan et al, 2012) has been that of any particle size range studied, copper enrichment is observed to occur in the intermediate ranges, and this is in line with observations made in the current study.

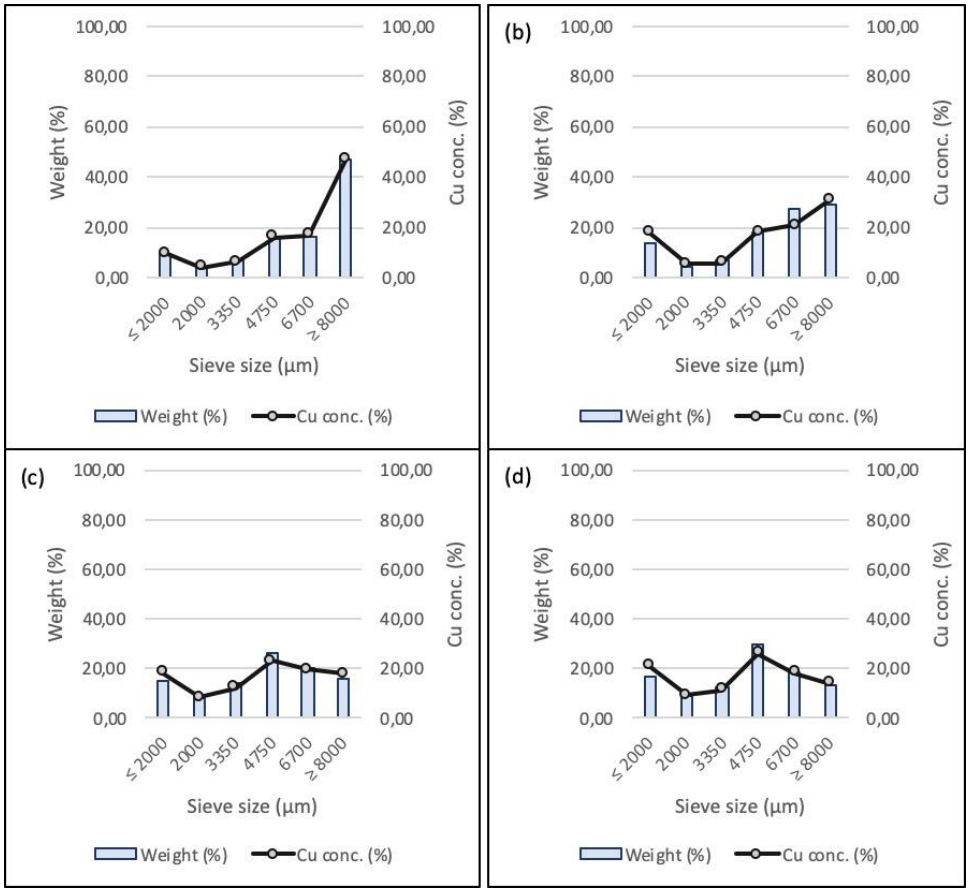


***Figure 9**. Copper concentration (as % of total Cu) and PCB weight % (a) – 2nd Shredding Cycle & 60 min milling; (b) – 2nd Shredding Cycle & 120 min milling; (c) – 4th Shredding Cycle & 60 min milling; (d) – 4th Shredding Cycle & 120 min milling*

The effectiveness of the different size reduction methods was then evaluated using ammoniacal leach tests. Figure 10 displays the copper extraction curves (%) from PCBs that were processed using the various methods using overhead stirred reactors. Method 1 (progressively shredded up to six times), Method 2 (shredded 2 & 4 times and milled in the planetary ball mill for up to 60 and 120 min), Method 3 (pre-treated in NaOH and progressively shredded up to six times), Method 4 (pre-treated in Liq. N_2 and shredded once) and Method 5 (shredded once and pulverized completely). It can be seen that PCBs processed using Method 1 performed better than the planetary ball milled and Liq. N_2 pre-treated PCBs but worse than the NaOH pre-treated PCBs. Moreover, PCBs processed using Methods 1 & 3 display an increase in extractions with progressive shredding. This is primarily a result of increased size reduction and subsequent copper liberation from the dielectric material with progressive shredding, as indicated by PSD in Figure 8. These observations were not what was expected. It had been anticipated that when the PCBs were treated using the outlined methods (Table 1) even without obtaining the smaller particle sizes reported in most leach studies, the delamination of the fibre glass layers owing to the clawing action of the industrial grab shredder used in the current study would result in copper liberation. Thus, the results from Figure 9 suggest that copper liberation from PCBs is primarily a function of size reduction rather than delamination. This is partly explained by the incomplete delamination shown in Figure 7, i.e. although the clawing action of the industrial grab shredder resulted in delamination and size reduction, the nature of the delamination was not significantly effective, with copper remaining covered by inner pre-preg layers which are impervious and thus prevent metal to lixiviant contact.

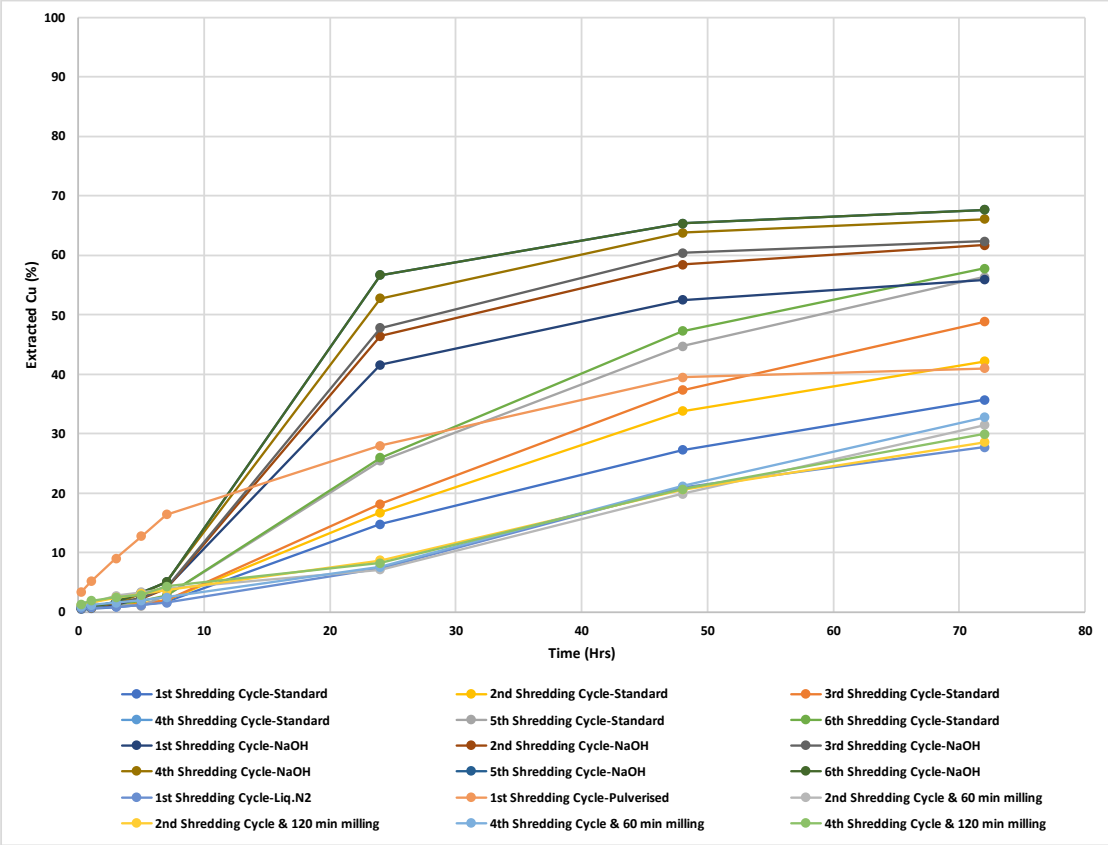


***Figure 10**. Copper concentration profile of the various size reduction methods in jacketed overhead stirred reactors. in 4 M NH_4OH +2 $(NH_4)_2CO_3$) over 72 hours at 25 °C and pH 10*

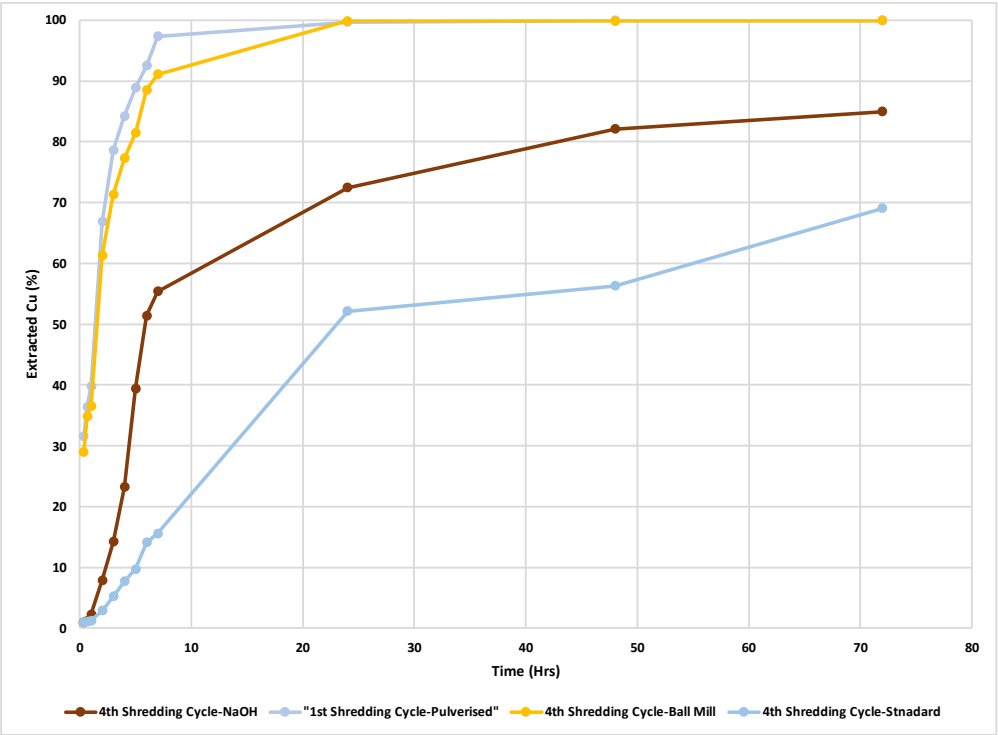


***Figure 11.** Copper concentration profile of selected size reduction methods in bottle roller tests in 4 M NH_4OH +2 M $(NH_4)_2CO_3$). 72 hours at 25 °C and pH 10*

A repeat of selected tests using bottler rollers instead of agitated reactors indicated improved extraction (Figure 11), with PCBs pre-treated via Method 2 (Shredded in 4 passes +Ball milled for 60 seconds) and Method 5 (Shredded in 4 passes and pulverised) showing 100% recovery, compared to the 33% and 41% respectively in the overhead stirred reactor tests. This significant difference in extraction is linked to the observed poor agitation in the overhead stirred reactors. It was observed that although more particles reported to the smaller size fractions, and with more visible copper, particles from Methods 2 and 5, tended to settle to the bottom of the reactor. Without effective agitation, it is expected that mass transfer would limit the reaction resulting in the settled particles leaching poorly. This was overcome by the bottle roller which effectively swirled all the contents of the reactor, overcoming mass transfer limitation, and hence improving extractions. In the bottle roller tests, Methods 1 and 3 resulted in 69% and 85% extractions compared to 51% and 66% respectively in the overhead stirred reactors. This confirms that effective agitation is an important parameter; thus, in the design of hydrometallurgical processes to leach PCBs it will be important to take into consideration the poor suspension of “highly liberated” metal particles, noting that this was not overcome by further size reducing the PCBs.

The improved extraction (100%) achieved in the bottle roller tests from PCBs pre-treated using Methods 2 and 5 align with literature that reports increased extractions with a decrease in particle size (Birloaga et al, 2013, Li et al, 2020, Yang et al, 2011). There is no consensus in literature on the effective particle size for leaching PCBs, but it appears different researchers report thresholds below which further size reduction has no significant improvement on copper extractions (Huang, 2014, Yang et al, 2011, Zhu et al, 2011).

In overhead stirred reactors, the NaOH pre-treated PCBs (Method 2) displayed the greatest degree of copper extraction (66%) over the 72 hrs leach period. This is as a result of the upper- and lower-most copper layers being exposed and hence accessible for leaching. However, these two copper layers only represent 44% of the total copper content on the PCBs used in this study (Kondo, 2023). This implies that the combination of shredding and NaOH pre-treatment allowed for the leaching of all the copper in the outer layers (44%) and the additional 22% came from the copper found in the two inner layers and the vias. In the bottle roller tests, 82% of the total copper on the PCB was leached. Since visual inspection of the leach residue showed that there was no copper on the outer layers, the unleached copper is that which remained sandwiched in the inner layers of the prepreg, which is confirmed by test that involved milling the sample without the NaOH pre-treatment resulting in 100% extraction.

The energy consumption of the shredding cycles was recorded throughout the experimental procedure and combined in succession to create the general power profile displayed in Figure 12. All power profiles start and end at a power consumption of 118.5 W which is relates to the idling power consumption of the grab shredder. Furthermore, it must be noted that the shredding time decreases considerably 14 seconds for the first cycle to about six seconds for the fourth cycle. The 1st cycle requires the most time due it being the preliminary size reduction cycle. The time required decreases thereafter as the size of particles progressively decreases. The time required for shredding then increases again to just above eight seconds for both the fifth and sixth shredding cycles. This is the result of particles having reached smaller sizes that actively choke the shredder chamber, requiring more time and effort to bring about size reduction and delamination.

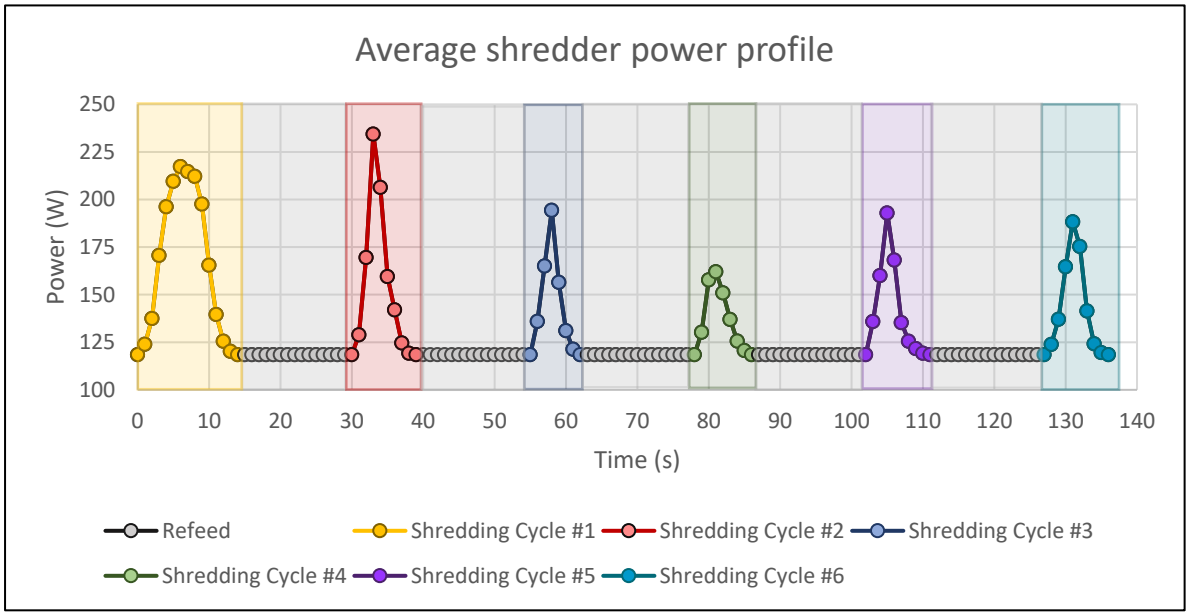


***Figure 12**. Power profile of the industrial grab shredder including intermediate re-feed times*

***Table 2.** Results of power measurements for different shredding configurations*

Shredding cycle	Cycle time	Energy per PCB (J)	kWh/kg	Cumulative Energy (kWh/kg)
1st	14	690	0.0037	0.0037
2nd	9	340	0.0018	0.0055
3rd	7	193	0.0010	0.0065
4th	7	158	0.0008	0.0073
5th	9	209	0.0011	0.0085
6th	9	237	0.0013	0.0097
Shredder + Ball Mill	-	336 170	1.7889	-
Shredder + Pulveriser (Ring mill)	-	450 690	2.398	-

Table 2 shows the energy consumption of the shredder and the combination of shredder and ball mill/pulveriser (Methods 2 and 5). This was determined by integrating over the length of each shredding cycle and adding the energy consumption from the ball mill or the pulveriser (Methods 2 and 5). From Table 2 it is apparent that significantly more energy (1.8 kWh/kg and 2.4 kWh/kg) was consumed to allow for the extraction of 100% of the Cu in the leaching step when Methods 2 and 5 were used. Furthermore, Method 5 was difficult to operate even at laboratory scale owing to the sample heating up causing smearing of the mill as components of the PCB melted. Shredding in 4 passes allowed for the extraction of 85% and 69% of the Cu with and without NaOH pretreatment respectively. The shredding in 4 passes consumed orders of magnitude less energy than that which was consumed in Methods 2 and 5.

4.4. Conclusion & Recommendations

The clawing mechanics of the industrial grab shredder have proven to be moderately effective in terms of the liberation of Cu. It has been shown that with progressive shredding an increase in the number of delaminated particles occurs simultaneously with the generation of finer particles. However, some particles favoured partial delamination which failed to effectively expose the Cu that is situated underneath the tightly woven (pre-preg) fibreglass layers. Although increasing the number of shredding passes improved extraction, at least in the first 4 shredding cycles, it did not maximise extraction with the highest extraction reached from shredding alone sitting at 69% and this improved to 85% when combined with NaOH pre-treatment in bottle roller tests.

Shredding of frozen (Liq. N_2) PCBs resulted in a higher degree of delamination but this was only partial delamination and did not result in increased copper leaching. Further size reduction using a ball mill or pulveriser led to 100% extraction of the copper while increasing energy consumption by four orders of magnitude. And thus, use of the industrial grab shredder shows significant potential as an energy efficient approach to liberating Cu from waste PCBs. Therefore, Method 3 which combined NaOH with shredding, is worth further investigation, looking at how extractions can be improved and evaluating the recyclability of the NaOH into the process.

5. Study 2 – Evaluation of solvent swelling pre-treatment for copper recovery from waste printed circuit boards

5.1. Introduction

A typical treatment route for treating waste PCBs is smelting in integrated pyro-hydrometallurgical operations such as the one at Umicore in Belgium 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, whereas such operations are unlikely to be efficient at the small to medium scale as would be desirable in a developing economy where challenges such as poor e-waste collection, high energy costs and poor supportive legislative frameworks prevail (Moyo et al., 2022).

In contrast, hydrometallurgical processing routes, such as solvent swelling for metal liberation and oxidative ammonia leaching, have proven to be promising for minimizing cost, environmental impact and maximizing 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 13.

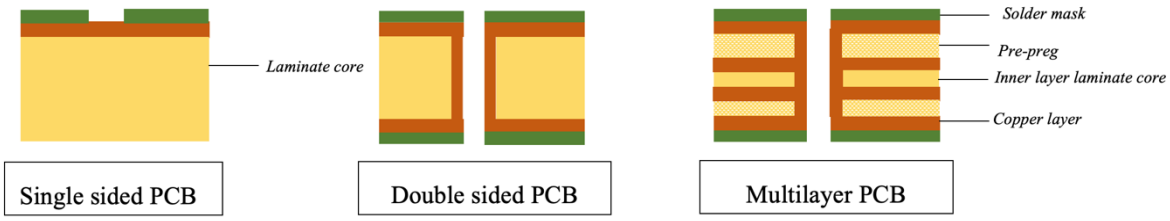


Figure 13. *Classification of PCBs by conducting layers*

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 12 conductive layers pressed together with semi-cured pre impregnated resin “pre-preg” which acts as glue between the copper layers to yield a tightly laminated composite as illustrated in Figure 14.

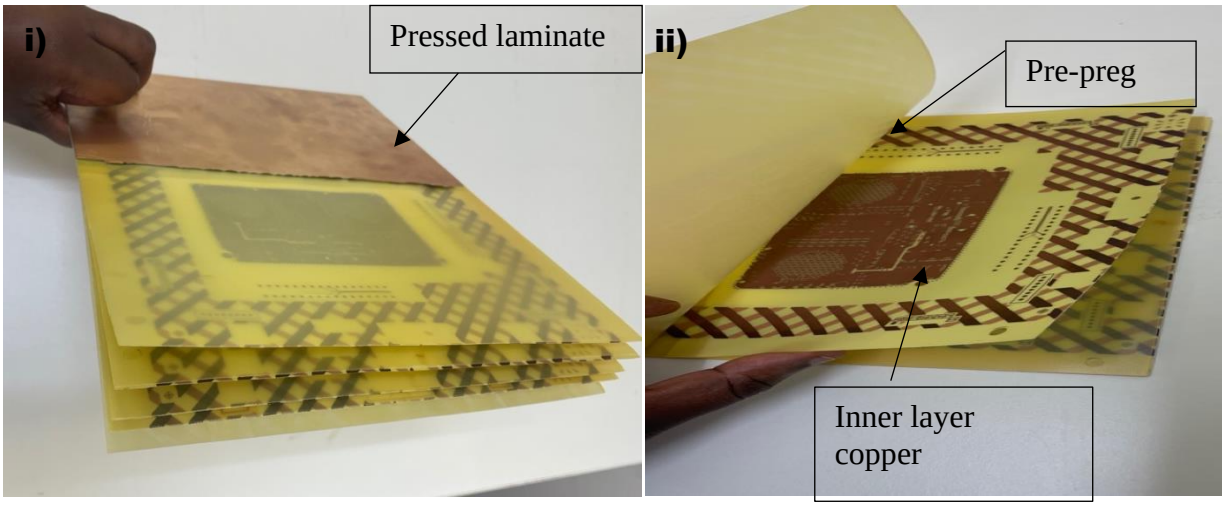


Figure 14. *Deconstructed illustration of a 10 layer multilayer PCB sample supplied by Trax Interconnect i) Top surface copper layer and 1st pre-preg layer ii) Inner layer copper*

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 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 pulverizing (Cui & Anderson, 2016; Sethurajan et al., 2019).

Prestele (2020) detailed the optimization 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 utilized 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 as detailed in Table 3 include N-Methyl-2-

pyrrolidone (NMP), dimethyl sulfoxide (DMSO), di-methyl formamide (DMF) and Dimethyl acetamide (DMAc).

Table 3. *Comparison of PCB Solvent swelling studies in literature*

Author	S/L ratio	Organic solvent	Temperature	Reactor configuration	Reaction time	Particle size	Degree of copper liberation
(Wath et al., 2015)	1:5	NMP	100 °C	Flask with condenser and manual stirring	90min	16mm^2	Complete delamination and separation
	1:2	DMSO	90°C			36mm2	
(Zhu et al., 2013)	1:7	DMSO	145°C	Flask with condenser and manual stirring	60 min	16mm2	Complete delamination and separation
(Monteiro et al., 2021)	1:3	NMP	200 °C	Microwave	10min	25 mm^2	Significant delamination and separation
			153 °C	Thermostatic	10min		Minimal delamination and separation
			60 °C	Ultrasonic	25hrs		Partial delamination and separation
(Tatariants et al., 2017)	300g PCB:1L solvent	DMF	25 °C	Ultrasonic	30-70hrs	100 mm^2	Complete delamination and separation
			50 °C		10-20hrs		Complete delamination and separation
			75 °C		5-10hrs		Complete delamination and separation
(Yousef et al., 2018)	300g PCB:1L solvent	DMF	50 °C	Ultrasonic	16hrs	Full size PCB	Complete delamination and separation

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 processes utilizing 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 Trax Interconnect (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). Reaction (1) shows how copper metal is dissolved by reacting with cupric ions in the cupric chloride ammonia complex solution (Chemcut Corporation, 2002; Koyama, Tanaka & Lee, 2006).

$$Cu + Cu(NH_3)_4Cl_2 \rightarrow 2Cu(NH_3)_2Cl \quad (1)$$

The resulting cuprous product is immediately oxidized by oxygen as illustrated in Equation (2).

$$2Cu(NH_3)_2Cl + \frac{1}{2}O_2 + 2NH_3 + 2NH_4Cl \rightarrow Cu(NH_3)_4Cl_2 + H_2O \quad (2)$$

The total reaction can be summarized by Equation (3).

$$Cu + \frac{1}{2}O_2 + 2NH_3 + 2NH_4Cl \rightarrow Cu(NH_3)_4Cl_2 + H_2O \quad (3)$$

The etching process in PCB manufacturing often generates excess amounts of copper-bearing waste etchant as is observed at Trax. The cupric ion present in this waste etchant acts as an oxidizing agent to dissolve metallic copper (Radmehr et al., 2013) through the redox reaction illustrated by Equation (4) (Habashi, 1963).

$$Cu + Cu(NH_3)_4{}^{2+} \rightleftharpoons Cu(NH_3)_2{}^{+} \quad (4)$$

An example of this can be seen in the study by Koyama, Tanaka & Lee (2006) where the percentage of dissolved copper after 4 hours of leaching increased from 1 to 82% by increasing the cupric ion concentration from 0 to 0.3 kmol/m^3. This concentration is up to five times less than the copper concentration of a typical PCB manufacturing etchant. Hence PCB manufacturing etchant contains abundant oxidant as the copper content can be as high as 150g/L as seen at Trax thus making it a promising lixiviant for waste PCB recycling.

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) as illustrated in Figure 15.

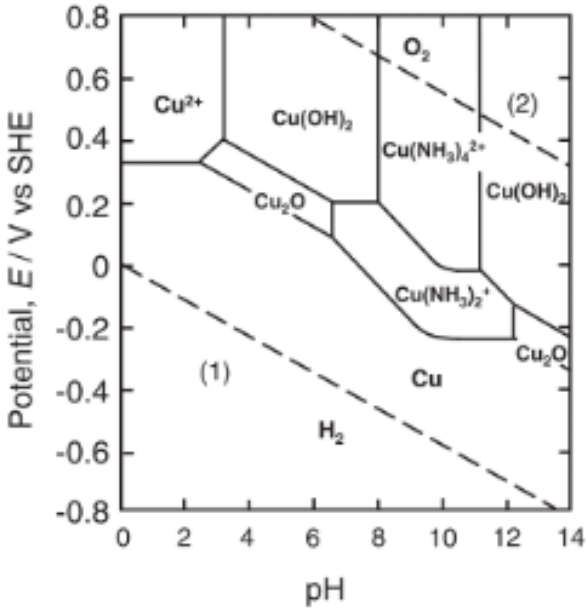


Figure 15. *Potential-pH diagram of the copper ammonia complex (Koyama, Tanaka & Lee, 2006)*

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. Thus, a significant part of the hydrometallurgical flowsheet for copper recovery from waste PCBs can be tested in a bench scale setup prior to future pilot scale testing. The chemistry required for this industrial process is well understood and currently in use in most PCB manufacturing factories, therefore it is of interest to investigate the ability of PCB manufacturing NMP based solvent to achieve sufficient metal liberation through solvent swelling for a viable industrial process.

5.2. Materials and methods

5.2.1. Printed Circuit Boards

The PCBs used throughout the experiments were unpopulated, solder-free 4-layer boards manufactured by Trax Interconnect. Figure 16a illustrates the top surface layer of the PCB and Figure 16b illustrates the bottom surface layer of the 142 x 102 x 1,55mm PCB.

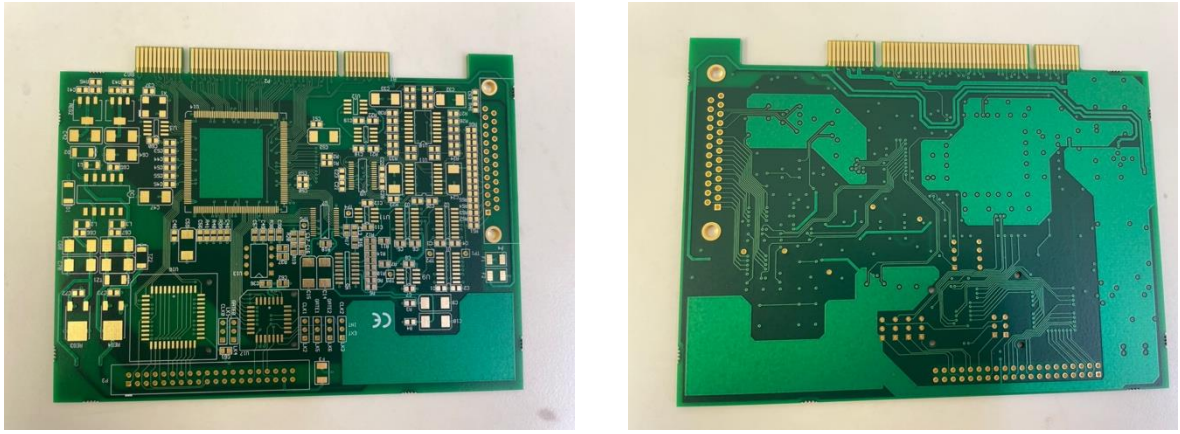


***Figure 16**. Images of the custom-made PCBs: a) top surface layer (Layer 1); b) bottom surface layer (Layer 4)*

The copper content of the PCB was determined by measuring the thickness of each of the 4 copper layers on the PCB (see **Error! Reference source not found.**).

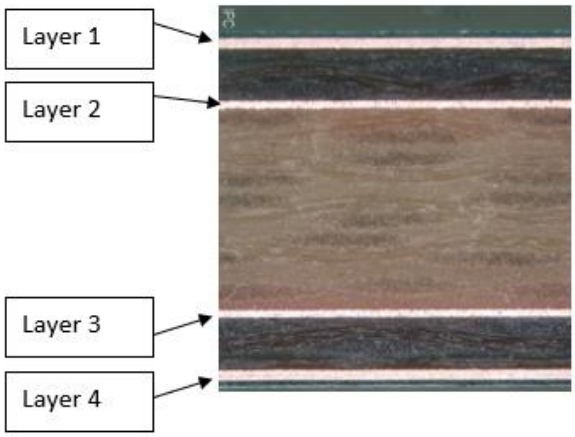


***Figure 17.** Coupon B X50 magnification view of copper layers*

A total of 5 samples were analysed and the resulting copper thickness of each layer measured using a metallographic microscope as detailed in Table 4. 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/cm^3 (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 agreeable with the theoretical copper mass determined by the PCB manufacturer from the design stack up and copper area with a 6% difference attributed to the allowable process tolerance. One of these custom-made PCBs was used in each test of the various solvent swelling methods described below ensuring repeatability.

Table 4. *Copper thickness measurements of each copper layer on coupons A-E in µm vs design stack-up thickness readings*

	A	B	C	D	E	Average measured Cu thickness [µm]
layer 1	40	50	45	40	35	**42**
layer 2	33	32	-	32	30	**32**
layer 3	33	32	35	32	-	**33**
layer 4	50	40	-	50	50	**48**
holes	25	-	-	35	-	**30**

5.2.2. 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 2x1.5cm pieces for the purposed of fitting into the 3L reactor (Figure 18). The PCBs were reacted in solvent for 90 minutes at a temperature of 150°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.

Figure 18. *Solvent swelling reactor setup*

<u>Solvent swelling NMP vs NMP based proprietary solvent (Solvent B)</u>

The laminate material used to manufacture the custom-made PCBs was FR-4 with a glass transition temperature (Tg) of 150 ^{o}C. The Tg is the temperature above which the rigid laminate material begins to soften (Pacáková & Virt, 2005), hence the solvent swelling temperature used was 150 ^{o}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 with 50g/L starting copper concentration. Synthetic etchant was utilized 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) (see also Section 4). 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.

5.2.3. Diagnostic copper leaching

Diagnostic leaching was carried out as an indicator of the extent of copper liberation from the preceding solvent pre-treatment processes. Two lixiviants were utilized, namely waste etchant collected from Trax with 150g/L copper content and synthetic etchant prepared as detailed in Table 5.

Table 5. *Preparation methods for lixiviants utilized*

lixiviant	Preparation method
Waste etchant	A sample was collected from the waste stream at Trax Interconnect. The copper content was analyzed by complexometric titration with EDTA and determined to be 150g/L.
Synthetic Etchant	50g/L Synthetic etchant was made up by dissolving 100g of pure copper foil in a solution with 200g NH_4Cl dissolved in 500ml de-ionized water and 500ml NH_4OH. Upon dissolution of the copper foil, the solution was made up to a final volume of 2L with DI water. The final pH was adjusted to 10 by adding ammonia. 10g/L Synthetic etchant was made up by dissolving 20g of pure copper foil in a solution with 40g NH_4Cl dissolved in 500ml de-ionized water and 150ml NH_4OH. Upon dissolution of the copper foil, the solution was made up to a final volume of 2L with DI water. The final pH was adjusted to 10 by adding ammonia.

The experiments were 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 1-6 L/day. The pregnant leach solution flowed through an outlet at the bottom of the column as illustrated in Figure 19 and was continuously circulated through the column.

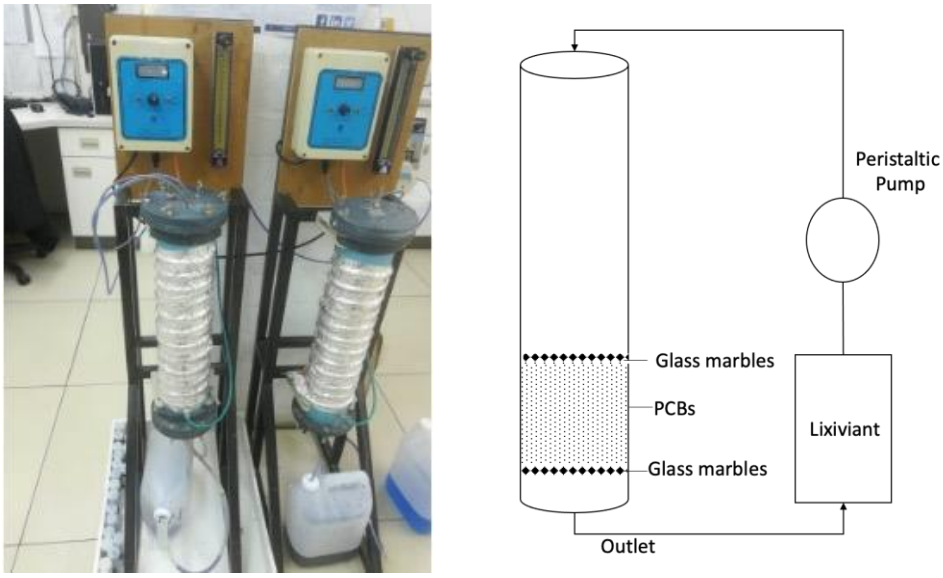


Figure 19. *Leaching column configuration*

The procedure utilized for diagnostic leaching was as detailed below.

1. Pre-treated PCBs were added to the reactor column.
2. 2L 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 (AAS) 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. Given the excess amount of copper present in the lixiviant, sufficient oxidant was present in the form of cupric ion to oxidize 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.

5.2.4. 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 experiment 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 20. Thereafter the cut pieces were charged to the leaching column.

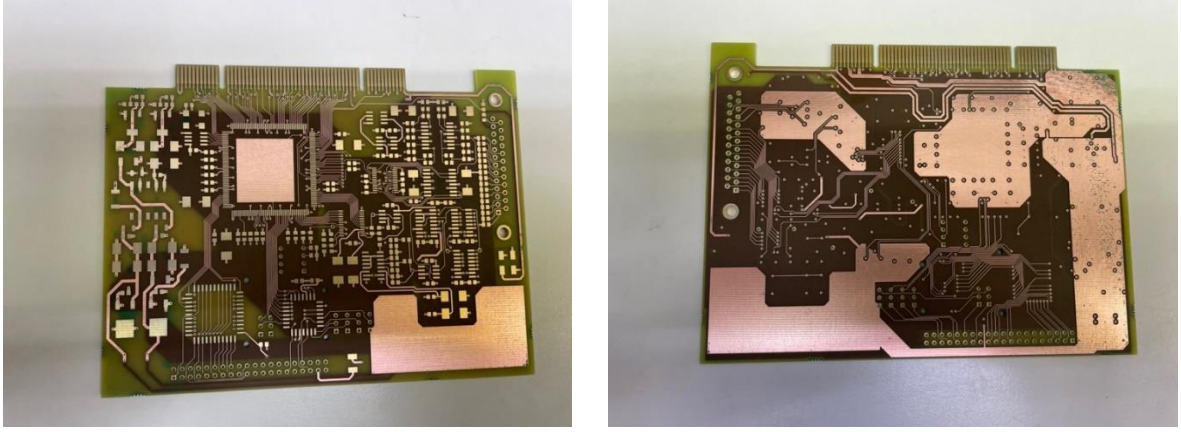


***Figure 20**. PCB after sodium hydroxide soak for solder mask removal*

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 utilized for leaching the mechanically shredded PCBs as illustrated in Table 6. The waste etchant collected from Trax was utilized in experiments 6 and 7.

***Table 6.** 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 min	Synthetic etchant-50g/L
2	Solvent B	150 °C	90 min	Synthetic etchant-50g/L
3	Solvent B	150 °C	90 min	Synthetic etchant-10g/L
4	Solvent B	150 °C	90 min	Synthetic etchant-10g/L
5	Untreated	-	-	Synthetic etchant-50g/L
6	Untreated	-	-	Waste etchant
7	Solvent B	150 °C	90 min	Waste etchant

5.3. Results and discussion

5.3.1. Evaluating of solvents NMP and Solvent B

Figure 21 illustrates the leaching profile of the pre-treatment comparison tests between NMP and Solvent B.

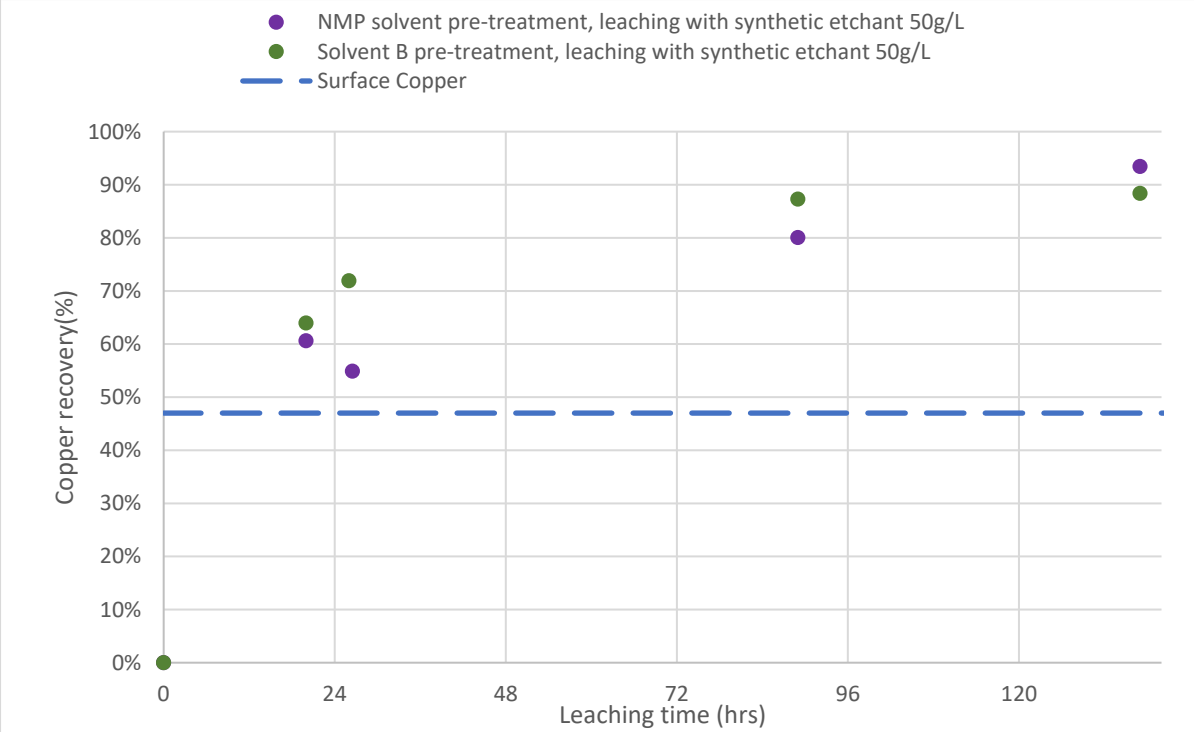


***Figure 21**. Comparison in performance of swelling with NMP in experiment 1 and Solvent B in experiment 2 at 150℃*

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 22). 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 2.** 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 23 illustrates residual pieces of PCBs after copper leaching. Some remaining inner layer copper was present as seen through the yellow laminate material.

Figure 23. *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 24. 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.

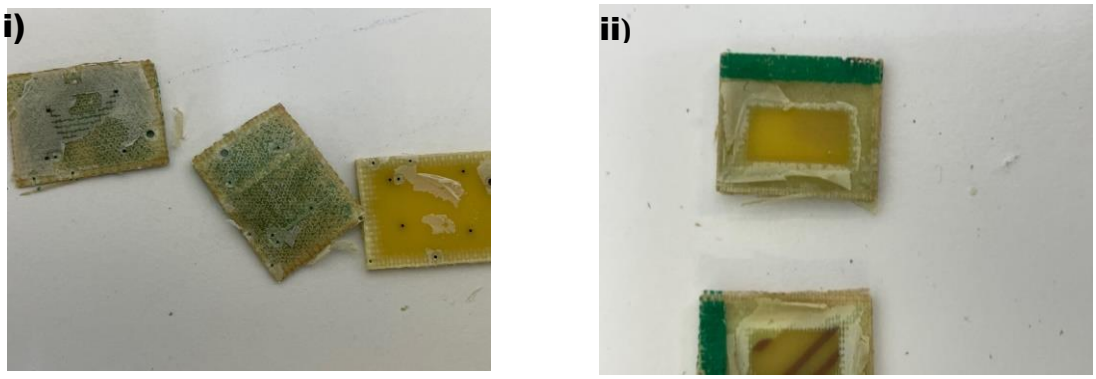


Figure 24. *i) Swelled PCBs with layers separated ii) residual copper trapped under pre-preg*

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.

5.3.2. 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 24.ii).

It was postulated that combining solvent swelling with mechanical shredding would aid in further delamination. Hence experiment 3 was conducted in which the PCB size was reduced from 2 x 1.5cm to < 8 mm thus increasing the surface area for subsequent solvent swelling. In addition, experiment 4 was carried out to determine the extent to which delamination was aided by shredding the boards to <8mm after swelling and prior to leaching.

Figure 25 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 minimize 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.

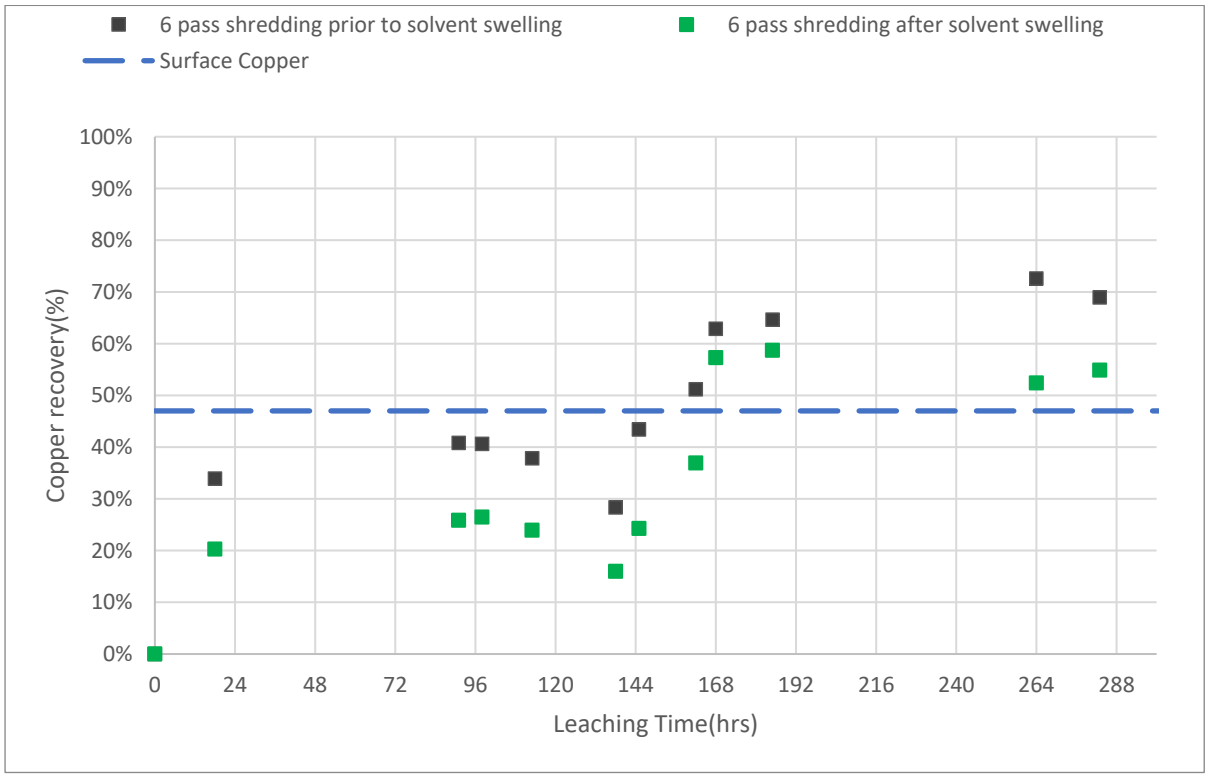


Figure 15. *Copper extraction curves for solvent swelled PCBs leached with synthetic etchant prior to solvent swelling in experiment 3 and after solvent swelling in experiment 4.*

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%.

5.3.3. Evaluation of diagnostic leaching

The performance of the lixiviant was measured by the leaching time required to completely extract the surface copper. Figure 26 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 1st 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.

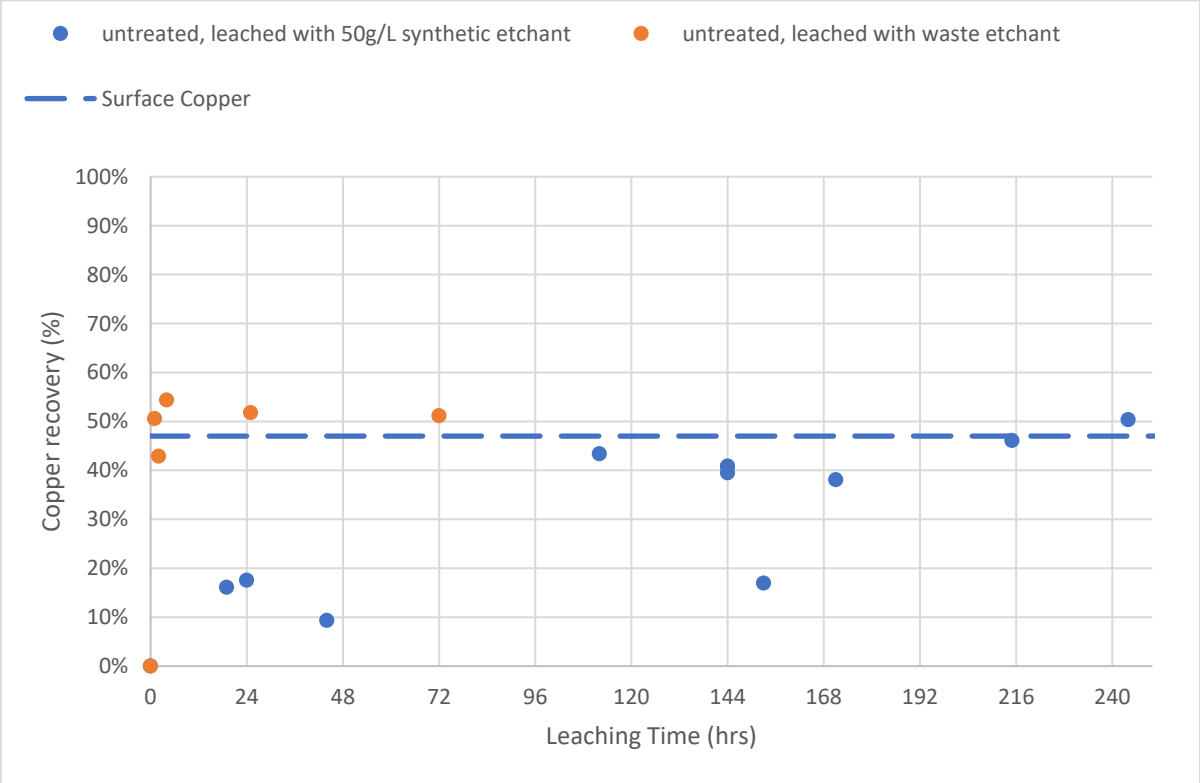


Figure 26. *Copper ectraction curves for untreated PCBs leached with synthetic etchant (experiment 5) and waste etchant (experiment 6)*

Analysis of the leaching curve for the waste etchant highlights an initial drop in copper recovery from 50.6% after 1 hour to 42.9% after 2hrs, 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 above 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 utilized 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 27 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.

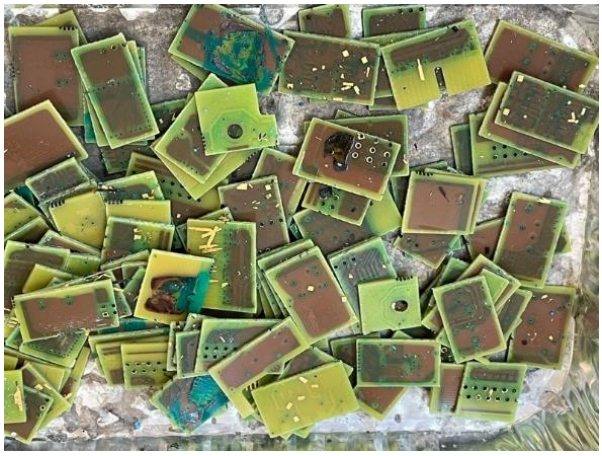


Figure 27. *Untreated PCBs in experiment 6 after leaching with waste etchant.*

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 PCB etching processes at Trax. This will aid in minimizing precipitation by maintaining the copper concentration of the lixiviant within a determined range. In addition, the copper extraction through solvent swelling

releases free ammonia back into the recycled lixiviant as illustrated, thus reducing reagent consumption.

5.4. Conclusions

In the current 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 utilized in PCB manufacturing, specifically waste etchant in the hydrometallurgical recovery of copper from waste PCBs. This required firstly the creation and characterization of a standard PCB due to the difficulties associated with characterizing 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 characterization 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 utilized in this study were ammonia/ammonium chloride-based waste etchant from 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. This highlighted the need for integration of the extraction stage with a unit for the recovery of copper from the lixiviant to maintain the copper content below saturation levels.

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.

6. Study 3 – Gold thiosulphate leaching from PCBs

6.1. Introduction

PCBs contain a large variety of precious and base metals. Base metals, such as copper and tin are found underneath the protective coatings of the board and precious metals, such as gold and silver are present on the surface of the board. On PCBs, gold is typically found in high concentrations, with some studies reporting figures as high as 903 g/t (Petter et al., 2014) while typical primary gold ores contain only between 10 to 90 g/t (Jeffrey, Breuer & Chu, 2003; Arslan & Sayiner, 2018). Although there is a trend to use less precious metal in the manufacturing of PCBs, the waste stream still outmatches primary ores, whose grades are decreasing, whose minerology has become more complex and which are much more difficult to mine.

There are many challenges to the processing of PCBs. Some of these challenges include their complexity and heterogeneity. Industrially, metal recovery of e-waste is carried out mainly via pyrometallurgical routes (Cui & Anderson, 2016) mostly by using PCBs as co-feed to a copper smelter. Though these routes do have disadvantages, mainly around the large energy requirements for processing and shipping collected WEEE over long distances, the precious metals can be recovered separately from the produced Cu through the processing of anode slimes from electrorefining. The overall recovery of Au through this route from the original feed is unclear, but unlikely to be more than 80% due to Au losses to flue dusts, slag, or incorporation into the cathode copper product.

Active research in the past 20 years has been carried out to find direct hydrometallurgical routes as a viable alternative for operation at small scale. Hydrometallurgy is perceived to have a lower environmental impact and is easier to manage (Cui & Zhang, 2008). The ammonium thiosulphate system is one such hydrometallurgical option. The system is non-toxic as opposed to its competitor, the cyanide system, and has been shown to extract gold at much faster rates (Sullivan & Kohl, 1997; Aylmore & Muir, 2001; Jeffrey et al., 2001).

The gold-thiosulphate complex is formed via two reactions in the ammonium thiosulphate system as per reactions (5) and (6). Initially the gold-ammonia complex is formed on the gold surface (5) with cupric acting as the oxidant, before converting into the gold-thiosulphate complex (6). The overall dissolution reaction of gold in an ammonium thiosulphate solution in the presence of cupric ions is represented in reaction (7).

$$Cu(NH_3)_4^{2+} + Au + 3S_2O_3^{2-} \rightarrow Au(NH_3)_2^{+} + Cu(S_2O_3)_3^{5-} + 2NH_3 \quad (5)$$

$$Au(NH_3)_2^{+} + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2NH_3 \quad (6)$$

$$Au + Cu(NH_3)_4^{2+} + 5S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3 \quad (7)$$

The heterogenous redox reaction between oxygen and copper is shown in reaction (8) (Fleming et al., 2003). Here the cupric ion concentration eventually reaches steady state and at this point the rate of reduction of the cupric ions through gold dissolution is matched by the rate of oxidation of the cuprous ions by oxygen. Thus, the cuprous ions serve as a redox catalyst in the leaching process and are not consumed.

$$4Cu(S_2O_3)_3^{5-} + O_2 + 16NH_3 + 2H_2O \rightarrow 4Cu(NH_3)_4^{2+} + 12S_2O_3^{2-} + 4OH^- \quad (8)$$

The overall redox reaction forming the gold-thiosulphate complex is shown in reaction (9). The cupric-amine complex and the ammonia within the system are recycled therefore need not appear in the overall reaction (9) (Xia, 2000).

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 4Au(S_2O_3)_2{}^{3-} + 4OH^- \quad (9)$$

However, cupric is also known to interfere in this reaction by slowly catalysing the oxidation of thiosulphate to higher oxidation products such as tetrathionate, thus effectively destroying the leaching reagent (Fleming et al., 2003):

$$2\ S_2O_3^{2-} +\ 2\ Cu(NH_3)_4^{2+} \rightarrow S_4O_6{}^{2-} + 2\ Cu(NH_3)_2^{+} + 4\ NH_3 \quad (10)$$

The leaching of a high-grade gold ore by ammoniacal solutions of ammonium thiosulphate was investigated by Abruzzese et al. (1995). They found the dissolution was favourable at ambient temperature, moderate copper concentration (0.1 M) at elevated concentrations of $(NH_4)_2S_2O_3$ (2 M) and NH_3 (4 M). The system has been used for the leaching of gold from waste cell phone PCBs by Ha et al. (2010) and Tripathy et al. (2012). Substantially better gold dissolution was achieved by leaching from whole boards compared to shredded boards, postulated to be due to the interference of copper which preferentially dissolved from the shredded material. The role of copper in the thiosulphate leaching of gold was investigated further in the present study with both pure gold powder as a base line and custom-made PCBs.

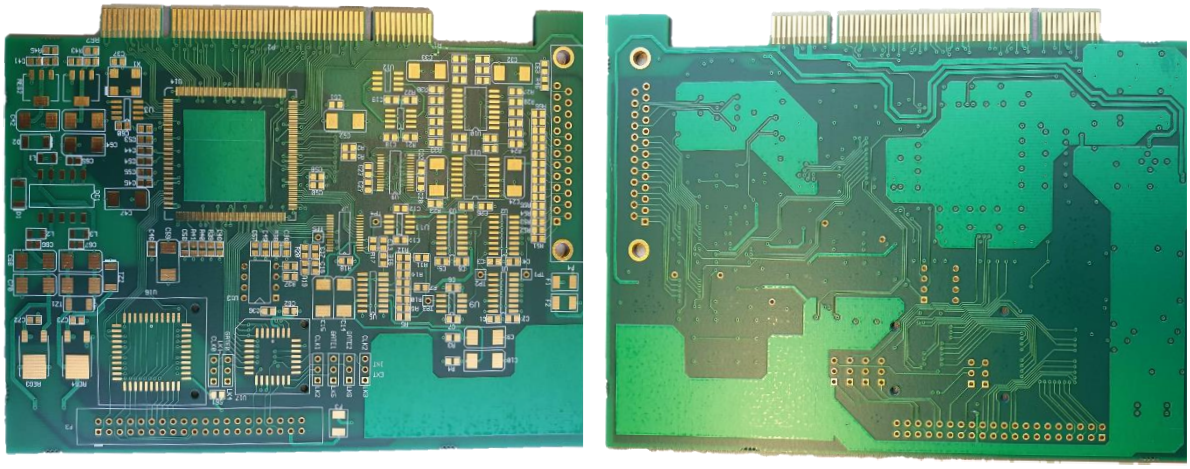
Active research in the past 20 years has been carried out on hydrometallurgical routes to find a viable alternative to the conventional cyanide route to extract gold from its sources. The ammonium thiosulphate system is one of these options. The system is non-toxic as opposed to the cyanide system, and has been shown to extract gold at much faster rates (Sullivan & Kohl, 1997; Aylmore & Muir, 2001; Jeffrey, Breuer & Choo, 2001).

The present work aims to provide a study of the thiosulphate dissolution of gold from gold powder as a reference and compare it to the leaching of gold from waste PCBs for the beneficiation of precious metals from the PCB waste stream.

6.2. Experimental

6.2.1. Materials

The PCBs used in all experiments were custom made boards manufactured by Trax Interconnect (Pty) Ltd. The dimension of the boards was 142 x 105 x 1.55 mm. All boards were of the same composition, dimension and framework and were manufactured from the same type of materials, thus ensuring that accurate comparison and reproducibility of the experiments could be accomplished. The following Figure shows both the top-side and the bottom-side of the board.



(a) *(b)*

***Figure 28**. (a) Top-side of the PCB (b) Bottom-side of the PCB*

The gold-coloured areas in Figure 19 indicate the gold-nickel alloy that has been plated onto the board as contacts. These contacts are initially exposed copper not covered by the solder mask which is electroplated with nickel and the nickel is subsequently electroplated with gold in the manufacturing process. Thus, the gold present on the board is partially in the form of a nickel-gold alloy. The contacts are thus exposed to allow any interaction between the gold and the leach solution.

The mass of gold on the board was quantified utilising the thickness of the gold plating on the board as well as the area of the gold-plated contacts on the top and bottom layers. The gold plating thickness was 0.07 µm as provided by the manufacturer. Incorporating the gold density, in addition to the gold area and thickness, produced the mass of gold for a single board. Table 7 contains both the area and mass of gold on the top and bottom outer layers.

***Table 7.** Gold distribution in area and mass on the top and bottom layer of a single PCB*

	Area (m^2)	**Au mass (mg)**	**Gold distribution (%)**
Top layer	2.33×10^{-3}	3.15	74.8
Bottom layer	7.87×10^{-4}	1.06	25.2
Total	3.12×10^{-3}	4.22	100

The mass of gold was thus determined as 4.22 mg per board which was taken as the initial gold concentration of the samples. The mass of copper present on a single board was 11.8 g.

Premion® 99.99% gold powder, supplied by Alfa Aesar, was utilised in the gold powder reference studies.

6.2.2 Methods

Leaching experimentation was carried out in a jacketed batch stirred tank reactor (BSTR) fitted with an overhead stirrer (400 rpm) and a water bath for temperature control (25°C). A total of three 1 L BSTRs were utilised and the experimental reactor set up is displayed in Figure 29. Air was used as the oxidant and was bubbled through each reactor. The air flow (0.07 L/min) was monitored by the flow meter shown on the right.

Figure 29: *Schematic illustration of leaching reactor (left) and experimental set up of batch stirred tank reactors.*

In the leaching experiments, ammonia and ammonium thiosulphate were used and copper (II) sulphate pentahydrate was added in small amounts to catalyse the reaction. Table 8 lists the various conditions for all leaching experiments on PCBs. A standard solution consisting of ammonium thiosulphate, ammonia and copper (II) sulphate pentahydrate was first prepared for the 24-hour gold powder experiment. The concentrations of the lixiviants used were as follows: 0.5 M ammonium thiosulphate, 0.5 M ammonia and 0.02 M background copper sulphate (II) pentahydrate.

Table 8. *Lixiviants and conditions for ammonia-ammonium thiosulphate leaching*

Lixiviants/Conditions	**Units**	**Values**
$(NH_4)_2S_2O_3$ concentration	M	0.5
$CuSO_4.5H_2O$ concentration	M	0.008/ 0.02/ 0.045/ 0.1
NH3 concentration	M	0.5
pH	-	9 - 10
Temperature	°C	25
Time	Hours (h)	6/24
Stirring speed	Revolutions per minute (rpm)	400
Volume	mL	500
Compressed air flowrate	L/min	0.07
Solid to liquid ratio*	-	1:10
Gold powder**	mg	56

*Applies only to PCB experiments. **Applies only to gold powder experiments

Leaching tests conducted on the PCBs followed the same procedure. One PCB cut to 2 x 2 cm pieces was leached in each reactor. The blade of the overhead stirrer was immersed into the solution allowing for it to be slightly above the cut PCBs whilst at the same time allowing continuous mixing of the solution.

6.3. Results and Discussion

Figure 30 depicts the gold extraction over 24 hours for gold powder dissolution. The curve for the dissolution of gold powder shows a sharp increase within the first 2 hours, thereafter a small but gradual increase until 21 hours with maximum extraction at 98.8%, after which the extraction declines again. Within the first 2 hours, a fast dissolution rate was expected due to the fast leach kinetics of the system as proposed by Breuer & Jeffrey (2000) in the presence of oxygen and this was evident.

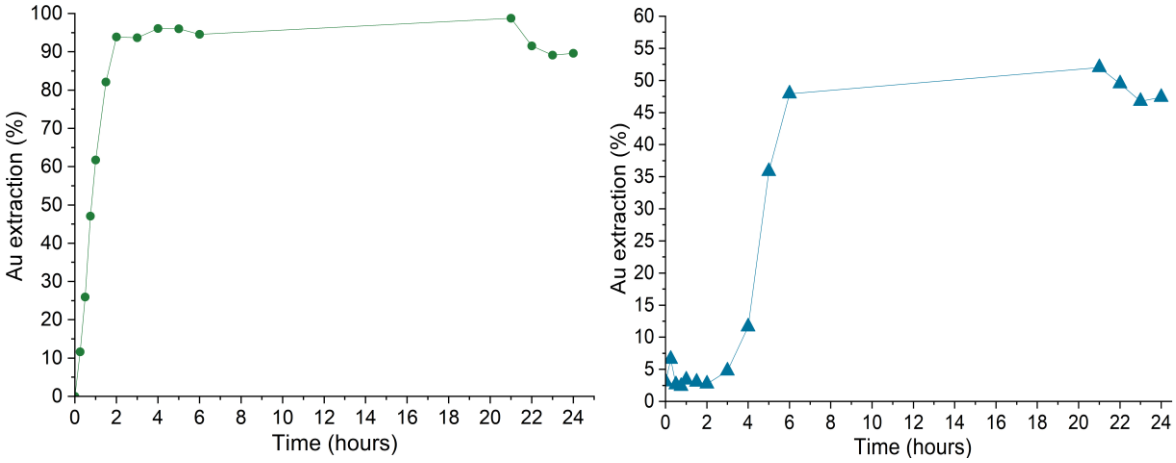


Figure 30. *Graph comparing the Au extraction from gold powder (left) and PCB (right) dissolution for 24 hours.*

These results serve as confirmation that ammonia-ammonium thiosulphate solutions were promising for the leaching of gold from PCBs. Within 24 hours, the gold powder was completely dissolved in the ammonia-ammonium thiosulphate system.

Results from the PCB leaching experiment in Figure 30 showed a similar trend to that of gold powder dissolution. There was an increase in extraction up to 47.9% at 6 hours after an initial delay. Further sampling at 21 hours suggests that the extractions showed only a slight increase (to 52%) and thereafter started to decrease, similar to the experiments with pure gold. The high rate of dissolution of gold powder was promoted by the absence of competing ions for the thiosulphate complex formation in the gold powder experiment. Background copper present in the solution at the start of the experiment was approximately 0.02 M. No additional Cu ions were present when the gold powder was dissolved. By contrast, additional copper leached from the PCB could have hindered the gold leaching process as copper is known to compete with gold in forming a thiosulphate complex (Ha et al., 2014). The decline in extractions for both the gold powder dissolution and gold from PCB leaching after 21 hours may be due to the consumption of thiosulphate as well as loss of ammonia in solution. Consumption of thiosulphate is attributed to the ion being meta-stable in addition to being “easily oxidised by the cupric ions” (Xu et al., 2017). Furthermore, both Molleman & Dreisinger (2002) and Xu et al. (2017) reported that thiosulphate consumption was a cause for low gold extractions.

Figure 31 shows the effect of background copper (II) sulphate concentration on gold extraction in the gold powder dissolution experiment. Four different background copper concentrations each were introduced into the system and the gold powder dissolution experiment was conducted over a 6-hour period.

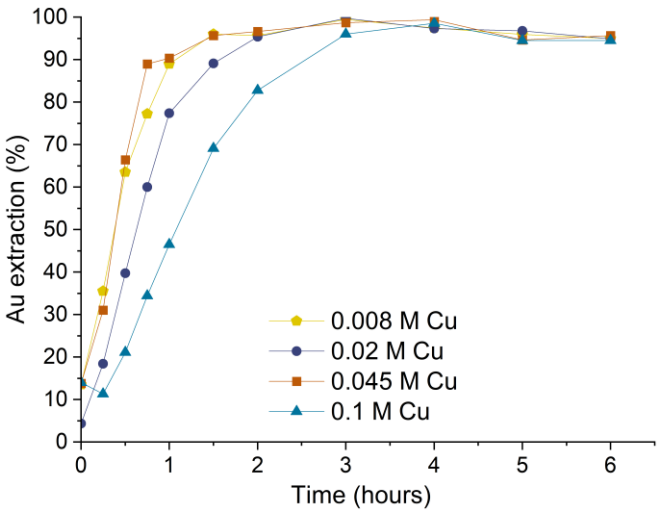


Figure 31. *Gold extraction from gold powder dissolution at various background Cu concentrations (0.008 M, 0.02 M, 0.045 M and 0.1 M)*

Table 9 summarises the gold extraction and the initial rate after 6 hours and 1 hour respectively for each background copper concentration. The fastest initial dissolution rate was that of the 0.045 M Cu concentration whilst the slowest was 0.1 M Cu after 1 hour. At high concentrations of background Cu (0.1 M), gold extraction increased more slowly after the first hour. This was in agreement with findings by Abbruzzese et al. (1995) where similar Cu background concentrations were used at a higher ammonia concentration (1 M) at ambient temperature. Figure 32 presents the same Cu background concentrations on PCB leaching experiments. In addition, 0 M background Cu concentration was introduced into the tests to determine the effect on the gold extraction rate with copper being extracted from the PCB only.

Table 9. *Gold extraction (after 6 hours) and initial dissolution rate (after 1 hour) at various Cu concentrations (0.008 M, 0.02 M, 0.045 M and 0.1 M)*

Copper concentration (M)	Gold extraction (%)	Initial dissolution rate (mg/h)
0.008	95	52.8
0.02	94.5	43.4
0.045	94.9	60.2
0.1	95.6	32.9

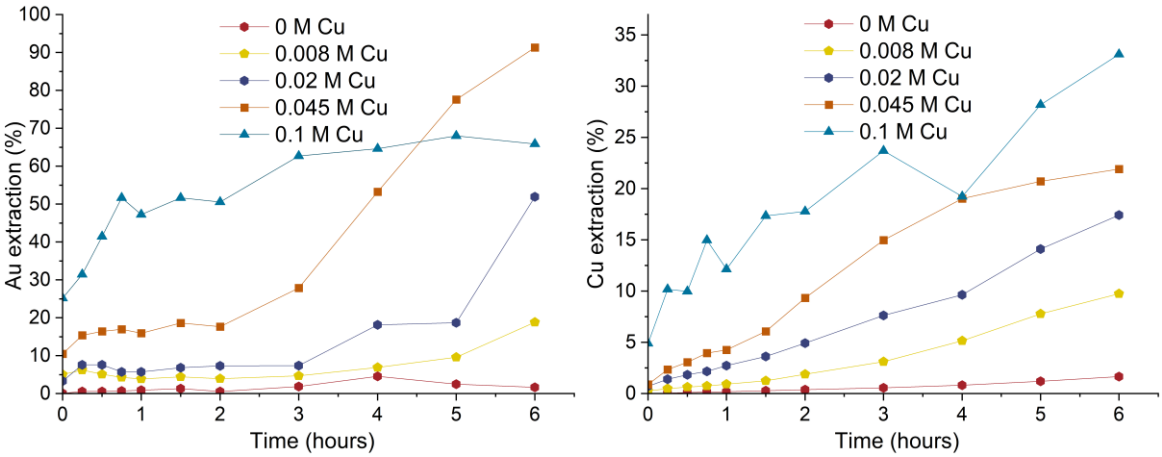


Figure 32. *left - Gold extraction from PCB leaching at various background Cu concentrations; right – Copper extraction from PCB leaching at various Cu concentrations (0, 0.008, 0.02, 0.045 and 0.1 M)*

The lowest extraction after 6 hours occurred in the absence of initial Cu thus showing that it is necessary to enhance the gold dissolution rate via the formation of the copper (II) amine complexes. The highest gold extraction was 93.7% at 6 hours in the presence of 0.045 M background Cu. A background copper concentration of 0.1 M was expected to have a similar gold extraction to 0.045 M however this was not demonstrated by the experiments. Therefore, it can be said that at very high background Cu concentrations, the gold extraction becomes independent of the copper concentration when incorporating PCBs. These results were consistent with those reported by Ha et al. (2010).

Figure 32.b illustrates the copper extraction during the thiosulphate leach tests. Copper extraction was significant, reaching 33%. The highest extraction was from the 0.1 M Cu experiment. The lowest extraction (1.64%) was attained from the 0 M Cu experiment. Gold extraction for the 0.1 M Cu experiment did not increase as fast that of copper and was slower than the other experiments after 2 hours, therefore indicating that it was indeed competing with copper to form a thiosulphate complex. The formation of the aurothiosulphate complex is thus a side reaction that may be promoted or inhibited depending on the conditions.

6.4. Conclusion

It was found that the ammonium-thiosulphate system was promising for the dissolution of gold as indicated by the high extractions of 89.6% after 24 hours of dissolving gold powder in solution but is still subject to improvements. Furthermore, from the gold powder dissolution experiments it was established that the presence of 0.1 M Cu resulted in the highest gold extraction whilst PCB leaching experiments achieved highest gold extractions at 93.7% using 0.045 M background Cu. The lower background Cu concentration needed for optimal leaching of the PCBs is attributed to the additional leaching of copper from the board as the reaction proceeds. This additional leaching of copper was not present in the gold powder dissolution experiment hence a higher background Cu concentration was needed. A threshold background Cu concentration of 0.045 M was recommended such that below this threshold the kinetics of the gold reactions were slow and above the threshold thiosulphate degradation and preferential leaching of copper over gold was prevalent.

In summary, Table 10 tabulates the gold and copper extractions for all PCB experiments where the background Cu solution concentration was varied.

Table10. *Gold and copper extractions from leaching PCBs with 5 different Cu concentrations*

Copper concentration (M)	Gold extraction (%)	Copper extraction (%)
0	1.7	1.64
0.008	18.8	9.76
0.02	52.0	17.4
0.045	93.7	21.9
0.1	65.8	33.1

7. Study 4 – Investigating Early-Stage Process Flow and Reactor Sequencing to Maximise Gold Extraction In the Thiosulphate Leaching of Waste Printed Circuit Boards

7.1. Introduction

In developed countries the more successful gainful recycling of metals from PCBs uses integrated pyrometallurgical and hydrometallurgical technologies. These hybrid technologies require significant capital injection for the installation of state-of-the-art gas scrubbers which prevent the emission of toxic flue gases. Additionally, their operational costs are high. Unfortunately, developing countries such as South Africa have insufficient e-waste volumes, poor energy supply and limited access to capital to implement advanced recycling facilities and models locally (Lydall et al., 2017; Moyo et al., 2020). The extraction of Au through the hydrometallurgical route emerges as the more viable route due to its high selectivity and high potential for the optimization of Au recovery from waste PCBs (Kasper et al., 2018).

In the preceding studies the extraction of Cu and Au from PCBs have been considered separately. However, Study 4 gave a clear indication that the presence of copper can potentially interfere with the thiosulphate leaching of Au. Hence the sequencing of Cu and Au extraction in a hydrometallurgical recovery process is of some potential concern. This is investigated in the present study.

7.1.1. Ammoniacal leaching of Cu

Several studies, mostly at laboratory scale, have been done on Cu and other BMs extraction prior to Au leaching from waste PCBs. The popular ones include the acids, chlorides and ammoniacal lixiviants. Despite usually high recoveries, acidic lixiviants have several shortcomings such as, poor selectivity, high corrosiveness and are difficult to deal with downstream. Alkaline lixiviants, specifically, ammoniacal systems, have many advantages over acidic leaching despite having the longest residence times (Chirume, 2019; Ficeriová et al., 2011; Koyama et al., 2006; Vijayaram et al., 2013). For one, the problems associated with equipment corrosion are eliminated (Radmehr et al., 2013; Rudnik et al., 2016). Ammonia also has a suitably selective capacity for metals such as Cu relative to other metals especially Fe and Al, which are highly soluble in acidic conditions (Chirume, 2019; Ficeriová et al., 2011; Koyama et al., 2006; Vijayaram et al., 2013).

Numerous studies have also been conducted on the alkaline ammonia-ammonium salt leaching of Cu and other BMs. Rudnik et al., (2016) showed that alkaline ammonia–ammonium salt solutions exhibit some advantages in the leaching of polymetallic materials such as PCBs, especially since dissolution of Cu is specific (autocatalytic). This characteristic enhances separation from co-extracted metals (Rudnik et al., 2016). Other metals (e.g., Ni) are also transferred into solution (electrolyte) as soluble ammine complexes, but the rate of their dissolution is determined by oxygen transport to the metal surface (Rudnik et al., 2016).

In the study by Bari et al., (2009) on various ammonium salts for Cu recovery from waste PCBs, highest recoveries of 64% and 92.6% Cu, were achieved for $(NH_4)_2SO_4$ and ammonium carbonate ($(NH_4)_2CO_3$) salts, respectively. Rudnik et al., (2016)'s study on different ammonium salt solutions, $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, showed the most favourable conditions for the Cu alloy ingots dissolution can be achieved

in the ammonia–ammonium carbonate system. This system favoured the leaching of Cu and Zn effectively, without uncontrolled alloy degradation. The same observation was made in the case of $(NH_4)_2SO_4$ where the same recoveries of 95% and 90% were obtained for Cu and Zn respectively. However, unlike $(NH_4)_2CO_3$, the same concentration of $(NH_4)_2SO_4$ was able to leach Ni under the same conditions, and this was shown by a recovery of 80%. This would be a good attribute if the goal is to remove BMs prior to PM leaching to minimise their interference. Chirume, (2019)'s results agree with Rudnik et al., (2016), as they concluded that the system with ammonium sulphate had the highest Cu recovery although carbonate salts proved to be a better buffer than sulphate as it had less fluctuations in pH.

7.1.2. Ammonium thiosulphate leaching of Au

A conventional method, and the leading choice for the recovery of Au from Au ores, is cyanide leaching. Cyanidation has been the dominant process for a century because of its simplicity, non-corrosiveness, robustness, and cost efficiency. However, cyanide application in e-waste has serious drawbacks that render it difficult to manage despite the high extraction capacity, especially in the context of extracting Au from waste PCBs with a high Cu concentration. Akcil et al., (2015), Kasper et al., (2018) and Tripathi et al., (2012) reported that, cyanide is not only toxic, and an environmental risk, but its wastewater is also difficult to process. The increasing environmental pressure on the use of cyanide and its limited selectivity is what motivated the ongoing research into non-cyanide alternatives. Amongst a variety of lixiviants ammonium thiosulphate shows potential because it is less toxic, highly selective, and cheaper (Akcil et al., 2015).

The dissolution of Au occurs through a formation of soluble aurothio-sulphate complexes that include $Au(S_2O_3)_2^{3-}$ and $Au(S_2O_3)^-$ (Kasper et al., 2018). The ammonia-thiosulphate system chemistry is very complex because of the simultaneous presence of complexing ligands such as ammonia and thiosulphate, the Cu(II)-Cu(I) redox pair and the oxidative decomposition reactions of thiosulphate involving the formation of additional sulphur compounds such as tetrathionate (Aylmore et al., 2001; Zipperian et al., 1988). Thiosulphate is a metastable anion which has a tendency of decomposing in aqueous solutions (Zipperian et al., 1988). It has therefore been established that neutral and alkaline media are conducive for the stability and solubility of the complexes (Aylmore et al., 2001; Zipperian et al., 1988). Moreso, adequate concentrations of ammonium thiosulphate, Cu and gaseous O_2 are what enable efficient extraction of the Au (Kasper et al., 2018; Tripathi et al., 2012). The presence of Cu in the form of cupric ions (Cu^{2+}) ions alongside ammonia form a copper tetramine complex $[Cu(NH_3)_4]^{2+}$, a beneficial catalyst for Au dissolution but also facilitates thiosulphate decomposition especially at higher Cu concentrations (Aylmore et al., 2001; Breuer et al., 2002; Senanayake et al., 2003; Sitando et al., 2018; Zhang et al., 2004).

7.1.3. Reactor Sequencing in the Thiosulphate Leaching of waste PCBs

In summary, from the literature survey there are two research domains on the thiosulphate-based leaching of waste PCBs. The first domain and more common one, utilised low Au content PCB sources, for example waste PCBs from computers. These first undergo pre-treatment and BM leaching in a bid to extract the Cu and other BMs prior to Au leaching (Figure 33). It is suggested by Veit et al., (2015) that during the dissolution of Cu, the metallic Au on the surface of waste PCBs is entirely inert. The other domain of research (red doted arrow in Figure 33) focused on high Au content sources, for

example mobile phones, which do not undergo prior leaching of Cu before Au leaching (Kasper et al., 2018).

A conventional leaching sequence when using the thiosulphate system to leach Au from waste PCBs involves physical pre-treatment, followed by base metal (BM) leaching ending with Au leaching (Albertyn, 2017; Ficeriová et al., 2011; Gámez et al., 2019; Petter et al., 2013; Tanisali et al., 2021). The physical pre-treatment is done to increase the leaching surface area to enhance BM extraction. However, it has been ascertained that it leads to the loss of a significant proportion of Au (between 50% and 90%) through the formation of fine flakes of Au during copper leaching (Kaya, 2019; Prestele, 2020). This contributes to an overall significant Au loss. Additionally, due to their dominance and dispersion on waste PCBs, primarily Cu and, to lesser extent, nickel (Ni) are more likely to compete with Au for the lixiviant, which thereby hampers the extraction of Au. Therefore, it appears that the extraction of Au is affected by the order in which the leaching processes are performed.

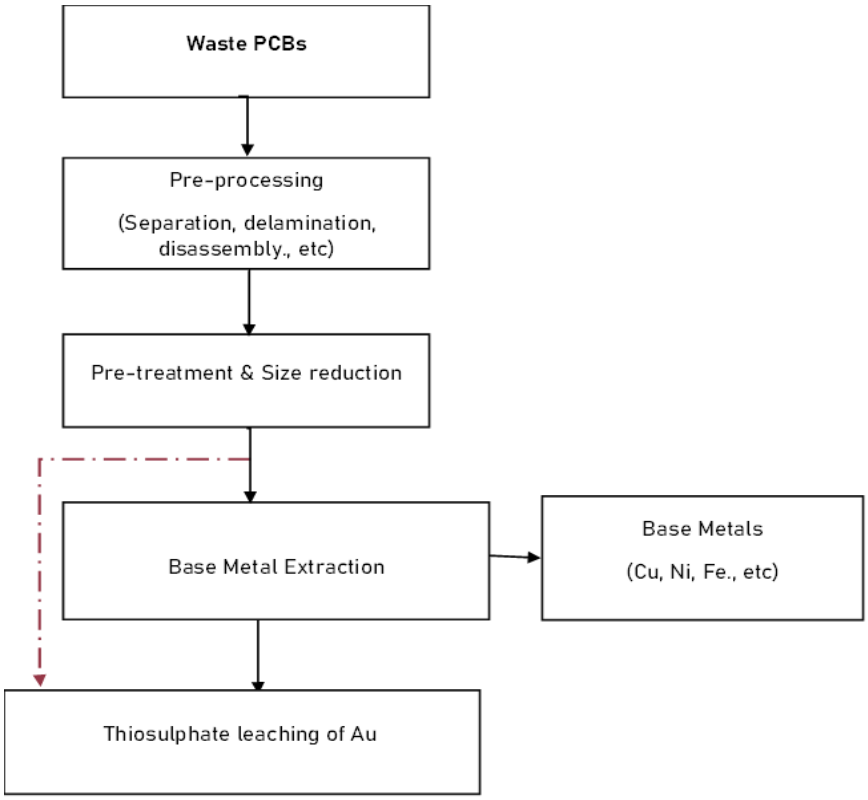


Figure 33. *Conventional Processing sequence for extraction of Au from PCBs. (The dotted line presents the unconventional route normally applied to High Au content PCBs).*

In the study by Petter et al., (2013) a 2% Au recovery was the maximum achieved after leaching the PCB fractions (less than 1mm) with 0.1M $(NH_4)_2S_2O_3$, 0.015M $CuSO_4$ and 0.2M NH_4OH. Using the same leaching conditions, Kasper et al., (2018) managed to extract 75% Au from whole boards that did not undergo any BM extraction (unconventional route). This demonstrates that, mechanical processing of waste PCBs results in a high rate of Au loss. Additionally, grinding exposes other metals that are present on the PCB (such Ni, Cu, etc.). Their surface area in contact with the leaching solution increases as a result, and they compete with the desired reactions of the Au leaching process. The study done by Gámez et al., (2019) revealed that waste PCB powder with residual 1% Cu can be successfully

leached using ammonia-thiosulphate solutions for PMs dissolution. However, 5% Au was lost during the prior leaching of Cu which was carried out using an acid solution of a 4M HNO_3 solution. 81% Au was extracted using: 0.7M $S_2O_3^{2-}$, 5% solids; pH of 10.5; and 6 hours of stirring at room temperature. More Au was lost during successive waste PCB size reductions during the pre-treatment process. Ficeriová et al., (2011) achieved a 16% Au extraction after leaching of whole PCBs without any prior pre-treatment and BM extraction, the conventional leaching sequence yielded 98% Au extraction. Despite attaining substantial recoveries of Cu due to the pre-treatment processes, Birich, (2020); Birloaga et al., (2013) and Kaya, (2019) found that during pre-treatment, around 50% of precious metals, including Au, are lost through the plastic and particle streams. Furthermore, Kasper et al., (2018) demonstrated that milling releases BMs (Ni, Cu, etc.) present on the PCB, thereby increasing their contact area with the leaching solution thus competing with the desired reactions of the Au leaching. A trade-off must be made between pre-processing waste PCBs to unlock Cu and avoiding size reduction to improve Au extraction primarily from the external layers. Another solution could be to extract Au before shredding and grinding, after which Cu can be rapidly extracted from shredded and waste PCB to improve efficiency.

In this study, four potential reactor sequences (order/flow of the leaching processes) were investigated to evaluate the extent of Au extraction, Cu and Ni co-extraction as well as associated Au losses in the ammonium thiosulphate leaching of waste PCBs. Specifically, this was achieved by; 1) performing a head grade analysis on the PCBs using Aqua Regia Leach and microwave assisted digestion to ascertain the metal concentration of targeted metals; Au, Cu, Ni , and Sn, 2) investigating the best reactor sequence that maximises Au extraction from waste PCBs, in an ammonium thiosulphate leaching system.

7.2. Materials and methods

7.2.1. Custom-tailored PCBs

The PCBs that were used throughout this research were made to order by Trax Interconnect (Pty) Ltd. in Cape Town, South Africa. This means that the same design, composition, and quality was maintained for each board to ensure reproducibility and precision in the comparison of the experimental results. A detailed description and characterisation of these boards has been given in the preceding sections of this report and is therefore note repeated here.

Each PCB is a four-layered FR-4 (fibreglass with epoxy resin) core board, weighing approximately 52 g. Each of four layers comprise of a laminate of FR-4 inner core sandwiched by two copper foils that are 17 µm in thickness. It has the dimensions; 142×102×1,63 mm. What connects the inner layers to the outer layers is the pre-preg (uncured FR-4 resin) which cures when the layers are combined. The total Cu grade on each board is 10.77g. Au is solely found on the vias (electroplated holes, connecting the copper layers in a PCB), the upper and lower surface of the board as well as the slot connectors on the sides, They present as an alloy of Au and Ni. The total Au mass on each board is 4.22 mg and that of Ni is 146 mg.

7.2.2. Au leaching sequences

Four reactor sequencing strategies, summarized in Figure 34, were examined with the goal of choosing one that yields the maximum Au extraction during the thiosulphate leaching stage.

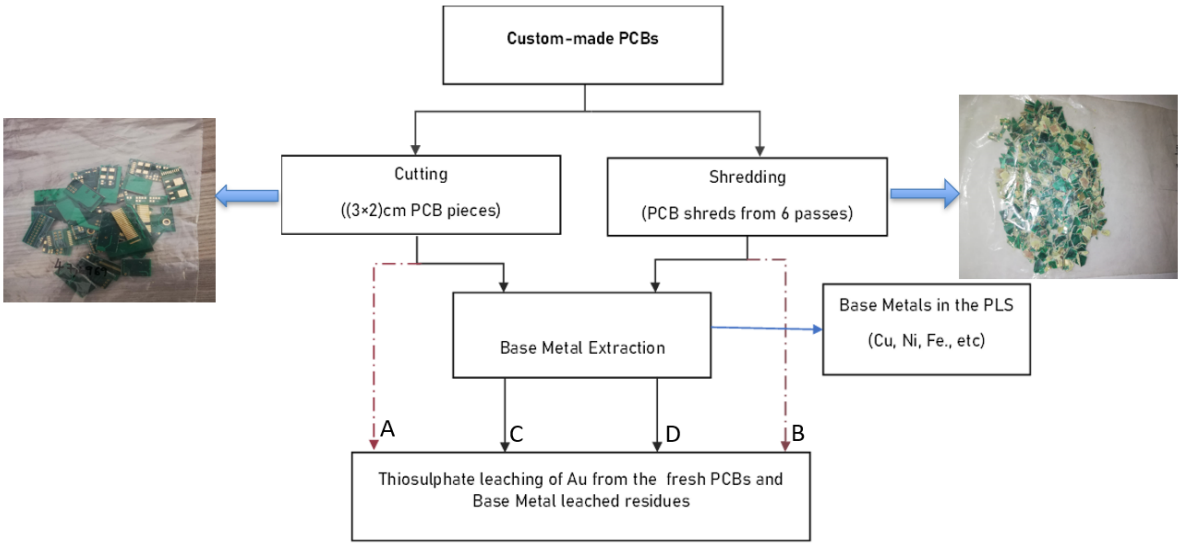


Figure 34. *Schematic of the reactor sequencing approaches investigated in this report. The red dotted lines (from far left to far right) present the unconventional sequence (A) and (B) respectively while the other two solid lines (left to right) present sequence (C) and (D).*

A. Sequence A- unconventional sequence where the PCBs are cut (3 cm x 2 cm) and then immediately move on to the Au leaching stage.
B. Sequence B- Similar to sequence (A) except in this instance the PCBs are shredded (in 6 passes) instead of being cut.
C. Sequence C- conventional sequence where the PCBs are cut (3 cm x 2 cm) and undergo BM extraction prior to the Au leaching stage.
D. Sequence D- Similar to sequence (C) except in this instance the PCBs are shredded (in 6 passes) instead of being cut.

The preferred size for sequence (A) and (C) were whole PCBs without any size reduction to minimise Au loss. However, for purpose of being able to fit the PCBs into reactors, each PCB was weighed and cut using a BS-200 bandsaw. The shredding approach was informed by the work of Prestele, (2020), who explained that it produces good Cu extractions during BM leaching by ammoniacal solutions while resulting in little losses compared to other pre-treatment procedures.

7.2.3. Cu leaching tests

For sequences (C) and (D), pre-treatment was followed by a Cu leaching stage using $(NH_4)_2SO_4$. The primary leach solution was analysed for extracted metals Au, Cu and Ni, although the product of interest were the leached PCB residues. This sequence was closed off by a Au leaching stage, using ammonium thiosulphate. The lixiviant was prepared by dissolving 2M $(NH_4)_2SO_4$, 4M of NH_3 solution and 100 ppm $CuSO_4{\cdot}5H_2O$ in a 2 L volumetric flask. The pH was measured and found to be 10.5. The bottle roller temperature was set at 25°C for the first run, and each PCB (cut) was put into a 2 L Schott bottle (three Schott reactor bottles ran concurrently in each run). Each Schott bottle was then filled with 750 mL of lixiviant. The commencement time was then recorded before the bottles were put on a bottle roller with constant mixing set to 250 rpm. To ensure that the reaction system had enough dissolved oxygen, compressed air at 0.1 L/min was bubbled into each reactor. 5ml samples were taken at 0, 1.5, 3.5, 6, 9, 24, 27, 48, and 72 hours. The aliquots were filtered through 0.2 µm syringe-driven

membrane filters before being taken for analysis using an MPAES. The loss in solution volume caused by sampling was accounted for by adding the initial lixiviant solution. The product of interest, the leached (PCBs) residue, was filtered off the leachate using a Whatman 40 filter paper. The residues were then air dried for 24 hours before being leached for Au. The process was repeated for the PCBs that had been shredded.

7.2.4. Thiosulphate leaching of Au from the fresh PCBs and Cu leach residues

The $(NH_4)_2S_2O_3$ lixiviant was prepared by mixing 1M NH_3, 0.5M $(NH_4)_2S_2O_3$ and 40mM $CuSO_4.5H_2O$ in a 2 L volumetric flask. The initial pH was found to be 10.4. The bottle roller temperature was set at 25°C, and each PCB (Sequence A) was put into a 2 L Schott bottle (three Schott reactor bottles ran concurrently in each run). Each Schott bottle was then filled with 500 mL of lixiviant and 1 PCB (~50 g) and put on a bottle roller with constant mixing set to 300 rpm. Compressed air was bubbled 0.1 L/min. The bottle roller set up is shown in Figure 35.

Figure 35. *Three parallel Schott bottle reactors, with identical leaching conditions, that used in the leaching reaction involving the bottle roller.*

For sequencing (A) and (B), pre-treatment was followed by a Au leaching stage using ammonium thiosulphate solution. 5ml samples were taken at 0, 0.5, 1, 2, 5, 8, 9, 20, 24 and 30 hours. 5 mL aliquot samples extracted for each selected time interval were diluted with 5 mL dilution solution. This dilution solution was prepared by dissolving and mixing 0.5 M $(NH_4)_2S_2O_3$ and 1 M NH_4OH. The pH of each sample was measured and recorded before dilution. The sampled solutions were filtered and then analysed for dissolved Au, Ni and Cu using the MP-AES. After a runtime of 24 hours the solution was filtered off using a Porcelain Buchner funnel. After filtration, the pieces were dried in an oven and the final PCB mass was measured. These leached residues were preserved for mass balance analysis and calculations. The sampled solutions were analysed for dissolved Au, Cu and Ni using the MP-AES analysis. The process was repeated for Sequence B and for Cu leach residues obtained from Sequence C and D.

7.3. Results and Discussion

7.3.1. Base Metal Extraction Results

During the ammonium sulphate-based Cu leaching stage, minute Au flakes suspended in the reactor were visible, 24 hours into the experiments. After 72 hours residence time , all the Au on the PCBs had completely peeled off and was visible at the bottom of each reactor. This is shown in Figure 36(a) depicts the bottom of the reactor just before leaching experiment and Figure 36(b) shows the bottom of the same reactor 72 hours later. These Au flakes were filtered off using a vacuum filter and 0.2 µm filter paper as shown in Figure 36(c). Thereafter, they were dried out in open air before being subjected Au leaching along with the PCBs they had peeled from, in the subsequent stage of Au leaching using $S_2O_3^{2-}$.

Figure 36. *(a)Reactor at time t=0 hours (b) Au flakes t=72hours (c) filtered flakes*

Figures 57 and 38 show the metal extraction results for the sequences C and D (cut and shredded), respectively, during Cu leaching using ammonium sulphate.

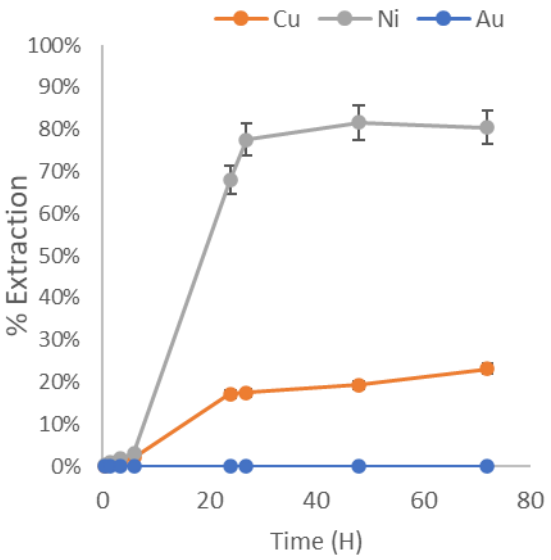


Figure 37. BM extraction for sequence C-cut PCBs
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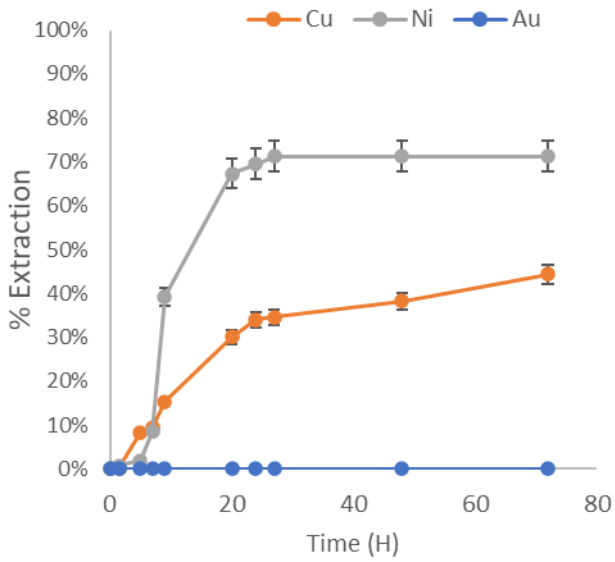

Figure 38. BM extraction for sequence D-Shredded PCBs

For both cut and shredded PCBs, Ni had the fastest leaching rates, with over 67% Ni being extracted within the first 24 hours. Cu rates of extraction were less than half of Ni extraction rates, with 34% and 17% Cu extracted within the same period for shredded and cut PCBs, respectively. The leaching studies demonstrate after a 72-hour residence time no Au was extracted during the Cu leaching stage, while a maximum of 71% and 80% Ni and 44% and 23% Cu was extracted for shredded and cut PCBs, respectively. The extent of Ni extraction was 9% higher for cut PCBs than shredded PCBs. This is likely because Ni is mostly on the surface, shredding exposes more Cu, therefore it leaches preferentially, and the Ni comes shorter. However, Ni had overall faster leaching rates than Cu because of its location of the PCBs. The Ni available on the PCB only exists in form of a Au-Ni alloy on the vias and upper and lower part of the PCBs. However, in the case of Cu, if the top and bottom masks are removed, approximately 31% of the Cu layers are accessible to the lixiviant. The maximum Cu extraction from PCBs that were shredded was greater than that from PCBs that were cut, and an additional 13% of the Cu deemed to be inaccessible was also extracted. This implies that shredding exposes Cu layers to the lixiviant more so than cutting.

7.3.2 Au Extraction Results

The summarized percentage Au extractions for sequences A through D is shown in Figure 39.

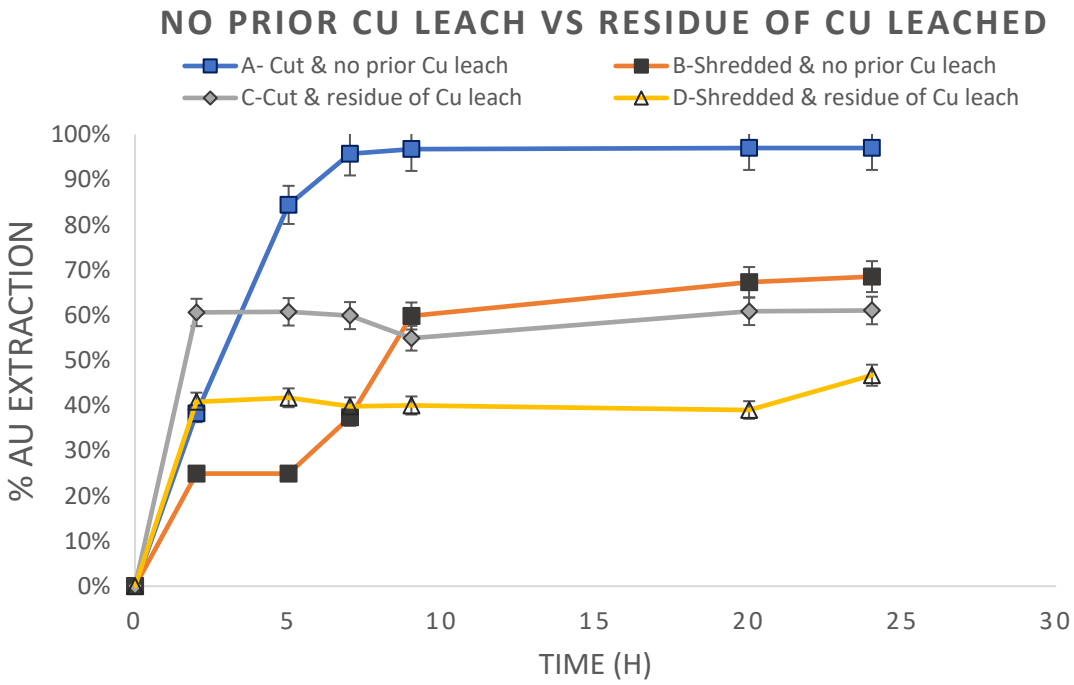

Figure 39. *The four reactor sequences investigated.*

The total Au extraction was standardized against the initial head grade, while the coextraction of Ni and Cu was standardized against the recalculated head grade, after the total mass of Ni and Cu extracted during the prior Cu leaching stage was subtracted. Sequences C and D demonstrated faster Au leaching rates over the first two hours, with 30% Au extraction/hour and 20% Au extraction/hour, respectively. Based on this rate, A and B were outpaced by C by a factor of 1.6 and 2.5, respectively. Thereafter, the plateau in C and D rate indicates that equilibrium had been reached. After 7 and 9 hours, respectively, A and B also reached a plateau. Sequence A had the maximum Au extraction of

nearly 97% after a total of 24 hours residence time, followed by B with 69%, and C and D with 61% and 47%, respectively.

Due to the previous Cu leaching step, Sequences C and D showed faster Au extraction rates and were able to reach equilibrium more rapidly than A and B. As was previously described, all the visible Au peeled off from the PCBs, generating very minute flakes of Au that were leached along the PCB residue they had peeled off from. The minuscule Au particles were consequently freely suspended, highly exposed to the lixiviant, and so easily dissolved in solution. Additionally, studies have shown that smaller particle sizes favor fast leaching reaction kinetics (Tuncuk et al., 2012). Contrarily, in sequences A and B, where there was no stage of prior Cu leaching, the Au was still intact on the fresh PCBs at the onset of the experiments. The low maximum Au leaching extractions demonstrated by C and D indicate that a large amount of Au was extracted. This was most likely due to the effect of shredding which exposes Cu into solution as previously mentioned, since no Au was dissolved during the Cu leaching stage, as indicated by Figures 37 and 38. As a consequence CuS precipitates can passivate the Au surface if there is a high concentration of Cu in the $S_2O_3^{2-}$ leach, which hinders dissolution of Au. (Aylmore et al., 2001; Breuer et al., 2002; Senanayake et al., 2003; Sitando et al., 2018; Zhang et al., 2004).

7.3.3. Reactor Sequencing A vs Reactor Sequencing C

Figures 40(a) and (b) show the focused, individual graphs for coextraction of Au, Cu and Ni of Sequence A and C, respectively in the $S_2O_3^{2-}$ leach. As shown by the individual curves in Figure 40, overall, the boards that were processed through sequence C were found to have the least amount of co-extracted Cu and Ni. Ni was barely leached after attaining a maximum of 7% extraction, whereas in Sequence A, a total of 97% Ni was coextracted. With regards to Cu, the total Cu extracted in sequence A was almost 4 times higher than the total extracted during Sequence C.

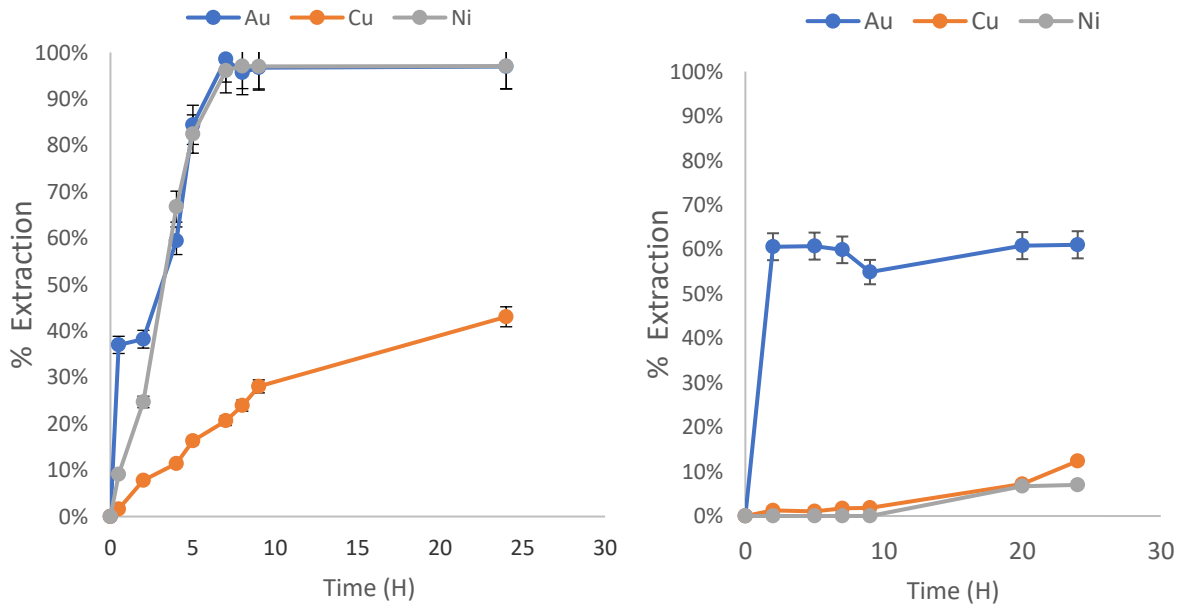

Figure 40. *(a)Reactor Sequence A, cut and no prior Cu leach PCBs & (b) Reactor Sequence C, cut and PCB residue of Cu leach, respectively.*

In sequence A, in the first 2 hours, Au leached 1.6 times quicker than Ni, but both metals reached equilibrium after 8 hours and a maximum of 97% of each metal was extracted. Cu was the least metal extracted, with a maximum extraction of 43% attained. Whereas in C, of the remaining Ni from the Cu pre-leach, only 7% of Ni was extracted. For Cu, an additional 12% of Cu was extracted from the Cu pre-leach. The differences in the extent of Au extraction was likely due to the losses incurred during the flaking and filtration. As for Ni, other than the presumption that it was lost during shredding (as a Ni-Au alloy), most of it had already been extracted during the prior Cu leaching stage.

7.3.4. Reactor Sequencing B vs Reactor Sequencing D

Figures 41(a) and (b) focuse on the different graphs for the coextraction of Au, Cu, and Ni from Sequences B and D, respectively.

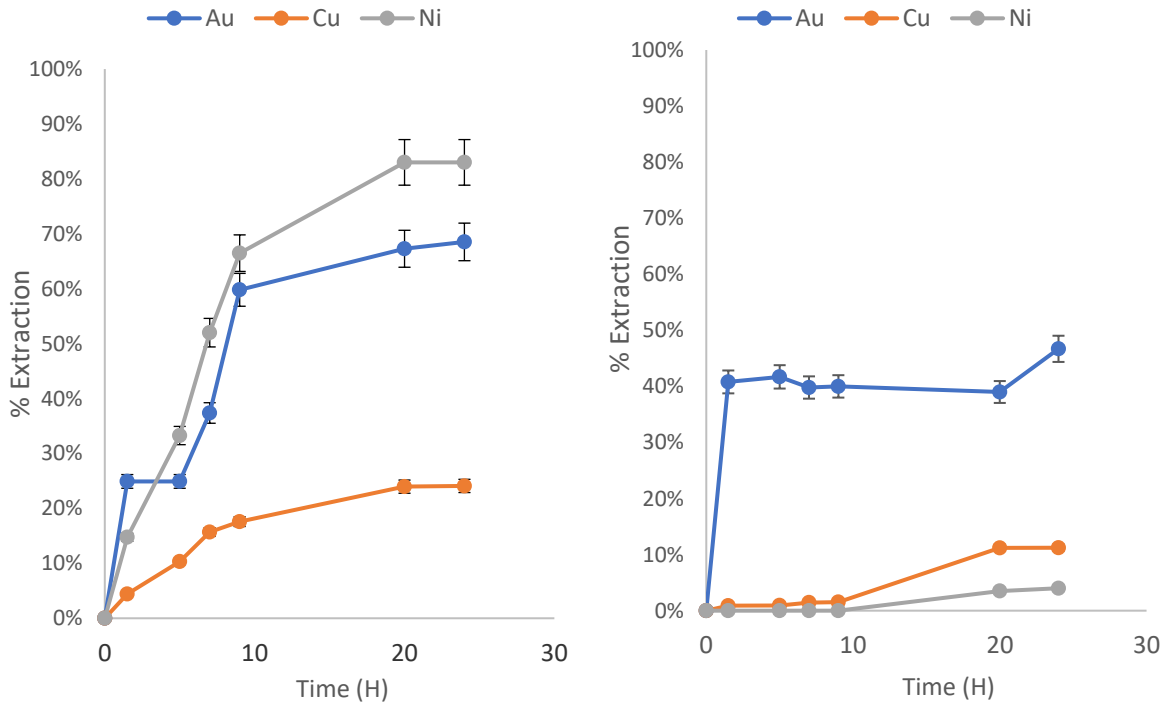

Figure 41. *(a)Reactor Sequence B, Shredded and no prior Cu leach PCBs & (b) Reactor Sequence D, Shredded and PCB residue of Cu leach, respectively.*

Figure 41 displays a pattern similar to Figure 40, except sequences B and D extracted less Au overall. The PCBs that were processed through sequence D had the least amount of co-extraction of Cu and Ni overall, as demonstrated by a closer examination of the individual curves in Figure 41.b. In contrast to Sequence B, where a total of 83% Ni was coextracted, Ni was barely leached after reaching a maximum extraction of 4%. With regards to Cu, the overall percentage extracted during Sequence B was two times greater than the total amount extracted during Sequence D. Au was extracted 1.6 times faster than Ni in the first 1.5 hours of Sequence B. Ni and Au were extracted to a maximum of 83% and 69%, respectively. While only, a maximum of 24% Cu extraction achieved. Whereas in D, only 0.14% of the remaining 29% Ni from the Cu pre-leach was extracted. An additional 11% of Cu was also extracted from the Cu pre-leach. Only 47% of the Au was extracted in total in D. Overall Cu

extraction variations in sequence B and D were largely due to the fact that most of the Cu had already been extracted during the prior Cu leaching stage for sequence D.

7.3.5. Selection of the Optimal Reactor Sequence

Sequence A was selected as the best route since it had the highest overall Au extraction. These findings differ from those of Ficeriová et al., (2011). Without BM extraction, they were only able to extract a maximum of 16% Au under the same leaching conditions. However, these results are an improvement over those of Kasper et al., (2018) , who under the same conditions only extracted a maximum of 79% from PCBs that did not undergo size reduction and BM extraction. The use of depopulated PCBs in this paper sets it apart from their studies.

Sequence A, however, had a higher rate of Cu and Ni co-extracted. 43% of Cu and 97% Ni were coextracted along with the highest Au extraction of 97%, after approximately 7 hours, which may not be favorable for downstream processes. On the other hand, sequence B has drawbacks such as significant losses during size reduction. Additionally, an increased coextraction of Cu, during Au leaching, results in larger losses of thiosulphate ions by its conversion to tetrathionate and other polythionates (Aylmore et al., 2001). As a result, there is a lower extraction of Au from shredded PCBs because such ions are not useful in the extraction of Au. BMs are removed in large quantities during the prior leaching stage of sequences C and D, which is advantageous for subsequent procedures. But it comes at a cost of Au loss during mechanical size reduction, especially for sequence D, and a further loss in the form of tiny flakes during filtration demonstrated by Figure 36.c. As a result, a total of 53% Au was lost during the methods used in sequence D. For the PCBs processed through sequence C, there was a 35% total in Au loss. No Au was extracted during the leaching of BMs, indicating that the loss of Au was a direct result of the stages that came before the BM leaching stage.

7.4. Conclusion & Recommendations

Sequence A, of cut PCBs without any prior Cu leach step, was selected as the best route, as it stood out as having the maximum Au extraction. However, compared to Sequence C-D, it had a higher percentage of Cu and Ni co-extraction. The results showed that through this sequence, 43% of Cu and 97% Ni were coextracted along with the highest Au extraction of 97%, after 7 hours of leaching. This translates to 21% Cu, 96% Ni and 97% Au extracted using 0.5M $S_2O_3^{2-}$, 1M NH_3 and 0.04M $CuSO_4$ solution mixture and a S/L ratio of 100 g/L. This co-extraction extent may not be favorable especially for downstream processes. On the other hand, other sequences have the key drawback of significant Au losses owing to size reduction. Sequence D suffered severe loss as high as 53% while Sequence C and B suffered a total of 20% and 26% Au. Furthermore, a higher coextraction of Cu, especially for Sequence B, led to depletion of thiosulphate ions, which was suggested to be the result of its conversion to tetrathionate and other polythionates. As a result, there was a decrease in the extraction of Au from shredded PCBs. The leaching results also demonstrated that no Au was leached during Cu leaching suggesting that it is inert and simply peels off during the Cu leaching step.

A few measures could be implemented to improve the extraction of Au from waste PCBs. The first step should be to perform leaching tests on completely whole waste PCBs that are not reduced in size. This would ensure that less Cu and other BM are not exposed to the leaching system during Au extraction using ammonium thiosulphate. It would be ideal to then apply the optimized Au leaching

process on real waste PCBs to see or test the practicality of the method on actual waste PCBs. In order to determine how much thiosulphate was degraded and the residual amount after leaching, it would also be helpful to do an iodometry-based analysis for residual thiosulphate. It would also be better to use fire assaying as it is more accurate to characterize waste PCBs and therefore accurately calculate the head grade of the waste PCBs.

8. Study 5 – Copper electrowinning from NH_3 solution – preliminary study

8.1. Introduction

Electrowinning is a key technology in Hydrometallurgy for the production of high purity metals directly from solution, often avoiding lengthy multi-step purification processes using alternative routes. However, electroplating is strongly influenced by the presence of less noble metals in solution relative to the one being recovered, as these will result in co-deposition or scavenging of current through side reactions. Therefore, often pre-purification of a leach solution is needed (for example through SX) in order to remove impurities. In the context of recovering Cu from leach solutions of waste materials direct electrowinning could therefore prove problematic. However, due to the limited solubility of many impurity metals in alkaline media, especially Fe, operating an electroplating process in ammoniacal solution, may offer advantages. Hence in the present study, the direct electrowinning of Cu from ammoniacal solutions was investigated under a variety of operating conditions to assess both the quality of copper cathode plated and the current efficiency of the process.

Direct electrowinning of Cu from ammonia leach liquor was attempted using a small batch electrowinning cell. The quality of the plated copper showed high purity, however at the relatively low Cu concentrations tested, interference from hydrogen evolution was significant affecting the mechanical quality of the electrode and reducing the observed current efficiency to around 40%. Preliminary tests with a flow-through cell using a high-tenor (15 g/L) Cu-NH3 solution show substantially better performance with smooth deposits formed at current efficiencies in excess of 90%.

8.2. Experimental

8.2.1 Electrowinning experiments

Electrowinning experiments were performed to evaluate the copper deposit according to Table 11. The system was performed with a stainless-steel electrode (working as a cathode) and a titanium mesh DSA (IrO_2 – Ta_2O_5 coated). The experiments were carried out for 90 minutes in a glass reactor at room temperature (22C) using an agitation of 500 rpm with a magnetic stirrer (Figure 42). Once the experiments were finished, pictures of the deposit were taken to have a visual inspection of the cathodic quality. The test solution came directly from PCB leaching test without any pre-concentration, containing approximately 15 g/L Cu^{2+}, 2 M NH_4CO_3 and 4 M NH_4OH. The pH of the solution was approximately 9.7.

To evaluate the purity of the copper deposited, the cathodes obtained were took off from the stainless-steel electrode to eventually dissolve them in 20 ml aqua regia (ratio 3/1). The spectrometer machine was used to analyse the copper contained in the liquid solution. A voltameter was used during the experiments to control the current of the experiments.

Table 11. *Electrowinning experiments carried out at different current densities.*

Experiment	Current density, A/m^2	Current, A
G3	500	0.8
G4	562.5	0.9
G5	437.5	0.7
G6	468.75	0.75

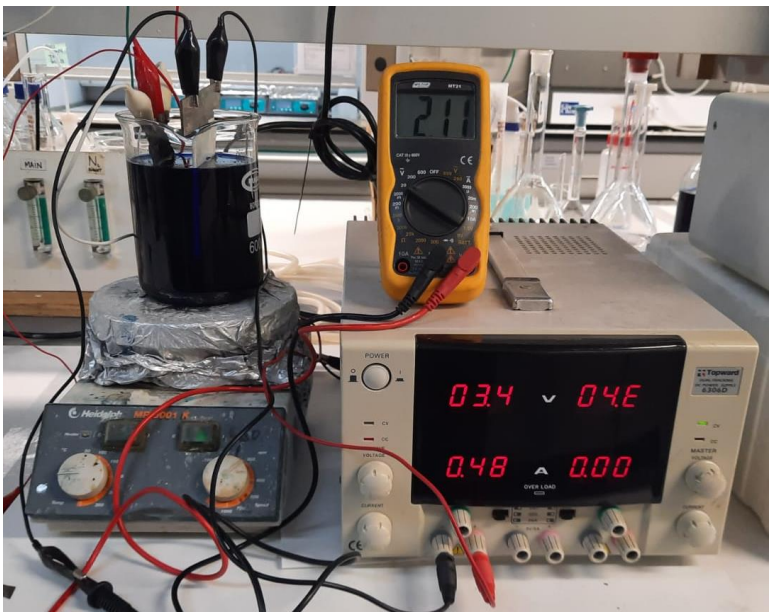

Figure 42. *Set-up of the EW experiments. At the left the magnetic agitator with the beaker reactor. At the right the power supply.*

8.2.2. Evaluation of current efficiency

The efficiency of the process was calculated using the first Faraday's law:

$$Teoretical\ Mdeposited = \frac{I * t * PMcu}{n * F} \tag{11}$$

$$Efficiency, \% = \frac{Experimental\ Mdeposited}{Teoretical\ Mdeposited} \tag{12}$$

The crystallisation of the plated copper is an important factor to be evaluated for the final product obtained. Winand (1992), proposed a way to characterise cathode quality. The adequate crystallisation is based on a plane texture without microporosity (FT zone). However, the quality of the cathodic deposit depends on various factors to be considered, such as current distribution in the cell, verticality of the electrodes, concentration of additives, etc. The quality of the deposit was analysed based on this diagram.

8.2.3. Development of a flow-through cell apparatus

A small size electrowinning cell was constructed as shown in Figure 43**.** This consisted of a 1 L plexiglass reactor holding 2 5 x 5 cm stainless steel cathodes between a similar sized anode plate. The solution

was systematically pumped between the cell and a reservoir to enable a smooth flow of solution across the electrodes (Figure 44).

Figure 43. *Flow-through cell apparatus*

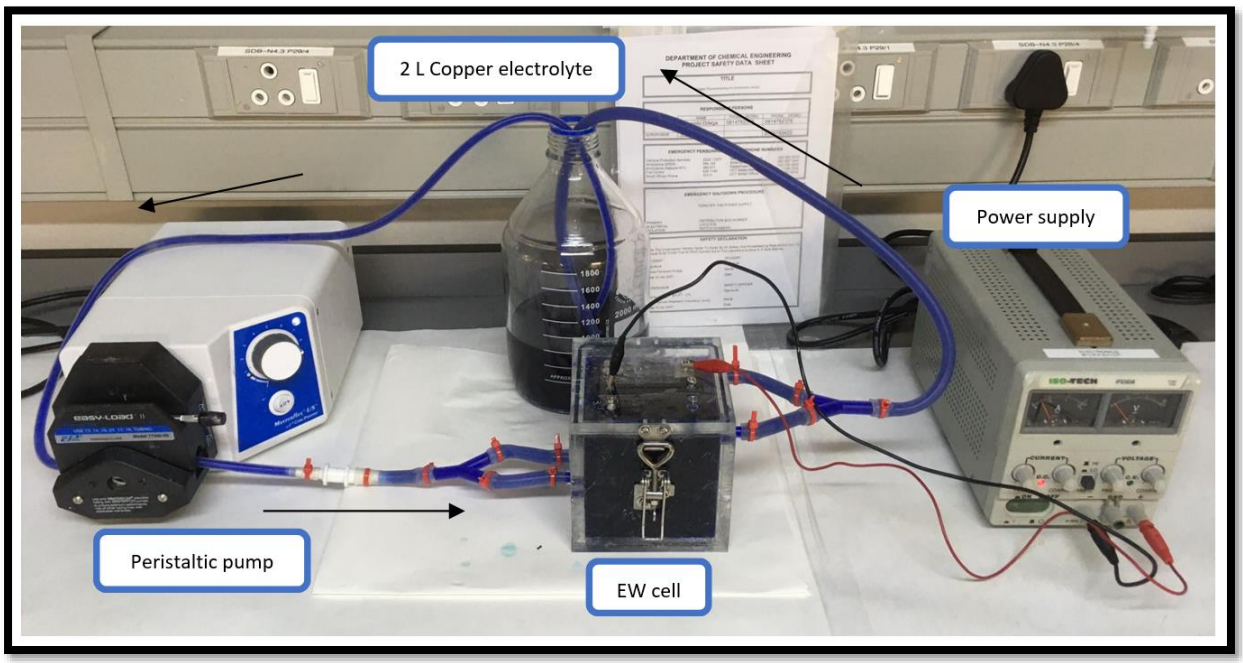

Figure 44. *Flow-through cell with pump circuit*

Preliminary tests were conducted plating from a solution containing 15 g/L Cu^{2+} + 2 M NH_4Cl over 1 hour at current densities ranging from 155 to 469 A/m^2. The deposit was investigated, and current efficiencies determined in each case.

8.3. Selected Results

The aims of this experimental work were as first instance, to evaluate the electrowinning of copper in ammonia solution using an industrial solution and to analyse the cathodic quality. The industrial solution came from a PCB's leaching process using a solution containing 2 M NH_4CO_3 + 4 M NH_4OH and initial 100 ppm Cu^{2+}.

The electrowinning was carried out in ammonia solution (2 M NH_4CO_3 + 4 M NH_4OH) over 1 hour. 4 experiments were designed to analyse visually the cathodic deposition (see Table 12) The currents set were 0.9, 0.8, 0.7 and 0.75 A. It was observed that while the current is increased, the efficiency remains constant. However, it was observed visually that the copper deposit was poorer in quality. For instance, the experiment G4 that was carried out using 0.9 A achieved 94% current efficiency, but the cathode was burned on the corners and the observed porosity is linked with the reduction of the hydrogen taking place on the cathode, directly affecting the copper quality deposit. On the other hand, the copper quality observed during the experiment G6 is optimal, the cathode was very easy to take off and it appears very clean (see Table 12). However, the efficiency of the process achieved just 38% which is not desirable for an industrial process.

Table 12. *Copper cathode deposit characterisation*

Experiment	Copper deposit	Efficiency, %	Purity, %
G3 (FI)		66	90.6
G4 (UD-FI)		94	95.7
G5 (FI)		10	97.7
G6 (FT)		38	97.7

Furthermore, the cathodic quality was evaluated through visual inspection. The table 5 below shows the deposits obtained during the experiments. The experiment G3 that was carried out at 0.8 A has a FI dendritic qualification which is a good quality deposit. This could be improved through changing the turbulence of the solution inside of the cell adding some baffles on the agitated reactors. Also tests G4 has a UD-FI classification due to the current 0.9 A being too high for the process, creating nodules on the surface due to competing reduction of hydrogen taking place on the cathodic surface at high currents. The experiments G6 has a FT qualification which is the most desirable, it looks clean, and it

was easy to take it off of the stainless-steel layer. However, the current efficiency of the process is merely 38%.

The complete set of images of the deposits generated at the different current densities is shown in Table 13, indicating good deposit quality at 250 and 280 A/m^2. A plot of the determined current efficiencies at is shown in Figure 45, indicating current efficiencies around 90% under the given operating conditions which is very encouraging.

***Table 13**. Pictures of deposits formed after 1 hour of electroplating a various current densities plating from a solution containing 15 g/L Cu^{2+} + 2 M NH_4Cl*

155 A/m^2	220 A/m^2	250 A/m^2
		
280 A/m^2	313 A/m^2	375 A/m^2
		
469 A/m^2		
		

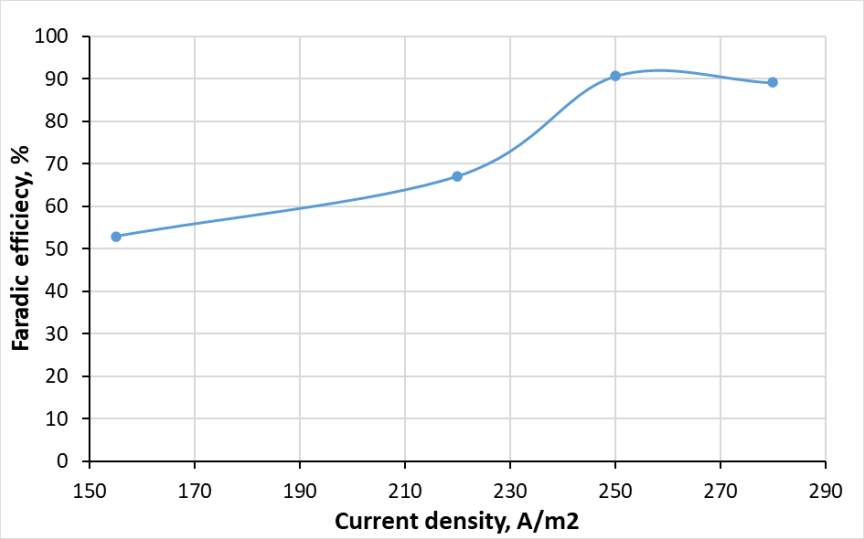

Figure 45. *Current efficiencies determined for the flow-through cell experiments.*

8.4. Conclusion

Preliminary electroplating tests have shown that the direct plating of Cu from ammoniacal solutions is feasible, and good quality deposits can be obtained, albeit at low current efficiencies for the low-tenor solutions employed in the batch tests.

On the other hand, a good quality deposit with current efficiencies in excess of 90% was achieved in preliminary experiments with a flow-through cell in which more constant operating conditions and a more homogeneous solution flow across the plates could be achieved.

9. Study 6 – Ion-exchange recovery of Au thiosulphate from model leach solutions

9.1. Introduction

Ion exchange as a separation method is still poorly explored, yet it offers effective and technically simple separation and does not require the use of hazardous or toxic chemicals. It therefore offers distinct advantages over precipitation and solvent extraction. A draw-back is the relatively low loading capacity and speed of many resins, necessitating large inventories in large contacting equipment.

Ion exchange recovery of cold from Cu/Au thiosulphate mixtures has been explored by Gomes et al. (2001), O'Malley (2002), Nicol & O'Malley (2002), Zhang & Dreisinger (2002, 2004) and Kotze et al. (2005) using a variety of medium and strong anion exchange resins, mostly with amine functional groups. This work was adapted for gold-thiosulphate leach liquors likely to be obtained from PCB leaching in the present study.

9.2. Experimental

Ion exchange experiments were conducted using three resins namely, the AuRIX®100 resin, which was available in chloride form, and the Purogold™ MTA5013SO4 and Purogold™ MTA5011SO4 resins, which came in sulphate form. Capacity, loading and elution tests were conducted on all three resins.

9.2.1 Capacity test experiments

Loading capacity was measured regularly and is a key parameter in evaluating ion exchange performance. The capacity tests determine the active sites available for attachment of the targeted ion. Capacity tests were conducted in the Zero Length Column (ZLC) reactor described by Nesbitt (2016), which is essentially a shallow bed of resin through which solution is pumped at a rapid rate. The experimental set up for an open circuit capacity test is illustrated in Figure 46. All experiments were conducted at ambient temperature and the flowrate was kept constant at 25 mL/min.

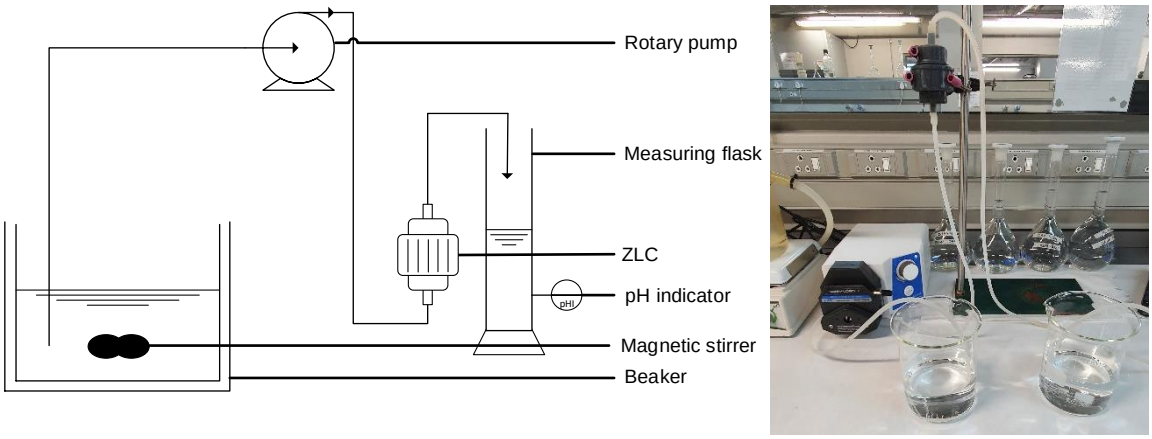

Figure 46. *Diagram of an open circuit ion exchange system and experimental set up for capacity testing*

Capacity tests, for the AuRIX®100 resin, were completed using two methodologies. The first method consisted of five steps. In the first step, 1 L of the 1 M NaOH solution at a flowrate of 25 mL/min was

passed through the ZLC using a pump. This was required to convert the resin from the chloride into the free-base form. Once the NaOH step was complete, deionised water was flushed through the ZLC until the pH was between 9 and 10. The third step utilised 1 L of the 0.1 M NaCl solution which was passed through the ZLC. Thereafter deionised water was used again to flush out any excess ions whilst the effluent pH was kept between 9 and 10. In the final step, 1 M NaOH at a volume of 1 L was pumped through the ZLC. The final step was necessary to detach any residual chloride ions attached onto the resin. A 10 mL sample of the NaOH effluent was analysed for chloride ions using a Gallery™ Discrete Photometric Analyser.

The second method employed the same solutions and concentrations as the first method however only the first three steps of the methodology were carried out. The final step 3 was conducted in a closed circuit such that the NaCl solution was circulated between the beaker and ZLC for 40 minutes at 25 mL/min. The solution was mixed using a magnetic stirrer at 300 rpm before extracting a 10 mL sample for analysis. The NaCl effluent sample was analysed using the photometric analyser to determine the final concentration of chloride ions in solution.

The capacity tests for the Purogold™ MTA5013SO4 and Purogold™ MTA5011SO4 resins were conducted in a similar manner. As both resins were available in the sulphate form, only three steps were required. 2 M NaOH and 0.5 M NaCl were used. The capacity tests for the Purogold™ resins included a titration experiment after the final step to determine the chloride ions in solution. The titration utilised 1 M HCl as the titrant for the MTA5013 and 0.1 M for the MTA5011 experiments using methyl red as the indicator.

9.2.2. Loading and elution experiments

Loading and elution experiments were conducted on all three resins using the standardised leached solutions from gold powder. Testing on the AuRIX®100 was first conducted in four steps in an open circuit. The conditions and lixiviants used are shown in Table 14. A 0.5 L solution of 1 M NaOH was pumped through the ZLC before passing 0.5 L of deionised water. Thereafter, the dissolved gold powder synthetic solution was loaded onto the resin by being pumped through the ZLC. A 5 mL sample of the dissolved solution was taken at 10-minute intervals for the duration of 20 minutes. The pH was recorded at the start and end of all steps. Deionised water was used to remove any excess ions present in the ZLC. Elution proceeded with NaOH. All samples were sent for ICP-AES analysis for gold and copper. The same resin sample was used for all loading and elution for the AuRIX®100 resin.

Table 14. *Loading and elution experiment conditions for AuRIX®100 resin*

Lixiviants/conditions	Units	Values
NaOH concentration	M	1/0.5
NaOH volume	L	0.5
Deionised water volume	L	0.5
Leachate volume	L	0.5
Flowrate	mL/min	25
Temperature	°C	25

Loading and elution experiments, on the Purogold™ resins, were conducted in a similar technique of four steps in an open circuit, except for the sodium hydroxide concentration. 1 L 2 M NaOH was used

to dislodge the large sulphate ions present on the resin. Loading and elution steps were conducted at a volume of 0.5 L. All experiments occurred at ambient temperature. Ammonium nitrate 2 M (NH_4NO_3) as eluant was introduced for experimentation on the MTA5013 resin at various flowrates (10 mL/min, 25 mL/min and 50 mL/min), The MTA5011 resin tests were conducted used the same eluant at a 25 mL/min flowrate. Samples were taken in the same manner as that of the AuRIX®100 resin. Effluent samples consisting of the eluant from the elution step were also collected and analysed using ICP-AES. Unless otherwise stated, all experiments were repeated three times.

9.3. Selected Results

9.3.1. AuRIX®100 resin

Two different methods were used to investigate the capacity of the AuRIX®100 resin. Table 15 shows the chloride ion concentration in equivalents per litre resin. Method 1 values were chloride ion concentrations that were eluted using 1 M NaOH solution. Method 2 values were chlorides ion concentrations loaded onto the resin after passing through NaCl solution in a closed circuit. The Method 2 values were the difference in chloride ion concentration in solution at the start and end of the experiments.

Table 15. *Comparison of two methods for capacity testing on the AuRIX®100 resin in terms of chloride ion concentration (eq/L)*

	Method 1 Chloride ions (eq/L)	**Method 2 Chloride ions (eq/L)**
Test 1	0.070	0.861
Test 2	0.125	0.439
Test 3	0.125	-
Average	0.107	0.650
Standard Deviation	0.031	0.299

Loading was done with 0.5 L of aurothiosulphate solutions made by dissolving 56 mg of gold powder in 0.5 M ammonia-ammonium thiosulphate solutions. Gold and background copper concentration was approximately 112 ppm and 0.02 M. Table 16 summarises the gold and copper loading of the resin. Loading values were based on the decrease in either gold or copper ions in solutions. The loaded resin capacity values were the percentage of resin active sites occupied by the aurothiosulphate and copper-thiosulphate ion respectively. The total resin capacity was the percentage of resin occupied by the gold and copper ions together.

Table 16. *Gold and copper loading values from AuRIX®100 testing*

	Au loaded (eq/L)	**Au-loaded resin cap. (%)**	**Cu loaded (eq/L)**	**Cu-loaded resin cap. (%)**	**Total resin cap. used (%)**
Test 1	0.00879	1.35	0.132	20.3	21.65
Test 2	0.00890	1.37	0.286	44.0	45.41

This data shows that the resin can recover much higher gold concentrations from the aurothiosulphate solution despite being suited for the aurocyanide system only. Test 2 loaded a higher concentration of the aurothiosulphate ion onto the resin than Test 1 despite Test 1 using fresh resin and Test 2 using the

resin eluted after conducting Test 1. While Test 1 and Test 2 give similar results for Au, more than double the Cu was loaded in Test 2. In both tests, the copper loading was much higher than the gold loading given a loading time of 20 minutes across all AuRIX®100 sets of experiments. Results from Gray, Hughes & Abols (2005) reported that in the cyanide system over an extended period of time (greater than 30 minutes) copper was adsorbed and eventually displaced by hydroxyl ions in solution whilst similar effects were not observed on resin loaded with gold. This indicates that the resin has a higher affinity for gold than copper as gold remained attached to the resin whilst copper was displaced. Provided that the resin would behave in a similar manner in a thiosulphate system it can be assumed that had the loading time been increased, the Cu ions could possibly be displaced by hydroxyl ions which would result in the aurothiosulphate ion competing with the hydroxyl ion for the active sites.

Table 17 compares the elution concentration values (equivalents per litre resin) for gold and copper. NaOH at 0.5 M was used as an eluant and the results reveal that the eluant was effective in removing gold in that 99.6% and 75.7% of gold loaded onto the resin were eluted for Test 1 and Test 2 respectively. Copper was not eluted as easily as the gold with only 43.1% and 18.5% of loaded copper for Test 1 and 2 respectively. being removed.

Table 17. *Gold and copper elution values from AuRIX®100 testing*

	Au eluted (eq/L)	**Au eluted from resin (%)**	**Cu eluted (eq/L)**	**Cu eluted from resin (%)**
Test 1	0.0087	99.6	0.057	43.1
Test 2	0.0067	75.7	0.053	18.5

NaOH proved to be an effective eluant for the gold ions however there was a significant amount of copper that remained on the resin after elution. Table 18 shows the recoveries for both steps and the overall ion exchange process from loading to elution. The overall ion exchange efficiency was calculated based on the concentration of gold or copper in the eluant relative to the concentration of gold or copper in the standard solution at the start of the loading step.

Table 18. *Average gold and copper recoveries from loaded solution*

	Recovery after loading (%)	**Recovery after elution (%)**	**Overall Ion exchange efficiency (%)**
Gold	3.46	87.7	1.09
Copper	5.05	30.8	0.67

Overall, the AuRIX®100 resin does indeed load Au and Cu onto the resin. However, given that only 6 ppm Au was removed from the gold solution, this makes for an adsorption efficiency of 3.5% which is very low. However, given the low gold mass present on a PCB (4.22 mg), the AuRIX®100 resin can indeed recover at least 50% of the gold present in a leached PCB (see chapter on thiosulphate leaching of PCBs). Cu was shown to be preferentially loaded onto the resin (at the expense of Au ions). Thus, it is concluded that the AuRIX®100 resin was not suited for the thiosulphate system.

9.3.2. Purogold™ MTA5013 Resin

Capacity tests were conducted in an open circuit to determine the operating capacity of the MTA5013 resin. A total of three tests were conducted to determine the capacity in terms of Cl^- ions. The results are shown in Table 19.

Table 19. *Capacity results on MTA5013SO4 resin*

Test	Chloride ions (eq/L)
Test 1	0.769
Test 2	0.769
Test 3	0.769
Average	0.769
Standard Deviation	3.98×10^{-15}

The general capacity provided by in the MSDS of the MTA5013 resin was 1.15 eq/L in chloride ion form and strong-base anion exchange resins with a quarternary ammonium group are known to be between 1 eq/L and 1.4 eq/L at volume capacity (Zhang & Dreisinger, 2002; De Dardel & Arden, 2012). The operating capacity calculated from the results presented in Table 19 is much lower at 0.77 eq/L. The significant deviation of the determined resin capacity relative to that specified by the manufacturer (1.15 eq/L) could be due to the difference in methods used to measure the resin capacity.

Furthermore, the actual capacity of the AuRIX®100 was 0.65 eq/L in comparison to the 0.77 eq/L obtained for the MTA5013 resin. Generally weak- to medium-base anion resins are often around 0.8 eq/L for general resin capacity and in the case of the AuRIX®100 resin specifically, the general capacity was 0.3 eq/L. According to Zhang & Dreisinger (2002), a higher resin capacity was expected for the strong-base anion resin and this was verified via the capacity tests which showed the actual capacity of the MTA5013 resin to be 0.77 eq/L.

Loading and elution tests were conducted on the MTA5013 resin at various flowrates (10 mL/min, 25 mL/min and 50 mL/min) as well as using two eluants (NH_3 and NH_4NO_3). The results are shown in Table 20.

Table 20. *Ion exchange loading results on MTA5013SO4 resin at 3 different flowrates: 10 mL/min, 25 mL/min and 50 mL/min*

Flowrate	Au loaded (meq/L)	Au-loaded resin cap. (%)	Cu loaded (meq/L)	Cu-loaded resin cap. (%)	Total resin capacity (%)
10 mL/min	8.06	1.05	150	19.54	20.58
25 mL/min	7.73	1.01	56.9	7.40	8.40
50 mL/min	6.97	0.906	69.6	1.34	2.24

The highest loading of gold onto the resin was at the flowrate of 10 mL/min. This correlated to 1.1% of the resin capacity being occupied by the aurothiosulphate ion. Whilst 20% was occupied by the copper-thiosulphate ion. The lowest loading was at the flowrate 50 mL/min with only 6.97 meq/L and 1.34 meq/L of gold and copper respectively being loaded onto the resin. Thus, it can be said that lower flowrates aided in higher gold loading ability onto the resin. The poor metal loading on the resin for

both gold and copper could imply that the resin required even lower solution flowrates so as to increase the contact time for the resin volume to be effective for the purpose of removing gold and/or copper from solution.

Table 21. *Ion exchange recovery values for gold and copper after loading step*

Flowrate	Au standard solution concentration (ppm)	Au recovery after loading (%)	Cu standard solution concentration (ppm)	Cu recovery after loading (%)
10 mL/min	143	3.84	1315	3.78
25 mL/min	119	4.43	1330	1.41
50 mL/min	119	4.02	1269	1.81
Average	127	4.09	1305	2.33

Table 21 provides the gold and copper recovery during the loading step of the resin. Only about 4.1% of total gold was recovered from the solution and in the case of copper 2.3% was recovered across all flowrates.

PCB leach solutions contained up to 4.22 mg of leached gold in solution from previous leaching experiments. Ion exchange results from gold loading experiments on the MTA5013 resin showed that all three flowrates (10/25/50 mL/min) had the ability to recover more than 50% of the gold present in a PCB leached solution (4.22 mg) in the loading step as indicted in Table 21 despite only occupying 1% of the resin active sites with the aurothiosulphate ion. However, on an industrial scale the gold leached solution would generally contain gold concentrations much higher than a single PCB thus indicating that the resin is ineffective in removing large amounts of gold given a high gold concentration solution in the loading step and the same resin volume. Furthermore, lower flowrates and higher resin volumes are indeed necessary to recover more gold in the loading step however flowrates below 10 mL/min can be seen as impractical on an industrial scale and high resin volumes can be expensive.

Table 22 shows the results obtained from the elution step using ammonium nitrate. The results from the 10 mL/min flowrate were obtained from an average of three tests while those from the 25 mL/min and 50 mL/min were obtained from 1 test each.

Table 22. *Ion exchange elution results on MTA5013SO4 resin at 3 different flowrates: 10 mL/min, 25 mL/min and 50 mL/min*

Flowrate	Au eluted (meq/L)	Au eluted from resin (%)	Cu eluted (meq/L)	Cu eluted from resin (%)
10 mL/min	4.96	65.6	22.4	24.4
25 mL/min	5.80	75.0	38.4	67.5
50 mL/min	5.11	73.3	20.3	29.1

Utilising a flowrate of 25 mL/min resulted in the highest amount of gold eluted from the resin (5.8 meq/L) with the 10 mL/min correlating to the least eluted gold of 4.96 meq/L. This was unexpected as

the loading results showed that a lower flowrate resulted in higher gold loading values and thus it was expected that the same would apply for elution.

Table 23 lists the total gold and copper recovered in the elution step for the overall process. It is thus clear that the method of eluting with ammonium nitrate is preferential for gold recovery. Copper recovery efficiency was much lower at 0.68% whilst gold was around 2.9%. Despite the low overall gold recoveries, the MTA5013 has been shown to have the ability to remove the aurothiosulphate ion from solution.

Table 23. *Overall gold and copper recoveries from loaded synthetic gold solution*

Flowrate	Au standard solution concentration (ppm)	Overall Au efficiency (%)	Cu standard solution concentration (ppm)	Overall Cu efficiency (%)
10 mL/min	143	2.36	1315	0.564
25 mL/min	119	3.32	1330	0.954
50 mL/min	119	2.94	1269	0.527
Average	127	2.88	1305	0.681

9.3.3. Purogold™ MTA5011 resin

Further experimentation was carried out on the MTA5011 resin obtained from Purogold™. These tests were conducted purely for confirmatory results of the MTA5013 experiments. The main difference noted between the MTA5011 and MTA5013 resin was the smaller particle size. The results obtained from the MTA5011 capacity test (Table 24) were similar to those obtained for the MTA5013 resin (0.77 eq/L). The operating capacity of the MTA5011 resin was taken to be 0.76 eq/L. This value was much smaller than the general capacity value of 1.15 eq/L reported in the MTA5011 MSDS.

Table 24*. Capacity results on MTA5011SO4 resin*

Test	Chloride ions (eq/L)
Test 1	0.796
Test 2	0.741
Test 3	0.741
Average	0.759
Standard Deviation	0.0321

The capacity result of 0.76 eq/L was expected, given the same method as the MTA5013 capacity experiment was employed. Despite the operating capacity being lower than the reported capacity, the method used by Nesbitt (2016) and incorporated in this study, is a well-established method and thus the operating capacity was considered to be acceptable.

Loading and elution experiments were conducted at a flowrate of 25 mL/min. Gold at a concentration of 10 ppm (14.7 meq/L) was loaded onto the resin, whilst copper loading amounted to 44 ppm (129 meq/L). The gold values were higher than that of the MTA5013 resin at the same flowrate whilst the copper values were lower (Table 25). Therefore, it is possible that a smaller particle size could result in

higher gold loading concentrations as 10 ppm was the highest concentration of gold loaded in all the loading experiments. The total resin capacity occupied by gold and copper was 19% and this fits well within the range of 8.4% - 29.8% obtained at the same flowrate for the MTA5013 resin. A possible explanation could be that gold adsorbs more rapidly and is then gradually displaced by copper or polythionates. The smaller beads have a larger surface area per unit volume, so the displacement will occur more pronouncedly than in larger resins where gold penetrates more deeply into the subsurface and would thus be more slowly displaced.

Table 25. *Ion exchange loading results for the MTA5011 resin at 25 mL/min*

MTA5011	Au loaded (meq/L)	Au loaded resin capacity (%)	Cu loaded (meq/L)	Cu loaded resin capacity (%)	Total resin capacity (%)
Test Average	14.7	1.93	129	17.0	19

Moreover, the loading of 5 mg in a gold dissolved solution substantiates the possible loading of gold from PCB leached solutions with a gold content of 4.22 mg. However, this loading recovery is still too low and thus a large bed volume of resin is required for higher recoveries when accounting for process design PCB leached solutions containing gold much higher than 4.22 mg found on a single board.

Table 26 shows the results from elution with 2 M ammonium nitrate. The results for gold were similar to the results shown in Table 9 for the 25 mL/min flowrate for the MTA5013 resin, with 75% of loaded gold being eluted. Copper results were the lowest elution results obtained over all experiments with only 21.8% of the loaded copper being eluted. This further substantiates the choice of 2 M ammonium nitrate being suited for gold elution recovery over copper elution recovery.

Table 26. *Ion exchange elution results for the MTA5011 resin at 25 mL/min*

MTA5011	Au eluted (meq/L)	Au Eluted from resin (%)	Cu eluted (meq/L)	Cu Eluted from resin (%)
Test Average	8.95	71	15.3	21.8

The MTA5013 and MTA5011 resins performed in a similar manner which was expected given the difference between the two resins was the particle size range. However, the highest gold loading and elution concentrations were recorded for the MTA5011 resin with 10 ppm being loaded and 6.3 ppm being eluted. This was associated with the nature of the resin bead and its effect on gold loading ability.

9.4. Conclusion

Three resins, a strong base MTA5013 and medium base MTA5011 and AURIX 100 were tested to explore the potential for Au extraction from thiosulphate leach liquors under a variety of operating conditions. The strong base MTA5013 was found to be the better performing resin. Overall, however, ion exchange tests showed very poor recoveries and selectivity to gold over the copper catalyst in the solutions, potentially due to limited residence times used in the test system.

The resins tested appear therefore not well suited for this gold-thiosulphate system without further study of potentially more suitable resins in more appropriate contact systems.

10. Study 7 – Pb/Sn solder leaching

10.1. Introduction

Solders on printed circuit boards (PCBs) connect the electronic components to the circuit boards. They are primarily made up of lead (Pb) and tin (Sn) alloys in varying proportions. The use of Pb in solder alloys has reduced in recent times due to environmental concerns, but since PCB wastes comprise materials of a wide range of ages, there is no immediate 'standard' composition of the solder alloys.
In line with the proposed process flowsheet, which envisages alkaline leaching processes for the main target metals Cu and Zn, the removal of solder (and with that of the electronic components) for separate recovery represents a separate process step. The process flowsheet envisages the solder leaching step to precede recovery of Cu and pre-treatment (size reduction, pyrolysis) thus keeping other value metals shielded from the lixiviants.

Bizzo et al. (2014) characterised the chemical composition of the PCBs and compared their values with previous data reported by other authors. They found that the total mass percentage of Sn and Pb fluctuate between 1.00-5.62% and 1.01-3.93%, respectively. Therefore, any solder removal process needs to investigate of both metals, preferentially selectively, through the targeted use of leaching reagents.

10.1.1. Sn leaching

Kim et. al (2014) performed experiments to separate Sn from waste Pb-free solder using hydrochloric acid and hydrogen peroxide (reaction (1)). They found out that the leaching efficiencies of Sn improved when H2O2 is added and at increased HCl concentration.

$$Sn + 2H_2O_2 + 4\ H^+ = Sn^{4+} + 4\ H_2O \quad (13)$$

Jha et al. (2012) found that the dissolution of Sn in HNO_3 under the optimized condition for lead leaching is negligible, this is confirmed by Yoo et. al (2012). The Sn precipitates as stannic acid during nitric acid leaching:

$$3\ Sn + 4\ HNO_3 + H_2O = 3\ H2SnO_3 + 4\ NO \quad (14)$$

$$Sn + 4\ HNO_3 = H_2SnO_3 + 4\ NO_2 + H_2O \quad (15)$$

The solubility of Sn is higher in hydrochloric acid than in sulfuric acid or nitric acid (Scott et al., 1997) Moosakazemi et. al (2019) investigated leaching of Sn and Pb recovery from PCB solder. They found out that Sn extractions with 2 and 2.5M HCl were 80% and 79%, respectively after 240 min of leaching. Finally, the highest dissolutions of Sn (88%) occurred at 75°C.

Kim et al. (2016) proposed a leaching method of Sn using stannic chloride (Sn^{4+}) in hydrochloric acid using Pb-free solder. Sn concentration remained low in the leaching solution without SnCl4, whereas the leaching efficiency of Sn with the addition of $SnCl_4$ addition dramatically increased to more than 99% within 60 min. Kim et al. (2016) also investigated Sn leaching in the presence of Cu^{2+} as a potential cement and found that Cu ions in solution can indeed be removed and dissolve Sn into solution.

$$Cu^{2+} + Sn = Cu + Sn^{2+} \quad (16)$$

$$2\ Cu^{2+} + Sn = 2\ Cu + Sn^{4+} \quad (17)$$

Lee et. at (2015) studied the dissolution of Sn using waste Pb- free (90.2% Sn, 4.11% Ag, and 0.65% Cu) solder in hydrochloric acid solution with ferric chloride as oxidant.

$$2\ Fe^{3+} + Cu = 2\ Fe^{2+} + Cu^{2+} \quad \text{at } 0.43V \tag{18}$$

$$4Fe^{3+} + Sn = 4\ Fe^{2+} + Sn^{4+} \quad \text{at } 0.76V \tag{19}$$

10.1.2. Pb leaching

The study by Jha et al. (2012) confirm that the percentage leaching of lead reached 99.99% using 0.5 M nitric acid solution at 90 °C in 30 min while only 0.19% and 1.24% lead dissolution is noticed in the case of 0.5 M sulfuric acid and 0.5 M hydrochloric acid respectively in 75 min. Moosakazemi et. al (2019) leached PCB with HCl and found out that the highest Pb recovery (87%) was achieved at 2M HCl concentration at room temperature and 98% of Pb extraction at 75° C.

10.2. Experimental Study

Two experimental campaigns were conducted, the first focussed on preliminary studies using solder wire of different compositions in stirred beaker experiments, the second focussed on the direct leaching of solders from batches of waste PCBs in column reactors.

10.2.1. Agitated beaker tests

Experiments with 4 different solder wires were carried out to find out some operational parameters and the best mix of reagents: Solder A (around 85% Sn - 10%unknown); Solder B (30%Sn – 70%Pb); Solder C (97%Sn – 3%Cu); Solder D (60%Sn – 40%Pb).

Solders A and C are solders recommended to use in PCBs and electronic circuits, whereas B and D are more commonly used in general applications. Tests were carried out in small beakers using 50 ml of magnetically agitated leaching solution with de-ionised water as solvent, hydrochloric acid at different concentration and oxidants such as ferric sulphate (Fe^{3+}), stannic chloride (Sn^{4+}) and citric acid (see Figure 47). The solid percentage used in all the experiments was 1%. In most experiments the experimental solution was exchanged after 24 hours of leaching for fresh solution to continue for a 2nd 24-hour stage of leaching.

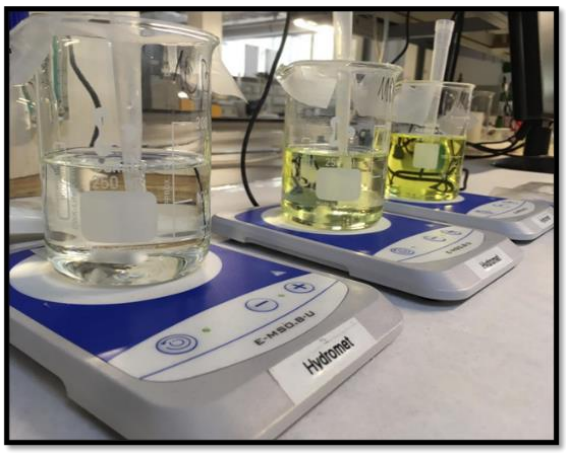

Figure 47. *Leaching set-up. Clear solution composed by hydrochloric acid + stannic chloride. Yellow solution composed by hydrochloric acid + ferric sulphate.*

10.2.2 Column Tests

Test on 500 g of whole waste PCBs were performed in columns (Figure 48); 3 types of set-ups were tested:

- Setup A: The leaching solution (or PLS) was recirculated being pumped from a container in the bottom until the top of the column in where the irrigation was through only 1 hole. The boards inside of the column were not submerged in the leaching solution.
- Setup B: The leaching solution was recirculated being pumped from a container in the bottom until the top of the column in where the irrigation was through a spiral configuration with many holes. The boards inside of the column were not submerged in the leaching solution.
- Setup C: The PLS was recirculated being pumped from the column's bottom until the top, in where the irrigation was through 1 hole. The boards were submerged in the leaching solution during the whole duration of the experiments.

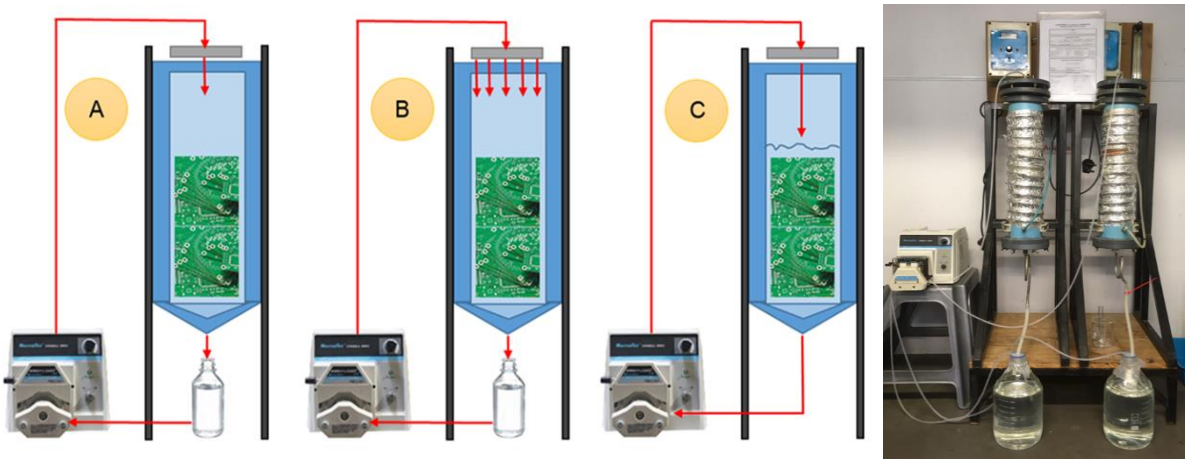

Figure 48. *Three different leaching setups in columns and column apparatus*

Each of the set-ups was tested with circulation of a standard 1M HCl and 5 g/L Sn^{4+} solution. Further column tests using set-up C were conducted to evaluate the effect of HCl and stannic concentration on the leaching performance.

10.3. Selected Results

10.3.1. Beaker studies

Leaching of the 4 types of solder in HCl in combination of various oxidants were investigated, the most promising combinations are shown in Figure 49, indicating that a combination of ferric and stannic ions as additives yielded the best results in terms of Sn extraction. The effect of varying the acid concentration is also shown in Figure 49. Pb dissolution stayed low under these conditions. Optimal dissolution was achieved with 2 M HCl in the presence of 0.5 g/L Fe^{3+} at room temperature, to selectively extract 100 % of the tin.

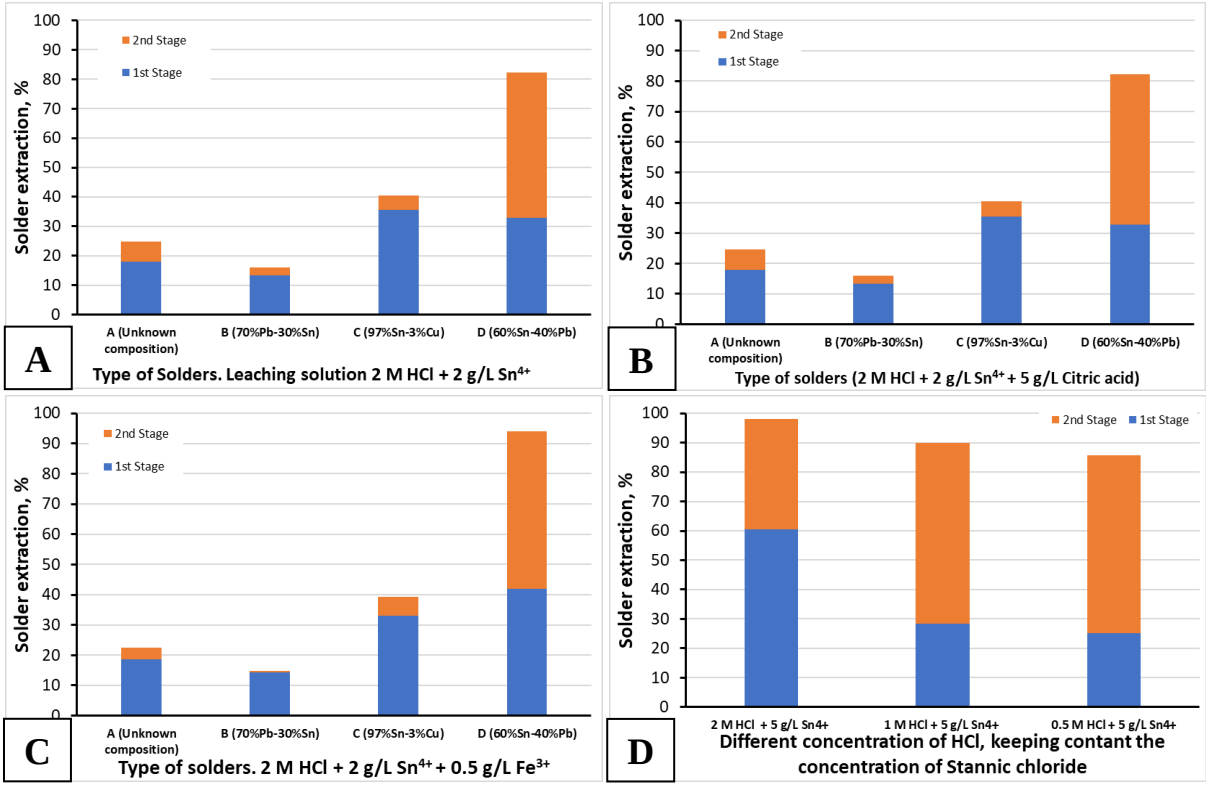

Figure 49. *Selected results from beaker solder leach stud (A-C) and results from varying the HCl concentration, solder C with high Sn (D)*

10.3.2. Column studies

4 individual waste PCB samples were characterised through grinding, acid digestion and ICP analysis, and average compositions computed as shown in Table 27.

Table 27. Metal wt% contained by each PCB sample

Element	PCB-A, %	PCB-B, %	PCB-C, %	PCB-D, %	Average,%
Sn	3.22	4.45	6.10	6.40	5.04
Pb	1.87	2.67	4.90	2.30	2.94
Cu	9.50	9.01	18.20	19.50	14.05

Leaching was carried out in the 3 column set-ups as shown in Figure 48 with 500 g of mixed waste PCBs charged and the standard solution. The Sn, Pb and Cu extractions were analysed from solution assays. It was observed that for the setup A, in which the irrigation was through just 1 hole, the Sn extraction was negligible (see Figure 50.a below) because the solution was not distributed homogeneously inside of the reactor and most of the PCBs were not touched by the leaching solution. For the case of the Pb extraction (see Figure 50.b below), the setup A achieved a value close 5% of Sn extraction. Furthermore, the setup B (irrigation by many holes) significantly improved the leaching extractions, achieving a Sn and Pb extractions of 80 and 19 % respectively. Although, it was noticed that the Sn precipitated during the CB setup experiments which is observed in the extractions obtained at the 6th and 8th day (see the grey curve on Figure 50). For the case of the Pb extraction, it was observed that decreased after the 6th day of leaching, which could also indicate a precipitation of Pb. On the other

hand, the experiments carried out with the setup CC (boards were completely submerged in the leaching solution, with recirculation of the solution at 6.8 ml/min) showed continuous metal extractions and precipitation was not observed. Furthermore, these experiments achieved a Sn and Pb extractions of 52% and 11% respectively.

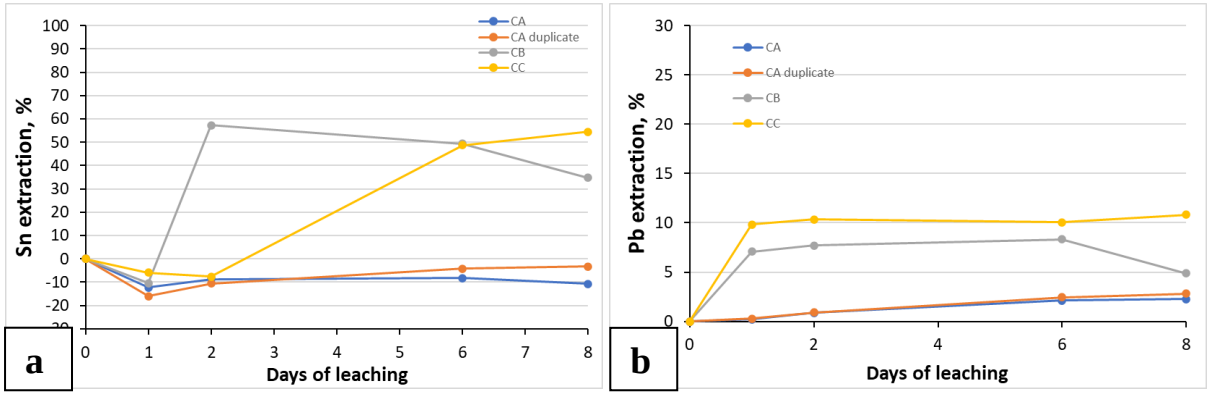

Figure 50. *Results from the three column set-up experiments: left Sn, right Pb extraction*

Further tests were carried out at different combinations of HCl and Sn^{4+} as per Table 28 using column set-up C. The results (Figure 51) clearly show the effect of initial $Sn^{4+,}$ although even in its absence some limited Sn leaching is achieved, potentially due to an autocatalytic effect. The linear progress of leaching indicates the limitation of oxidant regeneration by air. Pb extraction is not significantly affected by Sn concentration and remains consistently low around 10%. Cu extraction was negligible.

Table 28. *Description of leaching tests using different Sn^{4+} concentration*

Samples	Leaching solution	Populated boards wt, g	Non-populated board wt, g
Sn4	1 M HCl	240.10	129.66
Dsn4	1 M HCl	243.54	131.57
Sn5	1 M HCl + 1 g/L Sn^{4+}	231.54	125.10
Sn6	1 M HCl + 3 g/L Sn^{4+}	240.00	129.66
Sn7	1 M HCl + 5 g/L Sn^{4+}	240.00	129.66

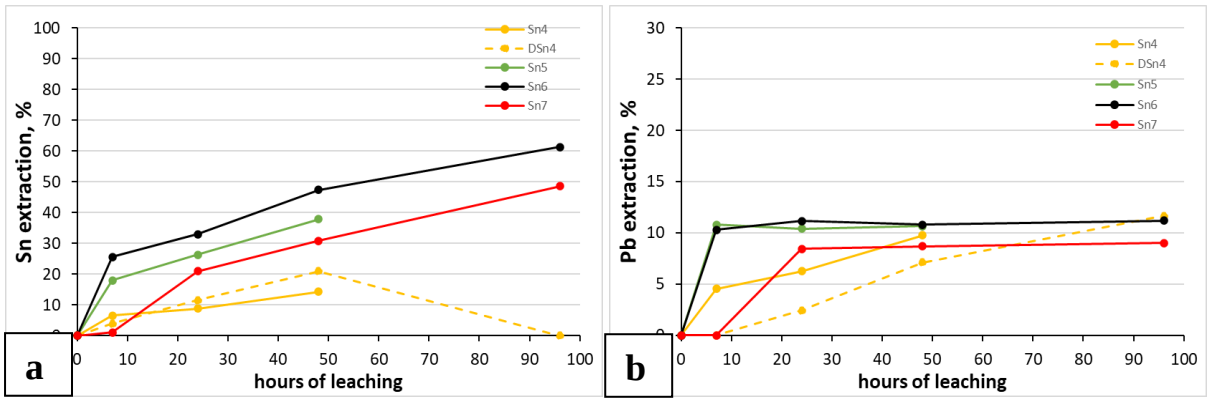

Figure 51. *Results from column leaching experiments in M HCl and various Sn4+ dosing; a) Sn and b) Pb.*

10.4. Conclusions

The experiments carried out with solder wire showed that Fe^{3+} and Sn^{4+} are strong oxidants affecting Sn dissolution. Even though the mix of Sn^{4+} + Fe^{3+} increased the leaching in 10% for some cases, it is not worth to have Fe as an impurity for the further purification process. It was concluded that, the stannic chloride is the best oxidant to use in hydrochloric acid, with 1-2M HCl and 5g/L Sn^{4+} showing the best results.

Column experiments that submerged leaching with a slow recirculation of solution showed the best results and again a combination of strong HCl and 5g/L Sn^{4+} gave the best performance. It was clear that extraction rate was limited by the supply of oxygen (through air) into the reactor system. Pb extraction was limited under these conditions, assumed to be due to re-precipitation as PbO_2 phases. This offers an opportunity for separate lead recovery through a secondary HNO_3 leach.

11. Study 8 – Considerations towards the development of an integrated flowsheet for the recovery and utilisation of metal values from waste PCBs

11.1. Introduction

The need to develop sustainable solutions for recycling e-waste has resulted in various effective methods of recovering valuable metals such as copper and gold which are found in abundance in e-waste particularly on printed circuit boards (PCBs). One of the challenges associated with PCB recycling is the variable metal content, however, it is estimated on a global scale, that up to 0.2 kilo tonnes of gold and 1800 kilo tonnes of copper can potentially be recovered from waste printed circuit boards alone (Forti et al., 2020).

Due to limited collection and recycling initiatives, Africa is significantly lagging with low collection rates that account to less than 1% of the e-waste generated (Balde et al., 2017). Despite this set back, there exists an opportunity for South Africa to overcome these challenges by the implementation of planned legislative framework targeted towards sustainable waste management practices that align with global standards (Kondo, 2023) . This is particularly important not only because of the lucrative value associated with e-waste recycling which is estimated to reach a global value of USD110.6 billion by 2030 (Global Electronics Recycling Business Report, 2023), but also to stimulate the down-stream use or re-use of the recovered metals in local industries. It was within the premise of the original project to consider re-utilising Cu and Au recovered from reject PCBs form its manufacturing process directly in the process and some opportunities for this are discussed in the following. However, the volumes of such reject material well exceed the potential waste stream of PCBs and thus the potential production of metal may well exceed the internal demand of a single manufacturer.

11.2. Assessing the steps of the initial process flowsheet

A preliminary process flowsheet had been developed at the initial stages of this project (Figure 1 of this report), and the various research studies presented in this project report aimed at deepening the science behind each individual process step and evaluate its feasibility and ease of integration with the proposed process. A number of aspects and limitations were identified though this work which are summarised in the following sections.

11.2.1. Ammonia leaching of Cu and recovery from solution

While the ammonia leaching process, which echoes the chemistry used in the etching of copper during circuit board manufacture, works well, its speed is strongly dependent on the mode of agitation, temperature and the overall back-ground copper concentration. Most laboratory test work was done at low background copper concentrations in order to make the achieved copper dissolution from a single model board (11.8 g) well discernible from the background. Extraction therefore reached completion only after days of leaching, whereas in an industrial setting one would expect much faster turn-around to justfy equipment utilisation. Industrial etchant solutions operate at 50-100g/L of copper background concentrations and etching proceeds with warm solutions (40-50 ‘C).

Also, reactor agitation plays a role, as moving from overhead stirred tank reactors in which cut or shredded boards mostly sat at the bottom to bottle rollers which provided constant physical movement of the pieces has demonstrated. In in industrial operation the etchant solution is actively

sprayed over the surface of boards and agitation is thus maximised. Some work was conducted in leach percolation columns which are non-agitated, more or less passive systems with good extractions achieved. These systems are an interesting option to consider for waste re-processing as they are simple and cheap to set up, easy to operate at various scales and minimise the use of solution inventory at the expense of speed. While in primary industrial production process timelines are of essence, this does not apply for waste-processing.

Recovery of Cu from an ammonia etching solution is well established in industrial practice, using an integrated SX/EW circuit which is easily scalable and can produce a high purity (>99.9%) Cu product. As the SX stage presents an additional process step, direct electrowinning of Cu form the ammonia solution was explored in Study 6 (Section 9) in the present project and found to be successful if operated under optimised conditions. However, the likely presence of impurities in the leach liquor from PCBs may interfere with the quality of the final copper cathode, requiring further investigations.

11.2.2. Thiosulphate leaching of Au and recovery from solution

The thiosulphate leaching of Au form circuit boards was studied in some detail (Study 2, Section 6) and found to proceed efficiently where the Cu background concentration could be kept within an optimal window of around 40-100 mM with near complete extraction achievable within 6 hours of contact time. However, maintaining this window in the context of treating PCBs is difficult as Cu concentration on the boards exceeds that of Au by orders of magnitude. Therefore, careful control of residual copper leaching during the Au thiosulphate process would be needed, for example by ensuring that there is no residual copper on the boards as they enter the Au leaching stage. An easier option would be to leach the gold form the boards before copper liberation by size reduction and delamination since all gold on circuit boards sits on the surface to make up contacts, whereas most copper sits within the board laminate or under protective coatings. This advantage of leaching Au from unpopulated circuit boards before Cu ammonia leaching was clearly demonstrated in Study 4 (Section 7), where rapid and complete Au extraction was achieved from PCBs before ammonia leaching, only partial recovery if run afterwards.

The recovery of Au from thiosulphate leach solutions was investigated using various IX resins (Study 5, Section 8), but the loading and elution were generally poor, achieving only marginal recovery of the gold into the eluate and considerable co-extraction of Cu. This was attributed primarily to the very low background concentrations of Au in the leach liquor (<8 ppm) relative to the background Cu concentration (40 mM = 2.5g/L) that is required for optimal Au leaching. Also, the resins tested for this study were not specifically designed for the thiosulphate system. Therefore further, more systematic study of Au recovery from such solutions is needed before the viability of the system in the given context can be ascertained.

It needs to be noted that the thiosulphate system was investigated primarily as an alternative to the well-established, but hazardous cyanide system for Au leaching. Interference by Cu plays a role also in this system, but here it is not an essential catalyst for the leaching reaction. Other Au leaching systems, including thiocyanate and thiourea could also be considered. Some test work done at UCT in a parallel study has focussed on using the iodine system for Au leaching form PCBs, which is showing promising results not only in terms of Au dissolution, but also direct Au electroplating and regeneration of the iodine regent, which makes this system substantially simpler to operate.

11.2.3. Solder removal

A preliminary study of the chemical removal of Pb/Sn solders form the surface of populated PCBs was presented in Study 7 (Section 10) using various combinations of HCl and $SnCl_4$ and nitric acid. A larger scale de-soldering study was conducted in a column percolation reactor with good results. Although optimal recipe and reactor configuration would still need to be established through further work, it becomes clear that the selective removal of Pb and Sn as the key solder materials through a simple leaching process is feasible in principle. Manual removal of electronic components following solder leaching was also found to be straightforward. However, in a parallel study the removal of solder melting through heat treatment was explored with later electrolytic separation of Pb and Sn, which yielded similar results, but required less use of chemicals. These two approaches therefore need still further exploration.

A key aspect of solder removal is the liberation of Au on contacts for subsequent leaching. As most Au leaching work in the present project was done on unpopulated boards, it remains to be seen to what extent this freeing-up can be achieved through different solder removal approaches.

11.2.4 Size-reduction and delamination

Size reduction of PCBs is aimed a liberating valuable metal components for subsequent leaching and in principle the finer the grind the better for subsequent valorisation. This principle applies also in the context of metal production from primary ores. However, the finer the grind the more costly the operation to achieve it. PCBs by their elastic nature are also not easy to grind, resulting in substantial energy loss to absorbed heat. Further, as the leaching work has shown, the early liberation of Cu may in fact negatively interfere with Au leaching.

In the present study size reduction using a grab shredder was explored (Study 1, Section 4) with and without removal of the surface protective solder mask through soaking in alkali solution. The effectiveness of the various parameters was investigated through subsequent diagnostic ammonia leaches of Cu. The solder mask removal was the critical factor in Cu liberation, whereas repetitively shredding the boards, while relatively low energy, did only modestly enhance Cu leaching through increasing mechanical de-lamination of the various layers of the board which allow access to the Cu.

Chemical de-lamination of shredded boards with NMP, on the other hand, resulted in remarkable improvement of Cu extraction from these difficult-to-access layers (see Study 2, Section 5). While the delamination process is relatively slow and conducted at elevated temperatures, it is a passive process, the solvent is relatively inexpensive and can be easily be regenerated through distillation.

Although not part of the present project, in a parallel study charring of the PCBs through pyrolysis was tested and its effectiveness confirmed in subsequent standard ammonia leach. However, this route would no longer preclude Cu from interfering in the Au leaching. Furthermore, the char, if not removed prior to leaching is likely to act as an adsorbent for the dissolved minerals, especially Au.

11.3. Revised process design and re-utilisation of metal values

Considering the critical discussion of the experimental work conducted in this project, the original flowsheet as proposed in Figure 1 needs to be revised before embarking on piloting work with any hope of demonstrating a successful process.

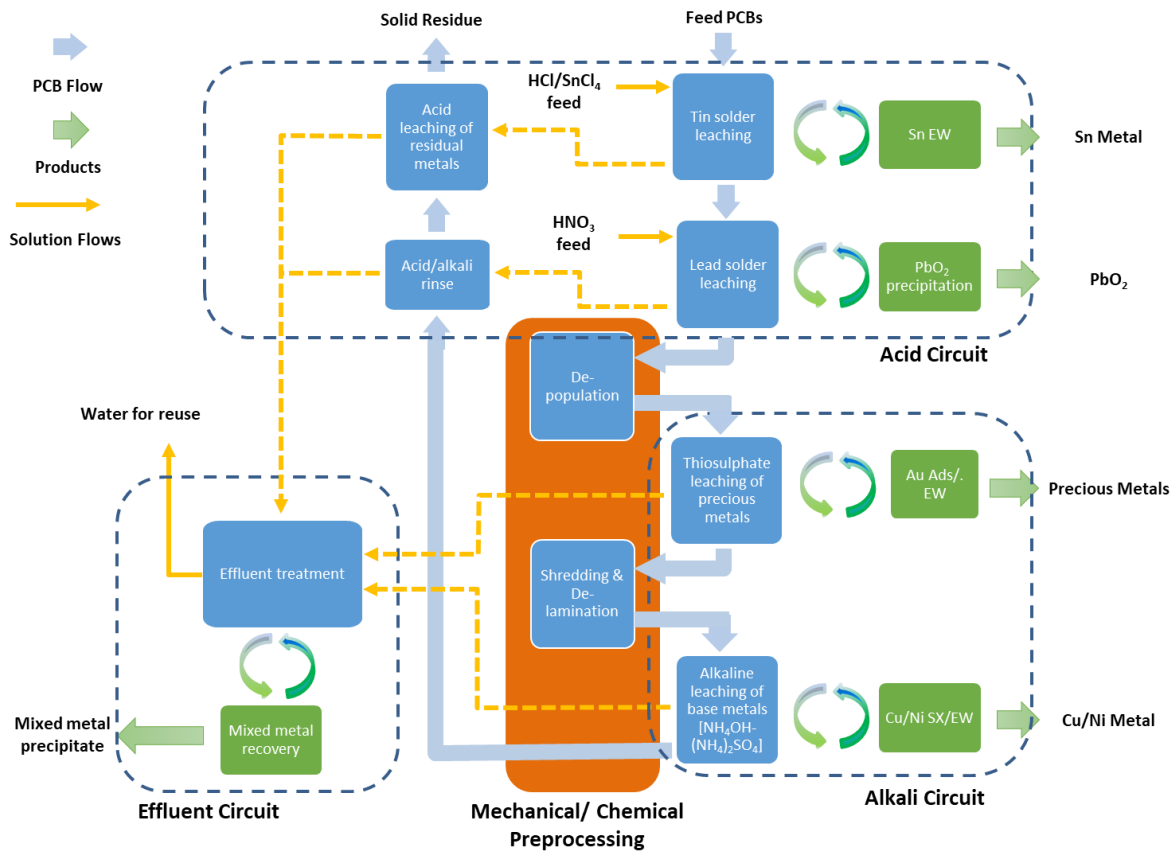

Figure 52. *Revised hydrometallurgical flow sheet for the recycling of waste PCBs*

A revised process flowsheet is shown in Figure 52. Here the flow of PCBs is from acid desoldering, via mechanical de-population to whole board Au leaching, followed by shredding and chemical delamination and then ammoniacal leaching with the leached PCB residues then rinsed with the bleed acid from the de-soldering stages to leach any residual metals. The solder stages will be operated in submerged columns/vats, whereas the Au-thiosulphate leach will probably be operated in batch tumbling drums – mimicking the bottle rollers. The Cu/Ni stage will be in a trickle column with recycle of the leach solution. The respective recovery stages will be operated in circulation with the main leach stage and all key metals will be produced by electrowinning which offer production of high-grade metal products for sale. All process solution bleed streams will be combined to effect overall neutralisation to precipitate any residual metals and the metal-rich waste sludge can be processed further or disposed. The leached bords consist of a largely clean waste material that can be used as filler material or potentially be incinerated.

Before embarking on a pilot study of the proposed revised project, the improved understanding of the process flows has also been translated into detailed process flow sheet design and associated mass and energy balances. This allows consistent updating of the process as new insights emerge and also allows for easy up-scaling of the process flowsheet.

By way of example this is shown for the two core leach stages (Au and Cu) as per Figure 53 and the associated mass balances in Tables 29 and 30 for a plant that processes 1000 kg/day of PCBs.

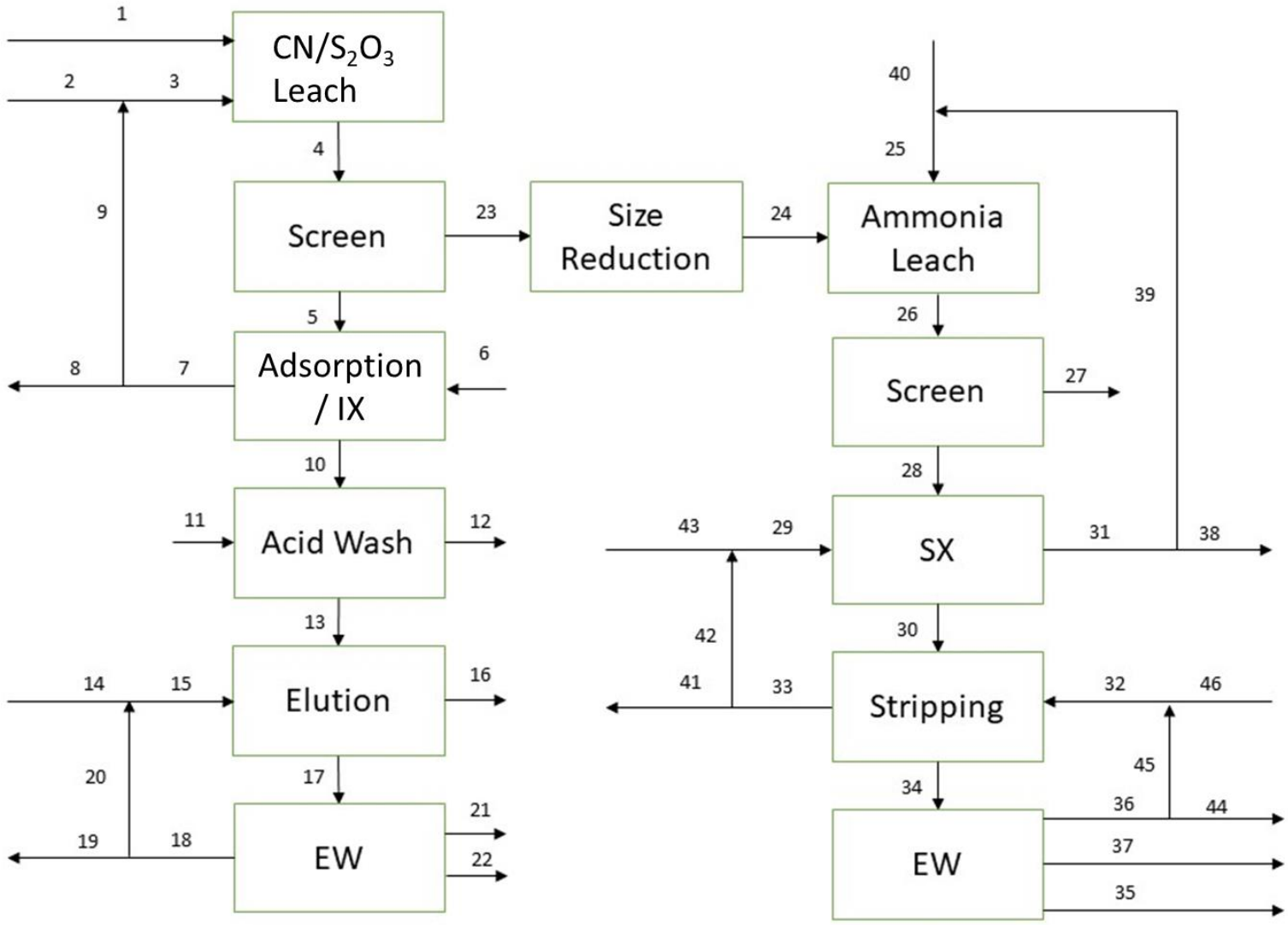

Figure 53. *Detailed Flowsheet design of Au and Cu leach circuits.*

Table 29. *Stream table for the Au-Cn leach circuit (all flows in kg/hr)*

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Au	Metals in Solid State	0.011	0	0	0.002	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.009	0	0.002
Ag		0.052	0	0	0.010	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.041	0	0.010
Cu		4.119	0	0	3.789	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.208	0	3.789
Ni		0.376	0	0	0.188	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.025	0	0.188
CaOH2 (lime)	Reagents and products for cyanide solution	0	0.001	0.029	0.029	0.029	0	0.029	0.001	0.028	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NaCN		0	0.741	1.354	0.645	0.645	0	0.645	0.032	0.613	0	0	0	0	0.494	0.587	0	0	0.098	0.005	0.093	0	0	0
O2		0	0.232	0.250	0.019	0.019	0	0.019	0.001	0.018	0	0	0	0	0	0	0	0	0	0	0	0	0.066	0
H2O		0	10.3	207	207	207	0	207	10	197	0	1384	1384	0	2.9	57.8	0	57.8	57.8	2.89	54.9	0	0	0
NaAu(CN)2		0	0	0.009	0.012	0.012	0	0	0	0	0	0	0	0	0	0.0012	0	0.013	0.0013	6.54E-05	0.0012	0	0	0
NaAg(CN)2		0	0	0	0.071	0.071	0	0	0	0	0	0	0	0	0	0.007	0	0.077	0.008	0.000	0.007	0	0	0
NaCu(CN)2		0	0	0	0.719	0.719	0	0	0	0	0	0	0	0	0	0.799	0	1.295	0.842	0.042	0.799	0	0	0
NaNi(CN)2		0	0	0	0.410	0.410	0	0	0	0	0	0	0	0	0	0.220	0	0.289	0.232	0.012	0.220	0	0	0
NaOH		0	0	0	0.347	0.347	0	0.347124	0	0	0	0	0	0	0.166	0.292	0	0.292	0.132	0.007	0.126	0	0	0
H2		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.160	0	0	0	4.33E-05	0
Carbon		0	0	0	0	0	4.17	0	0	0	4.17	0	0	4.17	0	0	4.17	0	0	0	0	0	0	0
CaAu(CN)2	Acid Wash and Elution Reagents and Products	0	0	0.0002	0.0002	0	0	0.0002	0.0000	0.0002	0.0118	0	0	0	0	0	0	0	0	0	0	0	0	0
CaAg(CN)2		0	0	0.007	0.007	0	0	0.008	0.000	0.007	0.069	0	0	0	0	0	0	0	0	0	0	0	0	0
CaCu(CN)2		0	0	0.074	0.074	0	0	0.078	0.004	0.074	0.699	0	0	0.210	0	0	0	0	0	0	0	0	0	0
CaNi(CN)2		0	0	0.160	0.160	0	0	0.168	0.008	0.160	0.392	0	0	0.118	0	0	0	0	0	0	0	0	0	0
H+		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HCl		0	0	0	0	0	0	0	0	0	0	0.229	0.005	0	0	0	0	0	0	0	0	0	0	0
CaCl2		0	0	0	0	0	0	0	0	0	0	0	0.341	0.224	0	0	0	0	0	0	0	0	0	0
HCN		0	0	0	0	0	0	0	0	0	0	0	0.166	0	0	0	0	0	0	0	0	0	0	0
AuCN		0	0	0	0	0	0	0	0	0		0	0	0.0098	0	0	9.8E-05	0	0	0	0	0	0	0
AgCN		0	0	0	0	0	0	0	0	0	0	0	0	0.051	0	0	0.0005	0	0	0	0	0	0	0
CuCN		0	0	0	0	0	0	0	0	0	0	0	0	0.323	0	0	0.0032	0	0	0	0	0	0	0
NiCN		0	0	0	0	0	0	0	0	0	0	0	0	0.178	0	0	0.0004	0	0	0	0	0	0	0
TOTAL		4.558	11.324	209	213	209	4.167	208	10.396	198	5.339	1384	1385	5.280	3.552	59.718	4.171	59.8	59.1	2.956	56.2	0.283	0.066	3.990

Table 30. *Stream table for the Cu-NH_3 leach circuit (all flows in kg/hr)*

		24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46
Au	Metals in Solid State	0.0022	0	0	0.0022	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ag		0.010	0	0	0.010	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu		9.968	0	0.299	0.299	0	0	0	0	0	0	0	9.22	0	0	0	0	0	0	0	0	0	0	0
Ni		0.188	0	0.056	0.056	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn		0.902	0	0.271	0.271	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH4+	Reagents and products for ammonia solution + EW	0	9.89	6.93	0	6.93	0	0	12.36	0	0	0	0	0	0	2.59	9.76	0.124	0	0	0	0	0	0
(SO4)2-		0	26.32	26.32	0	26.32	0	0	26.32	72.47	0	72.47	0	72.47	0	5.53	20.79	5.53	0	0	0	1.81	70.66	1.81
NH3		0	9.73	1.34	0	1.34	0	0	6.47	0	0	0	0	0	0	1.36	5.11	4.61	0	0	0	0	0	0
O2		0	3.70	2.43	0	2.43	0	0	2.43	0	0	0	0	0	2.32	0.511	1.92	1.78	0	0	0	0	0	0
H2O		0	98.02	99.50	0	99.50	0	0	99.50	473	0	473	0	471	0	20.90	78.61	19.42	0	0	0	11.76	458.79	14.37
H+		0	0	0	0	0	0	0	0	29.75	0	29.45	0	29.7	0	0	0	0	0	0	0	0.74	29.00	0.45
Cu(NH3)4		0	0.824	20.86	0	20.86	0	0	1.04	0	0	0	0	0	0	0.219	0.82	0	0	0	0	0	0	0
Ni(NH3)42		0	1.069	1.35	0	1.35	0	0	1.35	0	0	0	0	0	0	0.284	1.07	0	0	0	0	0	0	0
Zn(NH3)42		0	4.849	6.14	0	6.14	0	0	6.14	0	0	0	0	0	0	1.289	4.85	0	0	0	0	0	0	0
kerosene/	SX and stripping Reagents and Products	0	0	0	0	0	32.26	32.26	0	0	32.26	0	0	0	0	0	0	0	0.81	31.46	0.81	0	0	0
LIX54		0	0	0	0	0	75.28	0.94	0	0	75.28	0	0	0	0	0	0	0	1.88	73.40	1.88	0	0	0
CuA2		0	0	0	0	0	0	83.61	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AH		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu2+		0	0	0	0	0	0	0	0	13.48	0	23.04	0	13.83	0	0	0	0	0	0	0	0.346	13.48	0
ZnA2		0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0	0	0
TOTAL STREAM		11.1	154	165	0.64	165	108	117	156	589	108	598	9.22	587	2.32	32.68	122.9	31.46	2.69	104.9	2.69	14.7	572	16.6

The metals recovered from e-waste recycling are key raw materials in renewable energy technologies, the high purity copper attainable from waste PCB beneficiation lends it to direct reuse. It can be refined further and used to make copper foil, an essential anode material for lithium-ion batteries. This is of particular interest as, globally, the transition to renewable energy sources is of paramount importance. For South Africa, the need to transition to renewable energy sources is a daily reality which has resulted in significant demand for energy storage solutions. This has seen battery imports of lithium-ion cells and batteries skyrocketing from USD0.2 billion in 2021 to US1.1 billion in the first half of 2023 alone (Kuhudzai, 2023).

The conversation around South Africa broadening participation in the battery value chain is ongoing as the country is positioned well with several companies already assembling batteries using imported cells as well as manufacturing battery components (Montmasson-Clair, Moshikaro & Monaisa, 2021). Research into establishing battery cell manufacturing locally is limited but ongoing with AutoX and Megamillion exploring local manufacturing opportunities. Metair have gone as far as establishing a pilot plant for producing lithium-ion batteries in South Africa (Montmasson-Clair, Moshikaro & Monaisa, 2021), this is in addition to their battery manufacturing operations in Turkey and Romania. There exists an opportunity for the copper recovered from e-waste recycling to provide the high purity copper required for local lithium battery manufacturing as well as exports of battery grade copper. Beyond its use in lithium-ion batteries, copper is a key metal in the global green energy transition with the S&P Global Market Intelligence reporting the projected demand for copper to increase by 54% by 2030 on the backdrop of a 22 million tonne production shortfall in 2022 (Mills, 2023).

The metals recovered from PCB recycling can also be reused in the PCB manufacturing process directly which uses copper and gold as key raw material in the form of high purity copper anodes and as well as gold-based salts. This would be beneficial for local PCB manufacturing companies by promoting recovery of valuable resources that can be partially or fully fabricated internally into raw materials for re-use in critical PCB manufacturing processes.

12. Conclusions and Route Forward

Overall, the project has delivered substantial insights into the design of a hydrometallurgical process for the efficient recovery of metals from waste PCBs using ammonia-based leaching technology at its core. In this sense the process is based on the principles of the PCB manufacturing process and the work has shown that waste etchant solutions generated in this process can, in principle be used for the leaching of Cu from waste or reject circuit boards with opportunities for internal recycle of the recovered Au and Cu.

However, an integrated process for waste PCBs involves numerous steps that fall outside the PCB manufacturing process and therefore an immediate integration of the two appears less feasible. Although an evaluation of scale on overall process costs is still outstanding, it is unlikely that the process would be viable as an add-on to just process the reject and off-cut boards arising within a single small- or medium scale manufacturer. Consequently, a larger facility that is dedicated to the processing of waste PCBs collected at the regional scale (>1 t/day) that is carefully integrated with local industry to utilise the product palette generated by this process is the more likely option to consider.

Therefore, the challenge is now to develop the process further in terms of the various unit operations identified and evaluate it at the scale of a pilot process (at, say a few kg per day or per batch) that integrates all the process steps in a continuous chain from waste to end-product. Ongoing improvements to individual processing steps can be made while operating this process with some regularity. This will then allow the determination of the techno-economic feasibility of the process at different industrial scales and a decision on the next step.

A follow-on project to tackle these exact issues is currently getting underway. This sees our group collaborating with IME at the RWTH Aachen in Germany and Boku University in Vienna within the project ‘Short Circuits’ 2024-2027, supported by the VW Foundation.

Outputs from the Project

Publications

- Moyo, T. Ortega Jimenez, F., Prestele, M.P., Kondo, T.D. and Petersen, J. 2022. Evaluating pre-treatment methods to maximise copper recovery from printed circuit boards. Journal of Metallurgy and Materials Science, Vol. 64, No. 1-2, January-June 2022; http://jmms.nmlindia.org/volume-64-issue-1-2/
- Moyo, T., Chirume, B.H. and Petersen J. 2020. Assessing alternative pre-treatment methods to promote metal recovery in the leaching of printed circuit boards. Resources, Conversation and Recycling 152 (2020) 104545; DOI:10.1016/j.resconrec.2019.104545
- Moyo, T. and Petersen J. 2021. Pre-processing and characterisation of PCBs to unlock opportunities for local end processing in developing economies. IMPC 2020 Congress Proceedings; The Southern African Institute of Mining and Metallurgy (SAIMM), 2021, ISBN 978-1-928410-21-8, pp 3550-3558.
- Maharaj, D., Moyo, T. and Petersen, J.: 'Ammonium thiosulphate leaching of gold from electronic printed circuit boards – effect of copper concentrations'. 2024. Submitted to Minerals

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- Prestele, Mark (2020). Assessment of a shredding technology of waste Printed Circuit Boards (PCBs) in preparation for ammonia-based copper leaching. MSc Thesis. University of Cape Town.
- Maharaj, Dasmi (2022). Exploration of the thiosulphate process for the dissolution of gold from electronic waste and its recovery through ion-exchange. MSc thesis, University of Cape Town
- Kondo, Takunda (2023). Evaluation of solvent swelling pre-treatment combined with ammonia leaching using waste etchant from printed circuit board manufacturing for copper recovery from waste printed circuit boards', MSc thesis, University of Cape Town
- Gonte, Melissa (2023). Investigating Early-Stage Process Flow and Reactor Sequencing to Maximise Gold Extraction In the Thiosulphate Leaching of Waste Printed Circuit Boards. MSc thesis, University of Cape Town
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