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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

Submitted in fulfillment of the requirements for the awarding of a Master of Science Degree in Chemical Engineering

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Abstract

Electronic waste (e-waste) has emerged as a rapidly growing waste stream, growing at a global rate of 2 Mt per annum and is expected to exceed 74 Mt by 2030. E-waste contains a high content of precious and base metals which can be recovered for economic benefit. This has made the recycling of this waste stream of interest, with particular emphasis on the recovery of metals from waste Printed Circuit Boards (PCBs) as they contain a high content of copper as well as a significant quantity of precious metals such as gold, silver, and palladium. The major economic driver for the beneficiation of PCBs is the recovery of these precious metals followed by the recovery of copper which can constitute more than 20% of the value share. In the South African context, 5-7% of e-waste generated is collected and formally recycled. There exists potential to increase the proportion of e-waste recycled through the development of accessible beneficiation techniques that can be implemented by small scale industries.

This study builds on previously completed research on alkaline ammonia leaching for the recovery of copper from waste PCBs that have undergone various physical or chemical pre-treatment processes for metal liberation. Some PCB manufacturing processes employ a similar alkaline ammonia oxidative leaching system as one of the key process-steps in the manufacturing of PCBs as is evident by the case study of a local PCB manufacturing company. There exists an opportunity to utilize waste etchant from the manufacturing process as lixiviant for the recovery of copper from waste PCBs. This will enhance resource efficiency in line with the United Nations sustainable development goal 12, responsible consumption and production by extracting value from both the copper loaded waste etchant and waste PCBs.

The potential to recover copper from both waste PCBs and the waste etchant through a leach circuit that utilizes the excess lixiviant contained in the waste etchant is explored. To do this, the copper distribution of a custom-made 4-layer PCB is established through a breakdown of the readily accessible top and bottom surface copper, referred to as the “surface copper” as well as the tightly laminated inner layer copper inaccessible to the lixiviant. Pre-treatment utilizing chemistry from the PCB manufacturing desmear process is then explored as a viable pre-treatment method for liberating the inner layer copper with a key focus on solvent swelling with N-Methyl-2-pyrrolidone (NMP) and NMP based solvent (Solvent B).

The characterization of the custom-made PCB determined that 47.2% of the copper was located on the surface of the PCB and 52.8% in the inner layers. The success of the solvent swelling pre-treatment is measured by the extent to which this 52.8% is unlocked for access by the lixiviant. The degree of metal liberation by the chemical pre-treatment method employed was determined by diagnostic column leaching using primarily samples of waste etchant from a local PCB manufacturing factory as well as synthetic etchant modelled after a typical waste etchant stream. Solvent swelling yielded good recoveries above 90%, with NMP solvent swelling at 150°C achieving the highest copper recovery of the two solvents at 93.4%.

It was found that the PCBs that did not undergo solvent swelling yielded recoveries mostly from the surface copper with a recovery of 50% from boards that had been soaked in sodium hydroxide for removal of the solder mask coating. A combination of both physical and chemical pretreatment by combining 6 pass shredding with solvent swelling yielded a copper recovery of 68.9% using Solvent B. This was comparable to 88.4% obtained from solvent swelling with the same solvent. Solvent swelling alone was found to be an effective method for liberating copper from the inner layers and combining swelling with mechanical shredding was found to yield lower copper recoveries as a result of the preg-robbing phenomenon. Three lixiviant systems were analyzed for performance, namely ammonium sulphate, waste etchant and synthetic etchant. Of the three, ammonium sulphate with initial copper concentration of 100 ppm was significantly outperformed in leaching rate by waste etchant and synthetic etchant which required shorter leaching times to recover the readily accessible surface copper, however waste etchant was found to have limitations of copper saturation leading to precipitation due to its high copper content.

Table of Contents

List of Figures

List of Tables

Nomenclature

E-Waste	Electronic Waste
PCB	Printed Circuit Board
Lixiviant	Liquid leaching medium
Etchant	Liquid leaching medium used to define PCB circuitry in etching process
NMP	N-Methyl-2-Pyrrolidone
Solvent B	NMP based proprietary solvent
EPR	Extended producer responsibility
Pre-preg	Resin pre-impregnated material
FR-4	Flame retardant woven glass reinforced epoxy resin
Electroless copper	Chemical method of plating copper in drilled PCB holes
Direct metallization	Method of rendering PCB drilled holes conductive without electroless copper
Etch resist	Etchant resistant coating used to protect the desired copper circuitry on a PCB
Solder mask	Surface polymer coating on PCB
Tg	Glass transition temperature
BER	Brominated epoxy resin
UV-Vis	Ultraviolet-visible spectroscopy
Non-Populated PCB	Bare printed circuit board with no components
Populated PCB	Circuit board assembled with components
Mt	Million Tonnes
AAS	Atomic Absorption Spectrometry
Cu (II)	Cupric Ion
Cu (I)	Cuprous Ion

1 Introduction

1.1 Background

The Global E-Waste Monitor Report of 2020 (Forti et al., 2020) highlights electronic waste (e-waste) as one of the fastest-growing waste streams, growing at a rate of 2 Mt per annum. In addition, significant amounts of precious and base metals can be recovered from this stream for economic benefit.

The potential value from the beneficiation of e-waste for metal recovery has made this a stream of economic interest with particular emphasis on the recovery of metals from waste Printed Circuit Boards (PCBs) which contain one of the highest contents of copper in addition to precious metals such as gold, silver, and palladium compared to the metal content in natural ores.

The beneficiation of waste PCBs can be summarized into three general processing steps (Cui & Zhang, 2008), namely

a) Physical pre-treatment for component disassembly and size reduction.
b) Extraction of the desired metal fractions through mechanical processing and/ or pyrometallurgical or hydrometallurgical processing.
c) Refining through electrometallurgy for purification of the desired metal fraction.

Copper is reported as one of the metals with the highest economic value in e-waste due to its price and availability in large quantities (Golev, Corder & Rhamdhani, 2019; Forti et al., 2020). In hydrometallurgical beneficiation of PCBs for copper extraction, the process is reliant upon the lixiviant's ability to access the metal fraction. The majority of this copper is located within the inner layers of the PCBs tightly laminated between non-conductive resin and fibreglass layers, therefore, pre-treatment of the PCBs for metal liberation is an essential precursor. In contrast, the precious metals are mostly located on the top and bottom surface (the surface) of PCBs, readily accessible to lixiviants used in their hydrometallurgical extraction.

Pre-treatment for copper liberation 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, ranging from physical size reduction and delamination methods such as grinding, shredding and pulverizing (Cui & Anderson, 2016; Sethurajan et al., 2019). In addition, chemical pretreatment methods such as Bromine Epoxy Resin (BER) dissolution through solvent swelling have been used to facilitate delamination of the copper-bearing laminate (Kang et al., 2021).

To address the challenges associated with achieving lixiviant-metal contact with the inner layer copper, one can look to the PCB manufacturing process which employs solvent swelling for resin smear removal in a process known as desmearing prior to copper metallization of the through-holes of a PCB as detailed by European Patent 2287357A2 (Li et al., 2011). Commonly used solvents in both the PCB manufacturing desmear process and e-waste pre-treatment include N-Methyl-2-Pyrrolidone (NMP) and gamma-butyrolactone as detailed by US Patent No. 5,985,040 (Carano, Polakovic & LaFayette, 1999).

In addition to the commonality in the use of solvent swelling, both the manufacturing of PCBs and hydrometallurgical beneficiation of waste PCBs can employ the use of similar lixiviants for copper dissolution through oxidative leaching. An example of such a lixiviant is ammonia/ammonium chloride etchant which is used in PCB manufacturing for oxidative leaching of copper from the bare board. This process often generates excess amounts of copper-bearing waste etchant as is observed at a local PCB manufacturing company used as a case study.

Oxidative ammonia leaching 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) however, the feasibility of utilizing waste etchant from PCB manufacturing has not been detailed. Utilizing this waste stream from the PCB manufacturing process presents the opportunity to build on previous studies which explored the effects of various pretreatment methods on copper recovery using an ammonia-based lixiviant.

In contrast to pyrometallurgical processes, hydrometallurgical processing routes, such as solvent swelling for metal liberation and oxidative ammonia leaching, have proven to be promising for minimizing capital 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).

1.2 Problem statement

Depending on the chemistry of the manufacturing process, some PCB manufacturing plants which employ alkaline ammonia etching produce excess ammonia etchant with high copper concentration. This excess etchant solution, which is otherwise discarded as waste, contains free ammonia together with high amounts of copper in solution and may be usable as a lixiviant in the leaching of copper from waste PCBs, provided the copper in the boards is accessible for effective metal-lixiviant contact.

This would allow for a symbiotic operation in which effluent from the PCB manufacturing plant is used in a PCB recycling plant, thus promoting waste utilization, and providing an opportunity for diversification of income streams. In addition, this system would allow for the activation of extended producer responsibility (EPR) in that the PCB manufacturer can now take back their product, the PCB, and recycle it gainfully using mostly the same resources as that used in manufacturing. A key challenge in such a process is that a high fraction of the copper in waste PCBs is inaccessible owing to it being tightly laminated within the inner layers of multilayer PCBs. Hence, copper recovery is dependent on the effectiveness of pre-treatment methods such as solvent swelling for copper liberation to allow for lixiviant access.

Solvent swelling has been explored as an effective, eco-friendly pre-treatment method for copper liberation from waste PCBs (Verma, Singh & Mankhand, 2016). However, most research on solvent swelling pre-treatment focuses on BER dissolution and neglects to detail the effect of this pre-treatment on copper extraction (Kang et al., 2021).

1.3 Objectives

The research aims to investigate the feasibility of using NMP-based solvent for chemical pre-treatment of multilayer PCBs for copper liberation. To effectively leach copper from waste PCBs, organic solvent swelling to render the inner layer copper accessible to the lixiviant will be tested using a proprietary solvent hereafter referred to as Solvent B which is an NMP based organic solvent used in the desmearing process during PCB manufacturing.

The extent of copper liberation is established by leaching the pre-treated PCBs using ammonia/ammonium chloride-based waste etchant from PCB manufacturing. The proof of concept with regards to copper leaching using ammoniacal lixiviant is well established as is evident by its use as lixiviant in various applications such as copper recovery from ores (Tavakoli Mohammadi, 2012) , PCB recycling (Rudnik, Pierzynka & Handzlik, 2016) and PCB manufacturing (Melling, 1986).

The objectives of this study are as follows.

1. Establish the copper content of the custom-made PCB used in the study.
2. Carry out preliminary laboratory investigations to characterize a waste etchant stream from a local PCB manufacturer.
3. Evaluate solvent swelling pre-treatment and oxidation configurations modelled after the desmear process.
4. Determine the effect of solvent swelling on copper leaching and compare the performance of NMP vs NMP based Solvent B in exposing copper for access by ammonia/ammonium chloride lixiviant.
5. Evaluate the effect of combining solvent swelling with mechanical treatment by shredding using an industrial grab shredder.

2 Literature review

2.1 E-Waste Generation

The recycling of e-waste presents an opportunity for the development of a secondary resource economy from the recovery of metals. Globally 20% of e-waste was documented to be collected and appropriately recycled (Balde et al., 2017). An analysis of the e-waste generated and collected per continent highlights the challenges associated with the beneficiation chain, with Africa significantly lagging behind with a reported collection rate of 0.004 Mt which rounds off to 0% on a global scale (Balde et al., 2017).

According to the 2020 South Africa Waste Market Intelligence report by GreenCape (2020) a total of 25 100 t of e-waste was diverted from landfills in 2018. This represents a minor 7% of the estimated 360 000 t of e-waste generated in the same period according to the same study. The poor collection and appropriate recycling initiatives can be attributed to several factors, mainly the lack of access to feedstocks for collectors as well as expensive licencing regulations for e-waste recyclers (Sadan, 2019; Lydall, Nyanjowa & James, 2017). The challenges highlighted have significantly limited the growth of the South African e-waste recycling sector. However, there exists an opportunity to overcome these challenges due in part to the current legislative framework changes in South Africa that are geared towards more sustainable waste management practices that are in line with global standards.

One such framework is the extended producer responsibility (EPR) legislation implemented from November 2021 for the electrical and electronic industry, among other industries, which assigns end of life management to importers and producers of products such as e-waste (National Environmental Management: Waste Act, No. 59 of 2008, 2020). This together with the 2021 banning of waste electric and electronic equipment from disposal to landfill (National Environmental Management: Waste Act, No. 59 of 2008, 2013) creates an opportunity for increased access to feedstock with an anticipated annual increase in collection and recycling of 30% from the EPR regulations alone according to the act. These factors highlight the need for the development of local pre-processing and processing facilities as only 11% of e-waste diverted from landfills was processed locally as recently as 2020 (GreenCape, 2020). Currently, two local processors namely SA Precious Metals and Rand Refinery are active in South Africa with a combined processing capacity of 2 730 tonnes per year (GreenCape, 2020). Both these processors focus on precious metal recovery, leaving an estimated 22 379 tonnes of e-waste to be exported overseas (Lydall, Nyanjowa & James, 2017).

South Africa has an established network of formal and informal e-waste collectors, however, there is a lack of accurate data regarding the volumes, types, and trade flows of e-waste (GreenCape, 2020). This makes it challenging to accurately quantify the metal content for the development of large scale economically viable recycling processes. Table 1 illustrates a worldwide breakdown of selected metals contained in e-waste which amount to a potential value of USD 57 billion, with copper contributing the second highest amount in value.

Table 1 Selected raw material quantity and value in e-waste (Forti et al., 2020)

	Value (mill. USD)	Quantity (kilo tonnes)
Iron	24645	20466
Copper	10960	1808
Gold	9481	0.2
Aluminium	6062	3046
Palladium	3532	0.1
Cobalt	1036	13
Antimony	644	76
Silver	579	1.2
Rhodium	320	0.01
Osmium	108	0.01
Platinum	71	0.002
Indium	17	0.2
Iridium	5	0.001
Rhuthenium	3	0.0003
Bismuth	1.3	0.2
Germanium	0.4	0.02
Total	**57464.7**	

The value of e-waste is tied to the value of the precious and base metals found predominantly in PCBs. Copper and precious metals such as gold, silver and palladium contribute the most to the economic viability of e-waste recycling (Tuncuk et al., 2012). Currently, PCBs are graded according to the quantity of precious metals available for extraction, however, copper is estimated to have the second highest value contribution after gold. PCBs are a particularly rich source of copper, containing a significant amount of up to 30% as described below compared to 0.5% (Tuncuk et al., 2012) found in typical copper ores.

2.1.1 PCB substrate material characterization

The function of a PCB is to provide electrical connection and structural support to electrical components in a circuit (Bhunia & Tehranipoor, 2019). The main constituents of a PCB are non-conductive substrate material composites also known as laminates, resin pre-impregnated material (pre-preg), copper foil and precious metals such as gold, silver, and palladium. Many laminate materials are a composite of epoxy resin and fibreglass reinforcement, for example, FR-4 which is a commonly used laminate in PCB manufacturing. Additives such as flame retardants, curing agents, fillers and accelerators are added to the resin systems as required by the particular function of the PCB (Sanapala, 2018).

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

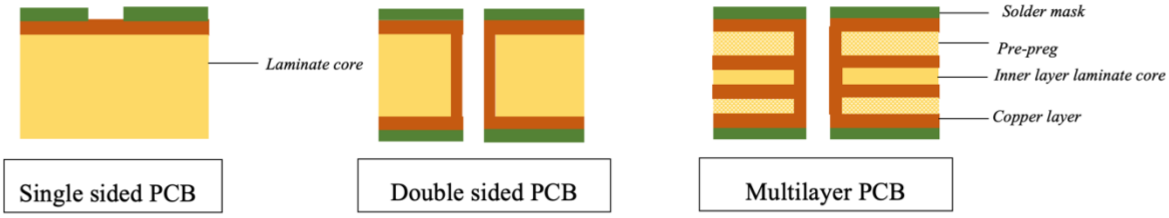


Figure 1 Classification of PCBs by conductive layers

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-preg to yield a tightly laminated composite as illustrated in Figure 2.

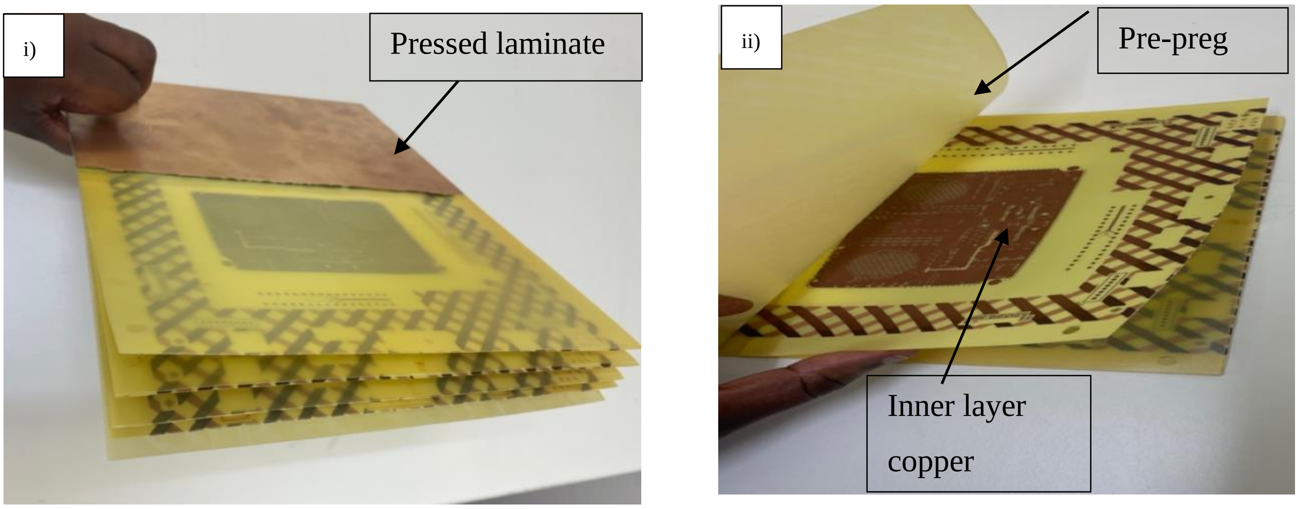


Figure 2 Deconstructed illustration of a 10 layer multilayer PCB sample supplied by Trax Interconnect i)Top surface copper layer and 1st pre-preg layer ii)Inner layer copper

2.1.2 PCB beneficiation

The heterogeneous nature of PCBs, in terms of the varying composition of metallic and non-metallic fractions, renders the beneficiation of this waste stream complex.

Table 2 illustrates the varying copper composition in PCBs from different sources with copper content ranging from 10 wt.% to 33.5 wt.% thus making this stream difficult to characterize.

Table 2 Copper content of various types of PCBs

	PCB Type	**Copper Content**
(Hageluken C, 2006)	Waste computer mainboards	20%
(Hageluken C, 2006)	TV boards	10%
(Oishi et al., 2007)	Generalized PCBs	26%
(Yang, Liu & Yang, 2011)	Waste computer mainboards	25.3%
(Silvas et al., 2015)	Printers	32.5%
(Sahan et al., 2019)	Mobile Phones	33.5%

Figure *3* illustrates the general approach to recycling PCBs, starting with disassembly and extraction of the PCBs from the bulk material, followed by processing for the recovery of metal through pyrometallurgical or hydrometallurgical processing in conjunction with mechanical pre-treatment for metal liberation and finally refining for metal purification.

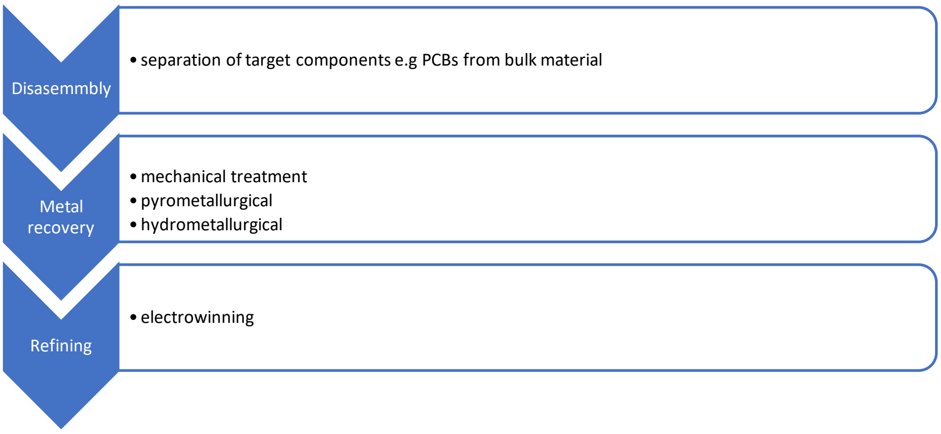


Figure 3 *PCB recycling schematic adapted from* (Cui & Anderson, 2016)

2.1.2.1 Mechanical dismantling and Pre-Treatment

The separation of high value fractions from the bulk e-waste material is carried out through mechanical disassembly. This is then followed by physical pre-treatment for size reduction and upgrading of materials using various methods such as grinding, magnetic separation, shredding, and electrostatic separation, depending on the subsequent treatment process (Cui & Anderson, 2016; Sethurajan et al., 2019). The amount of metal liberated is dependent on the particle size, for example, Zhang & Forssberg (1997) achieved almost complete copper liberation from particle sizes below 2 mm with a hammermill. Coarser fraction sizes achieved lower liberation due to encapsulation of metals in the non-metallic materials. Prestele (2020) employed shredding by means of an industrial grab shredder and noted that significant amounts of copper remained encapsulated in the non-metallic fraction with particle sizes below 8mm.

The mechanical size reduction methods used have a relatively low environmental impact in that they do not generate liquid effluent streams, however, the generation of hazardous dust particles is of serious concern (Tuncuk et al., 2012). In addition, to obtain the particle sizes suitable for maximum metal liberation, significant energy is consumed (Ruan & Xu, 2016). This is especially relevant within the African context where energy supply is expensive and unreliable, in addition, energy production is one of the major contributors to global carbon dioxide emissions thus impacting negatively on climate change (Ibrahim et al., 2021).

2.1.2.2 Pyrometallurgical processing

Primarily, PCB beneficiation methods employ pyrometallurgical processes with subsequent hydrometallurgical refining, or hydrometallurgical leaching preceded by physical pre-treatment for size reduction (Ilankoon et al., 2018). The methods used in pyrometallurgical processing are centered around aiding separation of metals using elevated temperatures.

Processing of e-waste in pyrometallurgical operations such as the one at Umicore in Belgium is carried out through smelting followed by electro-refining for the recovery of copper and precious metals. This is illustrated in Figure 4 which details the flowsheet utilized by Umicore for the co-processing of e-waste with various other metal rich streams (Cui & Zhang, 2008). This plant focuses on two primary processing steps, namely Precious Metals Operations (PMO) and Base Metals Operations (BMO). The primary step of the PMO is smelting which utilizes a significant amount of fuel for energy and organic materials from the feed stream as a partial substitute to coke as reducing agent for metals. The smelter separates precious metals which are further refined downstream after copper extraction in the electrowinning plant. The BMO unit focuses on processing the by-products from the PMO with the energy intensive lead blast furnace as the main process step followed by lead refining and further refining for the extraction of special metals such as Indium, Selenium and Tellurium (Hageluken, 2006). Various feed materials such as industrial metal containing waste, car exhaust catalysts and PCBs are fed into the process amounting to an annual processing capacity of 250 000 tonnes. These feed materials are fed into the process at the most optimum processing step which is determined by analysis of the physical and precious metal content of the streams.

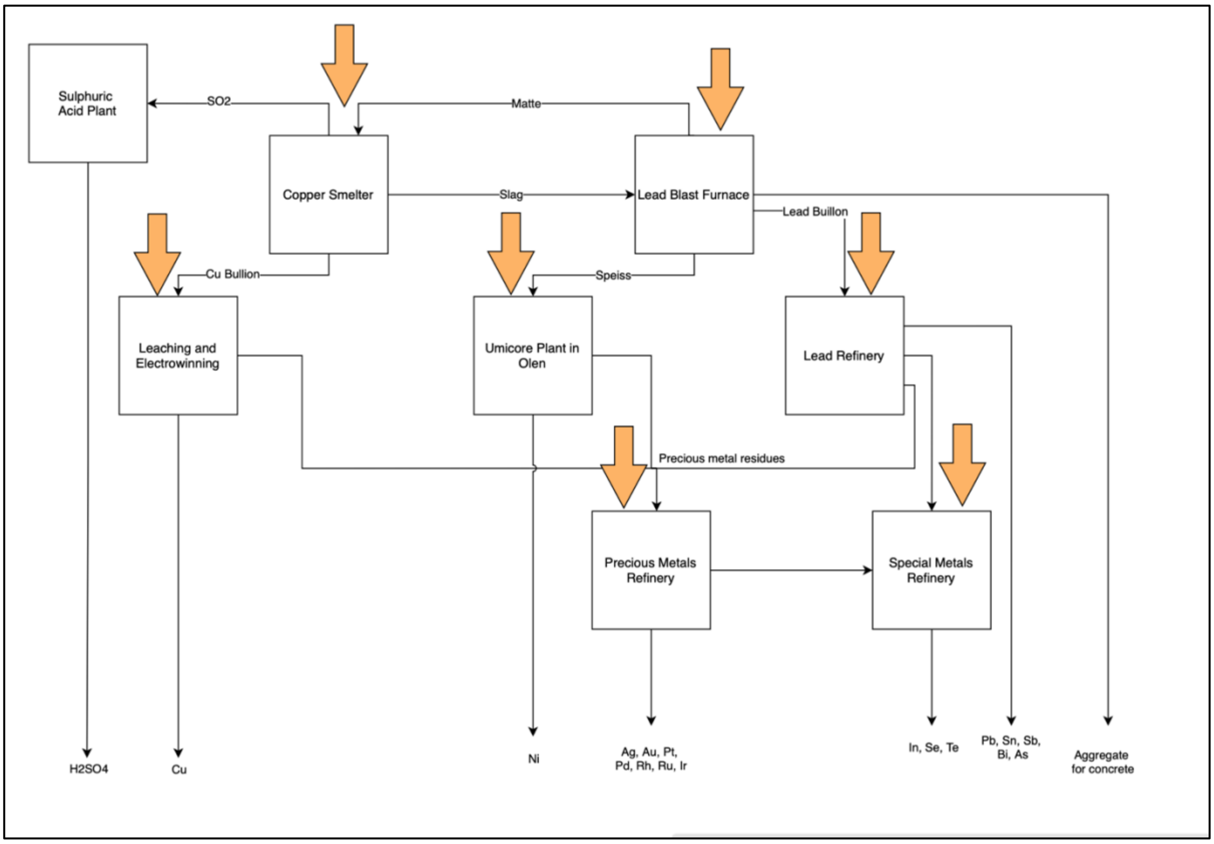


Figure 4 Simplified illustration of Umicore's integrated smelter refinery (adapted from Hageluken, 2006)

Large volumes of high metal content streams are essential for economic viability (Tuncuk et al., 2012) and the technology utilized in pyrometallurgical operations such as the one illustrated in Figure 4 requires significant capital input (Tuncuk et al., 2012). One of the major limitations in pyrometallurgical processing of PCBs is the presence of halogenated flame retardants in the laminate materials used in PCBs which require extensive off gas treatment installations to minimize environmental impact from the production of dioxins (Cui & Zhang, 2008). In contrast, hydrometallurgical processing routes have proven promising for minimizing capital 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 as detailed in 2.1.

2.1.2.3 Hydrometallurgical processing

Hydrometallurgical processing routes have been gaining momentum in e-waste recycling due to the challenges associated with traditional pyrometallurgical processing as highlighted in section 2.1.2.2 (Hsu et al., 2019). Figure 5 outlines a typical flowsheet for the potential hydrometallurgical processing of PCB's for the recovery of both base and precious metals.

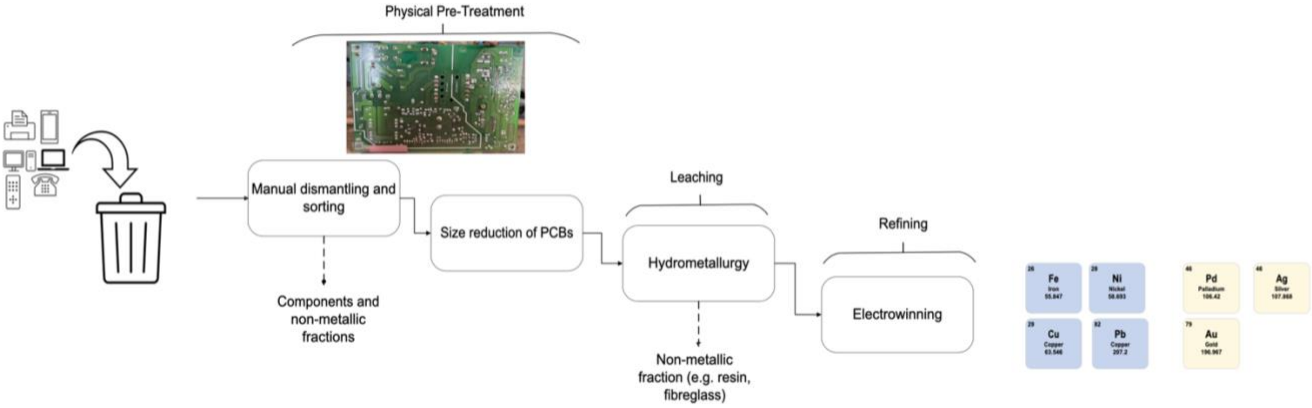


Figure 5 Typical hydrometallurgical process flowsheet for PCB beneficiation (Tuncuk et al., 2012)

Once collected, the PCBs are processed through various mechanical pre-treatment processes for size reduction to liberate the metallic elements enclosed by non-metallic materials such as ceramic, fibreglass and plastic. Size reduction is noted as one of the key factors in maximizing extraction efficiency in subsequent hydrometallurgical leaching processes (Tuncuk et al., 2012).

In light of the value contribution of copper, Tuncuk et al. (2012) detail various hydrometallurgical processing routes for the extraction of copper from waste PCBs which are complex to recycle due to the presence of various fractions other than the metals of interest. In addition, the composition of base and precious metals varies significantly depending on the type of PCB. The selective hydrometallurgical extraction of metals such as copper from PCBs has proven to be successful in various studies as reviewed by Cui & Zhang (2008) and Sethurajan et al. (2019).

Generally, oxidative leaching processes are commonly used for the extraction of copper and precious metals as reviewed by Tuncuk et al. (2012), with ammoniacal alkaline leaching and sulphuric acid/hydrogen peroxide leaching being common technologies for copper extraction (Yang, Liu & Yang, 2011; Radmehr et al. 2013). In these methods, subsequent purification steps are required after leaching to recover individual metal streams. These can include solvent extraction, precipitation and ion exchange followed by electrowinning (Cui & Zhang, 2008).

Ammoniacal leaching is credited as an ideal method for copper leaching from PCBs due to its selectivity to copper over impurities such as iron and aluminium (Oishi et al., 2007). This is an important consideration for the purity of the copper cathode produced in the final electrowinning processes as well as when considering reagent consumption by side reactions during leaching. Ammonia systems form stable amine complexes with copper whilst impurities such as tin, aluminium, and iron remain insoluble at certain pH ranges and thus are not extracted by the lixiviant (Oishi et al., 2007).

2.2 PCB Manufacturing

The PCB fabrication process consists of a series of subtractive and additive processes which bear similarities to the hydrometallurgical processing of waste PCBs. Figure 6 illustrates an example of a typical multilayer PCB fabrication process beginning with inner layer preparation using copper clad laminate.

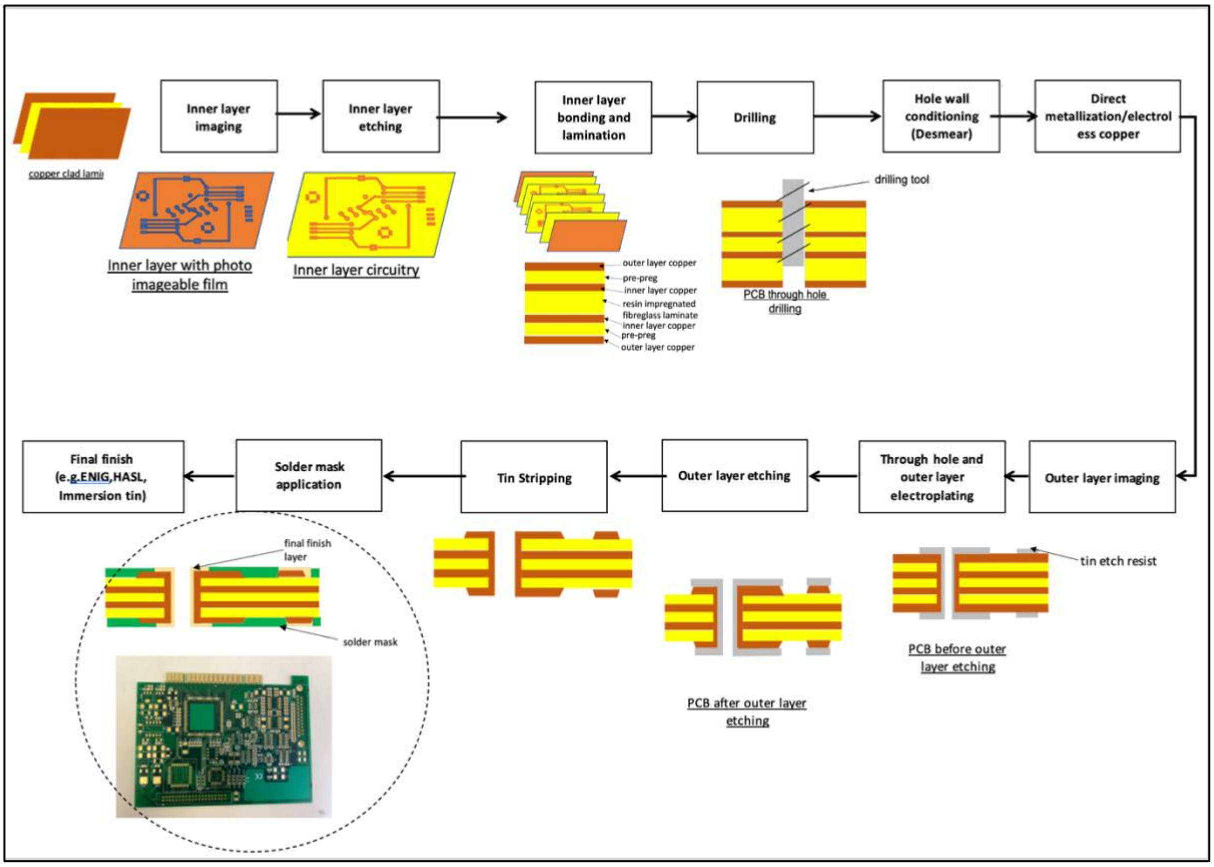


Figure 6 Typical PCB manufacturing process flowsheet for multilayer PCBs

The inner layers are imaged and etched to develop the inner circuit pattern after which they are stacked together with pre-preg and thermally pressed to form a solid laminate with multiple copper layers (Sanapala, 2018) as illustrated in Figure 6. Table 3 illustrates examples of the various inner layer copper foil materials commonly used as well as the minimum thickness obtained in the final PCB after processing.

Table 3 Processing tolerance for common inner layer copper foil materials used in PCB manufacturing adapted from (IPC-6012B, 2015)

Supplied inner layer copper foil material thickness	**Absolute Minimum copper thickness prior to processing (less 10% reduction)**	**Minimum thickness after processing**
½ oz(approx. 17 µm)	15.4 µm	11.4 µm
1 oz(approx. 35 µm)	30.9 µm	24.9 µm
2 oz(approx. 70 µm)	61.7 µm	55.7 µm

Typically, holes are drilled through the laminate to facilitate electrical connections between the copper layers as further illustrated in Figure 7i). This is then followed by a cleaning process known as desmearing where resin smear and debris generated from the drilling process is removed from the holes. In addition to cleaning the holes, the desmear process generates microcavities in the laminate material by etching a small amount of the epoxy resin thus creating a roughened surface which provides an anchoring surface for good epoxy/copper adhesion during copper plating (Ge, Turunen & Kivilahti, 2003).

The drilled holes are initially non-conductive and require either a direct metallization process or a catalysed non-electrolytic process that deposits a thin layer of copper in the holes to render them conductive for copper electroplating (Deckert, 1995). Once the drilled holes have been made conductive, the laminate material is coated with a photo sensitive film to produce the circuit image as illustrated by the blue film in Figure 7 ii) after which the material is processed through an acid copper electroplating bath where copper is plated on the exposed circuit image as well as inside the holes to establish electrical connection between the copper layers. After copper plating, the desired circuitry is electroplated with tin which acts as an etch resist for the subsequent copper etching process where the remaining excess copper on the surface is removed leaving behind the desired circuit image as illustrated in Figure 7 iii). The amount of copper etched from the surface often ranges between 50–70% of the total copper area depending on the design of the PCB (Shah, Gupta & Sengupta, 2018).

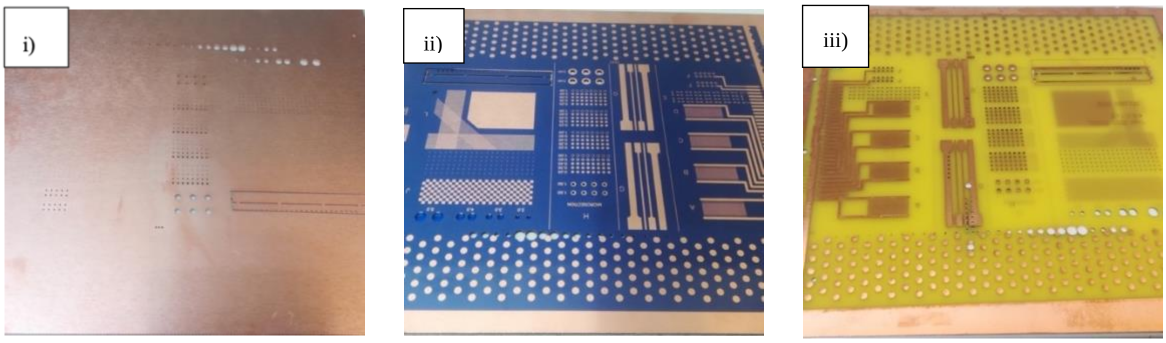


Figure 7 Illustration of the progression of a PCB during the manufacturing process i)Copper clad laminate ii)PCB with circuitry pattern before etching iii)PCB circuitry after etching

The manufacturing specifications for PCBs are standardized and regulated by the Institute for Printed Circuits (IPC) using three classes namely classes 1, 2 and 3 as illustrated in Table 4.

Table 4 PCB classification adapted from (IPC-6012B, 2015)

IPC class	**Definition**	**Examples**
Class 1	General electronic products	Toys, remote controls, flashlights
Class 2	Dedicated service electronic products with extended lifecycle	Microwaves, Televisions, laptops, smartphones
Class 3	High reliability electronic products	Military, Aerospace, Medical, Automotive

Prior to electroplating, the circuitry is deposited on the outer copper layers using the blue photo-sensitive film that hardens after exposure to UV light (see Figure 7ii). Table 5 illustrates the outer copper layer thickness ranges used in manufacturing with the corresponding processing tolerance depending on the copper foil material used. The electroplating process deposits a minimum average of 25 µm of copper in the drilled holes as well as on the outer copper surface of the copper clad laminate (IPC-6012B, 2015).

Table 5 Processing tolerance for common outer layer foil materials in PCB manufacturing adapted from (IPC-6012B, 2015)

Supplied copper thickness	**Minimum surface copper thickness after processing**	
	class 1&2	class 3
½ oz (approx. 17 µm)	33.4 µm	38.4 µm
1 oz (approx. 35 µm)	47.9 µm	52.9 µm
2 oz (approx. 70 µm)	78.7 µm	83.7 µm
3 oz(approx. 105 µm)	108.6 µm	113.6 µm
4 oz(approx. 140 µm)	139.5 µm	144.5 µm

Various chemical etching processes such as ferric chloride, cupric chloride and ammonia/ammonium chloride etchant are then employed to develop the final circuit pattern visible on the surface by leaching the excess amount of copper from the laminate during the etching process (Shah, Gupta & Sengupta, 2018; Patil, 2014).

The final stages of the manufacturing process are the application of an epoxy based solder mask layer to protect the copper surface from oxidation leaving only the copper area to be soldered (Sanapala, 2018). Lastly, a surface finish is applied to this remaining copper area to preserve the solderability of the copper by preventing oxidation. The most commonly used surface finish is Tin/Lead Hot Air Solder Level (HASL), however, this is increasingly being replaced by lead free alternatives due to the negative environmental and health effects associated with the use of lead. This has led to legislative restrictions such as the European Union Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS) directive which restricts the use of lead and other harmful substances in the manufacturing of electronics(Directive 2002/95/EC of the European Parilament and of the council of 27 January 2003, 2003). Typical lead free alternatives include Electroless Nickel Immersion Gold (ENIG), Lead free HASL, Organic Solderability Preservative (OSP), and Immersion Tin (ImSn) (Wei-Shan Chao et al., 2012).

2.2.1 Desmear process

According to a 2006 report by the United States Environmental Protection agency, approximately 70.4% of PCBs were manufactured using FR-4 laminate materials which are categorized according to their glass transition temperature (Tg) as detailed in Table 6. The Tg is the temperature above which the rigid laminate material begins to soften (Pacáková & Virt, 2005). Halogen free FR-4 laminates constituted only 4% of the overall laminate market (US EPA, 2015).

Table 6 FR-4 laminate material categories based on Tg (US EPA, 2015)

		% total market share
High Tg	Tg>170 °C	15.3%
Middle Tg	Tg approximately 150 °C	55.1%
Low Tg	Tg<130 °C	

During the drilling process illustrated in Figure 6, the drill bit generates high temperatures above the Tg of the laminate material thus resulting in the melting of resin. The softened resin is smeared down the hole wall depositing on the exposed inner layer copper and may inhibit electroless copper plating or direct metallization thus preventing electrical connection inside the hole (Clark, 1985). Removal of this smeared resin and debris through the desmear process is a critical process step; one of the most common desmear methods utilizes organic solvents such as NMP-based proprietary solvents for swelling and subsequent removal of the smeared resin with an alkaline permanganate solution.

During this desmear process, the PCBs are processed through a horizontal conveyorized process where they are soaked through the solvent in an ultrasonic bath at 60-90 °C for a duration that can vary between 1-10 minutes (Cheng et al., 2009) depending on the laminate and type of PCB. This is followed by an alkaline permanganate oxidizer which is used to remove the swelled softened resin at temperatures between 80-85 °C . Finally, an acidic neutralizer is applied to remove residual manganese by-product and permanganate (Carano, Polakovic & LaFayette, 1999).

2.2.2 Copper Etching

Chemical etching processes using acidic or alkaline ammonia etchant are commonly used in PCB manufacturing as discussed in 2.2. Alkaline ammonia etching systems are ideal for this purpose due to their high copper dissolution capacity, regeneration capacity, high etch rates as well as their non-selectivity to tin which is used as etch resist to protect the copper circuitry (Shah, Gupta & Sengupta, 2018; Çakır, 2007). Table 7 illustrates the composition of various ammonium chloride etching systems used in PCB manufacturing.

Table 7 Typical PCB ammonia etchant composition

Copper concentration [g/L]	Ammonium Salt concentration [g/L]	pH	Ammonia system	Author
30.8	38.5	8.5	Ammonia/ Ammonium Chloride	(Giannopoulou, Panias & Paspaliaris, 2003)
135	185	-	Ammonia/ Ammonium Chloride	(Fouad & Abdel Basir, 2005)
51.8	53.9	8.5	Ammonia/ Ammonium Chloride	(Shah, Gupta & Sengupta, 2018)

The disadvantages of alkaline ammonia etchants include crystallization on equipment and the sensitivity of the copper ammonia complex to process chemistry deviations leading to copper precipitation (Chemcut Corporation, 2002).

During the PCB fabrication process as detailed in 2.2, the exposed copper is etched via a series of reactions beginning with the dissolution of the copper on the PCB as illustrated in Equation 1.

$$Cu + Cu(NH_3)_4Cl_2 \rightarrow 2Cu(NH_3)_2Cl \qquad \text{Equation 1}$$

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

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

The total reaction can be summarized by Equation 3.

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

The resulting etchant from this process is gradually loaded with copper up to the maximum loading capacity determined by the process parameters for the etching process. For the PCB manufacturing factory considered in this study the maximum loading capacity for the etching process is 150 g/L. One of the key parameters in their etching process is the chloride to copper mass concentration ratio which is maintained at an optimum of 1.2-1.3. This ratio was found to ensure optimum performance with minimal risk of inaccurate etching as well as ensuring sufficient ammonium chloride to minimize the risks of sludging due to destabilization of the copper ammonia complex when etching PCBs.

Most PCB manufacturers integrate the etching process with a copper recovery plant for etchant recycling as illustrated in Figure *8*.

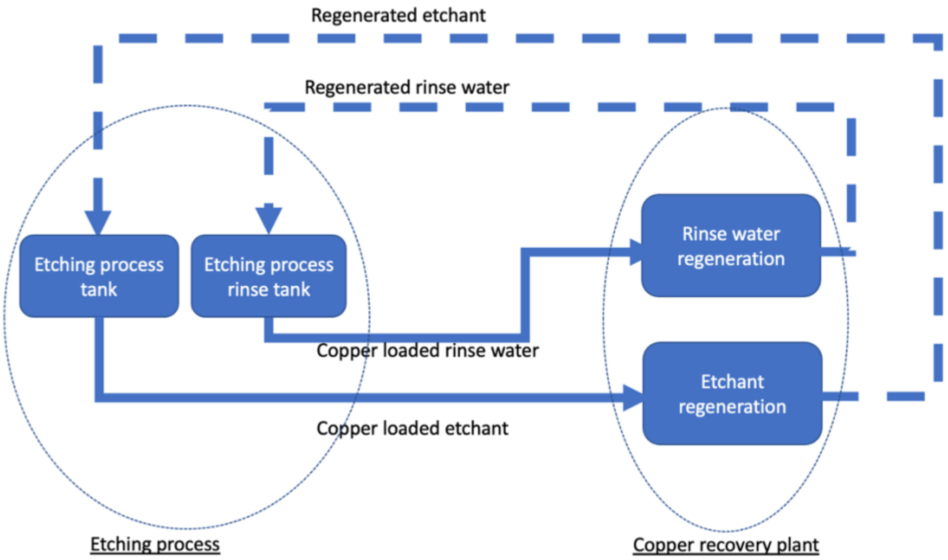


Figure 8 PCB manufacturing etching process integrated with a copper recovery plant adapted from (Sigma Engineering AB, n.d.)

In this process the copper loaded etchant and rinse water streams are individually contacted with an organic extractant, examples of these types of extractants include the hydroxy oxime based extractant LIX84 and beta-diketone based LIX54 represented by “R” in Equation 4

(Liang et al., 2011). The copper is extracted into the organic extractant forming a complex, ammonia is liberated during this reaction and is thus retained in the regenerated etching solution. The copper loaded organic extractant and the regenerated etching solution are immiscible hence they separate into individual streams.

$$Cu(NH_3)_4{}^{2+} + 2HR \rightleftharpoons CuR_2 \ + 2NH_4{}^{+} + 2NH_3 \qquad \text{Equation 4}$$

The copper loaded organic extractant is then contacted with sulphuric acid electrolyte which strips extracts the copper and regenerates the organic extractant compound as illustrated in Equation 5. The regenerated extractant is separated from the electrolyte and recycled back into the system for further extraction of incoming copper loaded etchant (Reinhardt & Ottertun, 1981).

$$CuR_2 \ + \ H_2SO_4 \rightleftharpoons \ 2HR + CuSO_4 \qquad \text{Equation 5}$$

The copper loaded electrolyte is fed to an electrowinning cell where solid copper is recovered and sulphuric acid regenerated for recycling back into the system (see Equation 6).

$$CuSO_4 + H_2O \rightleftharpoons Cu + \frac{1}{2}O_2 + \ H_2SO_4 \qquad \text{Equation 6}$$

One such system is the MECER system developed by Sigma Engineering AB which facilitates the regeneration and recycling of waste etchant while reclaiming electroplated copper through solvent extraction and electrowinning (Shah, Gupta & Sengupta, 2018). This closed loop recycling configuration minimizes waste generation; however excess etchant is generated from the replenishment of ammonium chloride as well as in systems where ammonia losses are replenished by the addition of aqueous ammonia. For example, the local PCB manufacturing company considered in this study has a significant volume available accumulated over a period of 5-10 years. Globally, the PCB industry is estimated to produce one billion cubic meters of waste etchant annually (Shah, Gupta & Sengupta, 2018). The copper present in this waste etchant acts as an oxidant which can be used in the leaching of copper from waste PCBs.

2.3 Oxidative Ammonia leaching

Oxidative ammonia leaching is widely used in the PCB manufacturing industry as detailed in 2.2.2. Similarly, oxidative ammonia leaching has been considered as an alternative to acid copper leaching of copper ores due to its advantages of higher selectivity to copper, reduced corrosion on equipment and lower reagent cost (Radmehr et al., 2013). In addition, various studies have detailed the use of ammonia based lixiviants for the recovery of copper from waste PCBs as illustrated in Table 8.

Table 8 Ammonia based copper recovery from PCBs in literature

Lixiviant system	Research focus	Author
Ammonia/Ammonium Sulphate	Copper leaching behaviour in ammonia system and the potential of an energy saving process by electrowinning the Cu(I) amine complex	(Koyama, Tanaka & Lee, 2006)
Ammonia/Ammonium Sulphate **Ammonia/Ammonium Chloride**	Selectivity of ammonia system for recovery of high purity copper cathode	(Oishi et al., 2007)
Ammonia/Ammonium Chloride	Metal interactions and investigation of various leaching factors on valuable metal recovery including copper, from smelted mobile phone PCBs	(Lim et al., 2013)
Ammonia/Ammonium Carbonate	Selective copper recovery from complex ICT waste	(Sun et al., 2015)

Commonly used salts in ammonia leaching systems are carbonate, sulphate and chloride; they provide a buffering effect by providing anions and protons during the ammonia complex formation (Sun et al., 2015). The ammonia/ammonium chloride system is of particular interest as it is common to both PCB recycling and PCB manufacturing.

2.3.1 Ammonia/Ammonium Chloride leaching chemistry

The copper oxidative dissolution in ammonia/ammonium chloride solutions as applicable to both the etching process and ammonia leaching of waste PCBs is as illustrated by Equation 1 in section 2.2.2, where solid copper is dissolved by reacting with cupric ions in the cupric chloride ammonia complex solution (Chemcut Corporation, 2002; Koyama, Tanaka & Lee, 2006). The resulting product is immediately oxidized by oxygen as illustrated by Equation 2 with the total reaction as summarized by Equation 3.

In PCB etching, the pH of the etchant is maintained between 8-8.5 at temperatures of 40-55 °C to maintain bath stability within the process (Chemcut Corporation, 2002). 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 9.

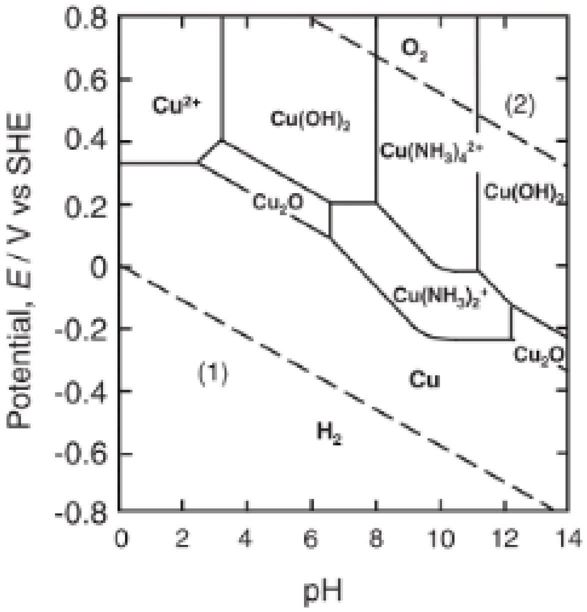


Figure 9 Potential-pH diagram of the copper ammonia complex (Koyama, Tanaka & Lee, 2006)

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). Previous research by Oishi et al (2007) and Sun et al (2015) has shown that ammonia leaching is affected by parameters such as initial Cu(II) concentration, pH and particle size as explored in greater detailed below.

2.3.2 Initial copper concentration

Initial cupric ion concentration significantly affects the copper leaching rate and this is significant to both waste PCB recycling as detailed by Koyama, Tanaka & Lee (2006) and Oishi et al. (2007) as well as in PCB manufacturing as detailed by Chemcut Corporation (2002). The cupric ion acts as an oxidizing agent to dissolve metallic copper (Radmehr et al., 2013) through the anodic reaction illustrated by Equation 7 (Habashi, 1963).

$$Cu + Cu(NH_3)_4{}^{2+} \rightleftharpoons 2Cu(NH_3)_2{}^{+} \qquad \text{Equation 7}$$

An example of this can be seen in the same 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 initial copper 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.

Sun et al. (2015) detailed results from their study of the kinetics of ammonia leaching of PCBs and other ICT waste such as copper cables with the view of producing results for a scale up to pilot scale. The results indicated that the copper leaching profile can be divided into the following three stages;

I. *Early low leaching rate stage* -where leaching is driven by oxidation from dissolved oxygen.

II. *Reaction high leaching rate stage*- where leaching is promoted by the increased concentration of cupric amine species. Here the intermediate cuprous ion is immediately oxidized by dissolved oxygen and converted to the cupric amine species, $Cu(NH_3)_4Cl_2$, which acts as a catalyst for the leaching reaction as detailed by Equation 2.

Final flat profile leaching stage-Koyama, Tanaka & Lee (2006) studied the effect of initial copper ion concentration and found that the cupric ion enhances the leaching rate, however by carrying out the experiment under a nitrogen atmosphere, the oxygen content was limiting thus enabling for the presence of the cuprous ion which was found to decrease the leaching rate. In the etching process during PCB manufacturing, at optimum etch conditions, the cuprous amine complex forms a film that acts as an etching inhibitor on the sidewall of the copper tracks (Chemcut Corporation, 2002), this is highly dependent on the pH and cupric ion concentration.

2.3.3 Ammonia and pH

Ammonia is present as a complexing agent to maintain the stability of the copper ion species in solution as ammine complexes (Sun et al., 2015; Radmehr et al., 2013). Figure 10 illustrates the effects of pH on the distribution of copper species in spent circuit board etchant. At a pH value of 8.5, which is within the typical operating range of 8-8.5 for PCB etching systems (Chemcut Corporation, 2002), copper was present predominantly in the cupric ion form as $\mathrm{Cu(NH_3)_4}^{2+}$ (Shah, Gupta & Sengupta, 2018) . This reiterated that the cupric form is the dominant copper species in ammoniacal solutions containing excess ammonia due to its high formation equilibrium constant over other ammine complexes.

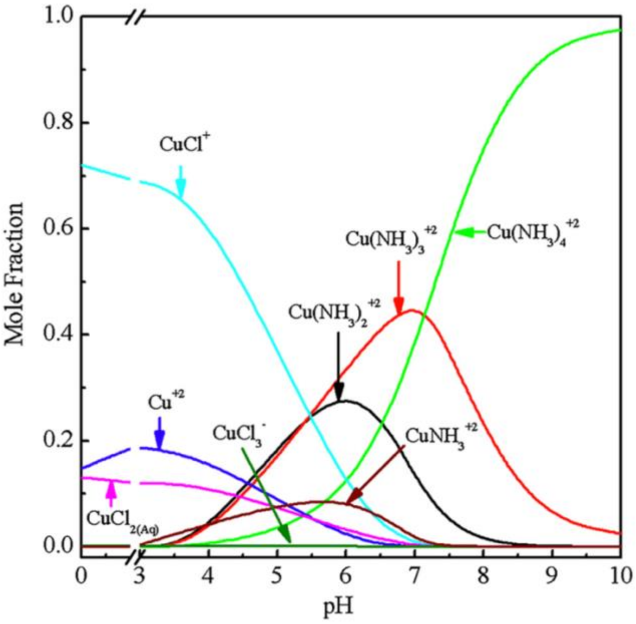


Figure 10 Speciation diagram of copper in spent printed circuit board etchant as a function of pH (Shah, Gupta & Sengupta, 2018)

The pH of the leaching solution is indicative of the relative amount of free ammonia available for the etching reaction (Chemcut Corporation, 2002) as illustrated by Equation 8.

$$NH_3 + H_2O \rightleftharpoons OH^- + NH_4{}^+ \qquad \text{Equation 8}$$

Sun et al. (2015) studied the recovery of copper from shredded ICT waste using ammonia-ammonium carbonate lixiviant, reporting that as the leaching reaction progresses, the final stage of the copper recovery profile flattens due to the influence of mass transfer or diffusion on the leaching kinetics (Habashi, 1963). This is attributed to a diminished activity of the leaching solution due to a reduction in ammonia which is required to complex the dissolved copper as the reaction progresses.

2.3.4 Particle Size

Particle size was identified as having a significant effect on copper recovery in various studies with Yang, Liu & Yang (2011) reporting a maximum recovery of 96% for particle size <0.5mm in comparison to a recovery of 50% for sizes 4 – 8 mm after copper leaching with sulphuric acid and hydrogen peroxide for 5 hours at 23 °C. Their conclusion was that the recovery of copper increased with decreasing particle size down to 0.5 mm below which the increase in recovery was minimal and was offset by the energy required to reduce the particle size further. Similarly, Koyama, Tanaka & Lee (2006) also concluded that decreasing particle size increased copper recovery, however the experiments conducted were limited to two particle sizes 3.4 and 1.5 mm.

Oliveira et al (2012) analyzed the effect of particle size on the leaching yield of various metals from shredded PCBs. It was determined that copper was the element most influenced by particle size, moreover, the leaching yield of copper in nitric acid lixiviant increased with a decrease in particle size from 2 mm to 0.2 mm as illustrated in Figure 11i). In addition to the influence of particle size, the same study highlighted that increasing temperature from 40 to 90 °C was found to significantly increase the degree of copper leaching by up to 60 % for a particle size of 1.2 mm compared to an increase of 40% from decreasing particle size from 1.2 mm to 0.55 mm as illustrated in Figure 11ii).

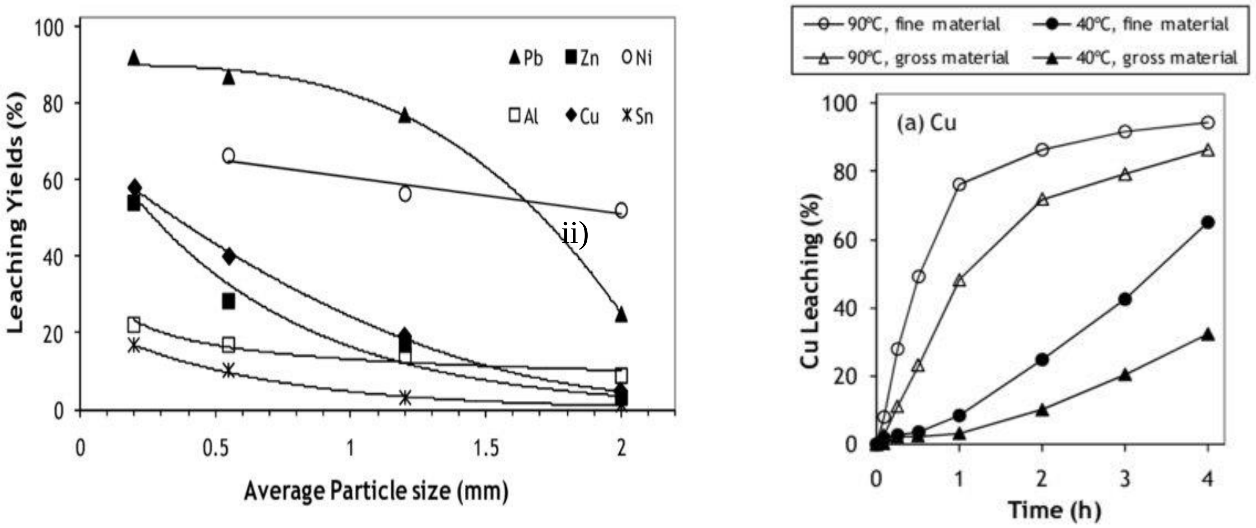


Figure 11 Results from leaching shredded PCBs with nitric acid i) Influence of particle size on leaching yield for varying elements; ii) Influence of particle size and temperature on copper leaching of fine material-0.55mm, gross material- 1.2mm (Oliveira et al., 2012)

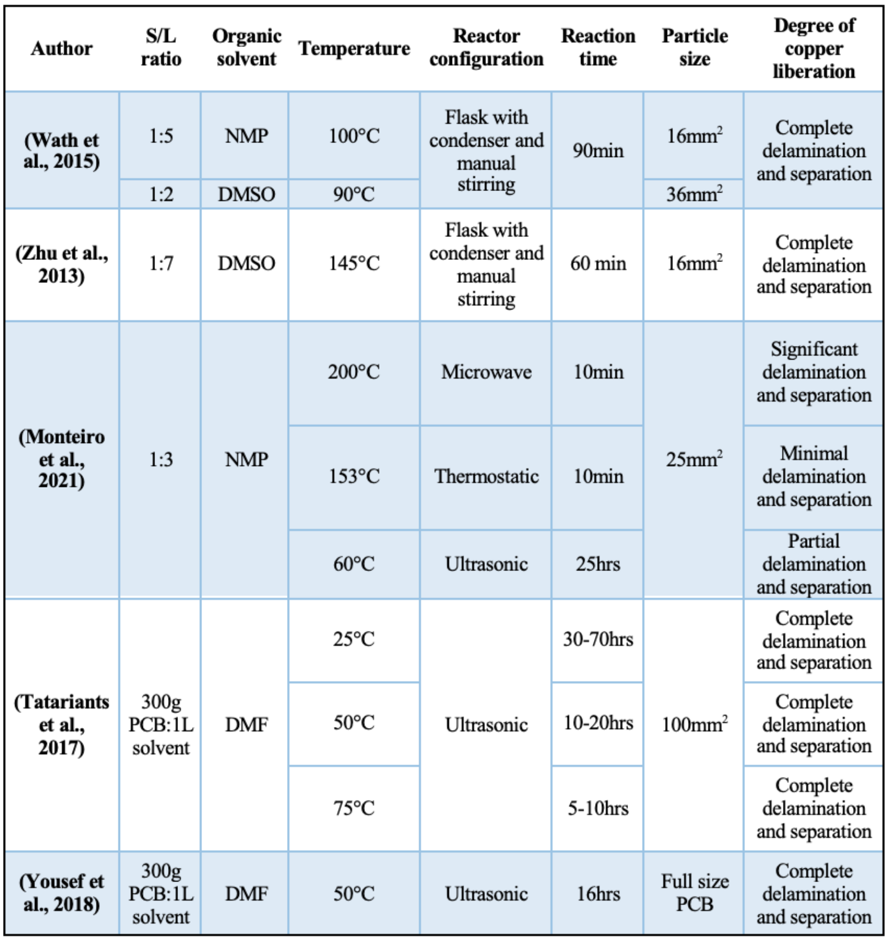
2.4 Solvent swelling

The hydrometallurgical extraction of copper from waste PCBs by lixiviants such as ammonia is dependent upon the lixiviant’s ability to access the inner layer copper as detailed in 1.1. The non-metallic fractions illustrated in Figure 2 typically comprise of thermally cured epoxy resin, brominated flame retardants, curing agents, fillers and accelerators (Monteiro et al., 2021; Sanapala, 2018). Once the dismantling of components has been achieved through mechanical or metallurgical processing, the most critical step from an economic and environmental perspective is the further processing of the stream to liberate the metal from the non-metallic fraction (Wath et al., 2015).

Solvent swelling has been explored as an environmentally friendly method of liberating the encapsulated copper in waste PCBs due to the ability to regenerate and recover the solvents utilized (Zhu et al., 2013). In addition, these solvents have the advantage of dissolving the non- metallic fractions such as BER without attacking the metal, thus preventing metal losses (Wath et al., 2015). Some of the solvents of interest explored in literature as detailed below include NMP, dimethyl sulfoxide (DMSO), di-methyl formamide (DMF) and Dimethyl acetamide (DMAc).

Table 9 details various studies undertaken on the solvent swelling of waste PCBs. The main parameters evaluated were the effect of solid to liquid (S/L) ratio, temperature, reaction time and particle size on the degree of BER dissolution which was related to the degree of delamination and separation of the PCB layers.

Table 9 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			36mm^2	
(Zhu et al., 2013)	1:7	DMSO	145°C	Flask with condenser and manual stirring	60 min	16mm^2	Complete delamination and separation
(Monteiro et al., 2021)	1:3	NMP	200°C	Microwave	10min	25mm^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	100mm^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

The studies highlighted in Table 9 established that solvent swelling is an effective method for dissolving BER, the main constituent of the epoxy resin found in PCB laminates as well as PCB pre-pregs which act as the “glue” between the desired copper inner layers.

Verma, Singh & Mankhand (2016) achieved optimized BER dissolution and complete delamination and separation of PCBs into copper foil and the non-metallic fiberglass fraction for particle sizes of 1 x 1 cm with a solid to liquid ratio of 300 g solid per litre of solvent in 4 hours at a temperature of 135 °C using DMF. It was noted in their study that DMF had the benefit of ease of regeneration due to its relatively high vapor pressure of 2.7 mm Hg and a low boiling point of 153 °C.

Monteiro et al. (2021) completed an extensive study on several solvents including NMP, DMSO, DMF and DMAc using the parameters and configurations detailed in Table 9. It was concluded in their study that microwave assisted solvent swelling with NMP was the most effective method for delamination. Similar to Verma, Singh & Mankhand (2016), Monteiro et al. (2021) measured delamination through the dissolution of BER which was measured by tracking the concentration of bisphenol A (BPA) in the solvent using ultraviolet-visible spectroscopy (UV-Vis) in addition to providing photographic images of the separated metallic and non-metallic fractions. The images provided illustrated complete separation of the metallic layers from the non-metallic layers for the best performing solvents in the order NMP > DMSO > DMF > DMAc which corresponded with the results obtained from quantifying the BPA concentration in each solvent.

Similarly, Wath et al. (2015) determined that NMP was the superior performing solvent compared to DMSO for BER dissolution and separation of metallic from non-metallic fractions. This study optimized temperature, time, S/L ratio and particle size to determine the degree of BER dissolution by measuring the amount of BPA. In addition to yielding the best delamination results with the parameters as detailed in Table 9, NMP was identified as having low volatility due to its high boiling point of 202 °C allowing for its use at higher temperatures that enhance delamination without being released to the environment.

The high boiling point of NMP is an advantage in the delamination of the commonly used FR-4 laminates in that NMP swelling can be operated at temperatures above the glass transition temperature of 130-140 °C of conventional FR-4 detailed in Table 6. This is a benefit as it enhances softening of the laminate to facilitate delamination because at these temperatures the solid structure of polymers such as those found in FR-4 begins to transition to a rubbery state (Pacáková & Virt, 2005) thus aiding in the destabilization of the mechanical structure (Lall et al., 2012).

In all cases of solvent swelling, the reactions are mass transfer controlled, hence the interfacial surface area drives the process, leading to higher BER dissolution rates with increasing surface area and decreasing particle size (Wath et al., 2015). In light of this, in this study it is considered worthwhile to combine mechanical pre-treatment with solvent swelling as a means of enhancing metal liberation from mechanical treatment. Han et al. (2019) utilized scanning electron microscopy to determine the improvements in crushing efficiency from prior solvent swelling. This was carried out by evaluating the sectional morphology of the printed circuit boards after swelling with dimethylacetamide (DMAc) at 100 °C for 2 hours followed by crushing to sizes below 0.5 mm compared to untreated PCBs crushed to the same size under the same physical conditions. Their study found that PCBs that were treated with solvent followed by crushing showed a greater degree of structural damage compared to those that were untreated, thus enhancing the degree of metal liberation. In addition, their study revealed that the metal to non-metal interface of the untreated PCBs remained intact.

2.5 Research Approach

Previous studies have detailed the optimization of various size-reduction methods for copper liberation (Prestele, 2020; Sethurajan et al., 2019; Ruan & Xu, 2016). Prestele (2020) for instance made use of an industrial grab shredder with reported maximum copper recoveries of 57.8% from 6 pass shredding alone. It has been 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 recovery by 10% (Prestele, 2020). To achieve significant copper recoveries with mechanical methods alone, finer particle sizes are required which increases the energy consumption. Thus, mechanical methods have a high capital investment input and operating cost in addition to having an environmental impact from the generation of dust.

Solvent swelling presents a viable alternative that can achieve complete metal liberation through delamination as detailed in literature. However, most of the research presented in 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 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 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. 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.

2.5.1 Hypothesis

Metal liberation from waste PCBs is a critical aspect in the recycling process. Through solvent swelling with an NMP based solvent, sufficient metal liberation from the inner layers beyond the surface copper can be achieved.

2.5.2 Key Questions

- How much copper is available on the PCBs?
- What is the copper distribution throughout the PCBs? What percentage constitutes the inner layer copper to be accessed?
- To what extent does treatment with NMP based solvents expose inner layer copper to the lixiviant?
- How does NMP based solvent compare with pure NMP in its ability expose copper to access by lixiviant?
- Is waste etchant from PCB manufacturing a suitable lixiviant for PCB recycling? What are the challenges and advantages associated with this lixivant?
- How much more copper, if any, is liberated by introducing mechanical shredding?
- What are the costs associated with using NMP based proprietary solvent vs using pure NMP?

3 Experimental materials and methods

This section details the experimental methods and materials utilized to achieve the objectives set out in this study. The experimental procedure was conducted in the following phases;

1. Characterization of the custom-made PCBs to determine their copper content as well as the copper distribution throughout the layers.
2. Collection of waste etchant samples from a local PCB manufacturer, analysis for the main components and using samples of this waste etchant to leach waste PCBs.
3. Solvent swelling test work modelled after the desmear process using NMP solvent swelling followed by oxidation with alkaline potassium permanganate at 80-85 °C with varying swelling reaction conditions. Diagnostic leaching carried out using Ammonia/Ammonium Sulphate.
4. Solvent swelling test work modelled after the desmear process using Solvent B, followed by oxidation with alkaline potassium permanganate at 80-85 °C. Diagnostic leaching carried out using Ammonia/Ammonium Sulphate.
5. Baseline diagnostic leaching of untreated (i.e. have not undergone solvent swelling) PCBs using freshly made synthetic etchant compared to leaching with waste etchant from PCB manufacturing.
6. Solvent swelling test work with pure NMP and Solvent B at FR-4 Tg temperature, followed by diagnostic leaching with both freshly made synthetic etchant and waste etchant from PCB manufacturing.
7. Test work combining mechanical shredding with solvent swelling using Solvent B followed by diagnostic leaching with freshly made synthetic etchant.

3.1 Materials

3.1.1 Reagents

The following reagents were utilized to prepare the ammonium sulphate lixiviant, potassium permanganate oxidant and neutralizing solution used in the desmear process modelled test work;

I. Ammonium Sulphate AR Grade (Supplied by Merck)
II. Ammonia 25% AR Grade (Supplied by Merck)
III. Potassium Permanganate AR Grade (Supplied by Merck)
IV. Sodium Hydroxide (Supplied by Cameron Chemicals)
V. Solvent B (as used by Trax Interconnect)
VI. Sulphuric Acid 98% (supplied by Protea Chemicals)
VII. Proprietary Neutralizer solution (as used by Trax Interconnect)
VIII. 1-Methyl-2-pyrrolidinone anhydrous (NMP), 99.5% (supplied by Sigma Aldrich)

The experiments were carried out at Trax Interconnect, a local PCB manufacturing factory. In order to closely model the composition of the reagents used in the PCB manufacturing process, the additional reagents used to prepare the synthetic etchant were the same chemically pure reagents used in the factory as follows;

IX. Ammonia 25% chemically pure grade (supplied by Protea Chemicals)
X. Ammonium Chloride chemically pure grade (supplied by Protea Chemicals)
XI. Copper Foil (as used by Trax Interconnect)

Table 10 summarizes the lixiviants and pre-treatment solutions prepared from the reagents listed. Detailed preparation methods are as outlined in Appendix A.

Table 10 Prepared lixiviants and pre-treatment solutions

Pre-treatment solutions	
Potassium Permanganate solution	Experiments 1-4
Neutralizing solution	Experiments 1-4
Lixiviants	
Ammonium Sulphate lixiviant	Experiments 1-4
Synthetic Etchant-50g/L copper concentration	Experiments 5,7,8
Synthetic Etchant-10g/L copper concentration	Experiments 10-11
Waste Etchant	Experiments 6,9

Waste etchant samples for leaching were collected from a local PCB manufacturer. The waste etchant ranged in composition as detailed in Appendix A. The samples were collected from the loaded etchant holding tank prior to etchant regeneration at the copper recovery plant as illustrated in Figure 8.

Analytical tests were performed using the reagents detailed below;

XII. 0.1N Silver Nitrate (supplied by Cameron Chemicals)
XIII. Dichlorofluorescein (DCF) indicator (supplied by Cameron Chemicals)
XIV. 0.1M EDTA (supplied by Cameron Chemicals)
XV. Murexide powder (supplied by Cameron Chemicals)

3.1.2 PCBs

The PCBs used throughout the experiments were unpopulated, solder-free 4-layer multilayer boards manufactured by Trax Interconnect. Figure 12 illustrates the top surface layer of the PCB and Figure 13 illustrates the bottom surface layer.

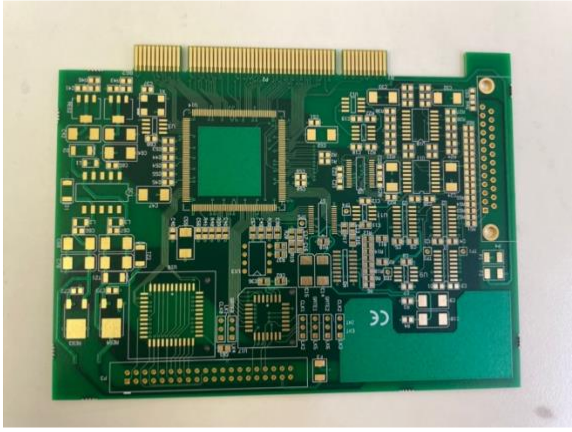


Figure 12 Custom-made PCB with dimensions 142 x 102 x 1,55mm top surface layer (Layer 1)

Figure 13 Custom-made PCB with dimensions 142 x 102 x 1,55mm bottom surface layer (Layer 4)

The boards are comprised of NY2150 mid-Tg FR-4 laminate core material clad with 35 µm copper on both sides sandwiched between 1080 and 7628 pre-pregs with thicknesses of 70 µm and 187 µm respectively. Within the manufacturing process the surface copper prior to electroplating as well as the copper inner layers are processed through a series of etching processes that reduce the initial copper foil thickness as illustrated in Table 3. The surface comprises a starting copper foil thickness of 18 µm copper which is plated up to 36 µm. The core and pre-preg materials used by the manufacturer were supplied by Shanghai Nanya.

Parts of the exposed surface copper area are covered with green solder mask supplied by Electra Polymers. The remaining exposed copper surface comprising of tracks and pads for soldering is plated with a chemically deposited nickel phosphorus alloy with thickness ranging from 3.6 - 6.3 µm. This nickel layer is covered by a thin microporous protective gold layer (Xiao et al., 2018) ranging from 0.05 - 0.08 µm. The degree of porosity of the electrochemically deposited gold layer increases with decreasing gold thickness (Advanced plating technologies, 2018), therefore, for PCBs with an ENIG surface finish such as that of the custom-made PCBs the thickness of the gold and nickel phosphorus layers may impact the leaching rate of the outer surface copper.

3.2 Equipment

The equipment utilized in this study is as detailed in the subsections below.

3.2.1 Size reduction

The size reduction of the PCBs prior to solvent swelling and leaching was mainly achieved through cutting the PCBs into 2 x 1.5 cm pieces using a PCB cutter. This was done to obtain a workable size to facilitate fitting into the solvent swelling reactor and leaching column.

Mechanical treatment for metal liberation and further size reduction to smaller particle sizes for the experiments that employed physical pre-treatment was achieved by shredding the swelled PCBs through 6 passes as the maximum number of cycles as determined by Prestele (2020).

3.2.1.1 PCB cutter

The PCB cutter illustrated in Figure 14 was used to individually cut the PCBs into 2 x 1.5 cm pieces along the cutting lines illustrated in Figure 15.

Figure 14 PCB cutter used to cut custom PCBs

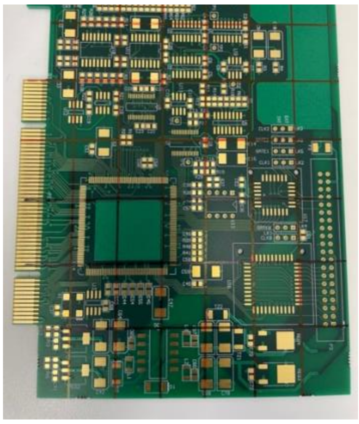


Figure 15 PCB with cutting lines

3.2.1.2 Industrial grab shredder

The shredding of the PCBs for delamination and further size reduction was carried out using an industrial grab shredder with a 1.1kWh motor and a 50Hz frequency converter. The maximum number of shredding cycles tested in this study was 6 passes. Prestele (2020) achieved a recovery of 57.8% with the same number of passes and noted residual resin and fibreglass coverage on the inner layer copper of the partially delaminated PCBs.

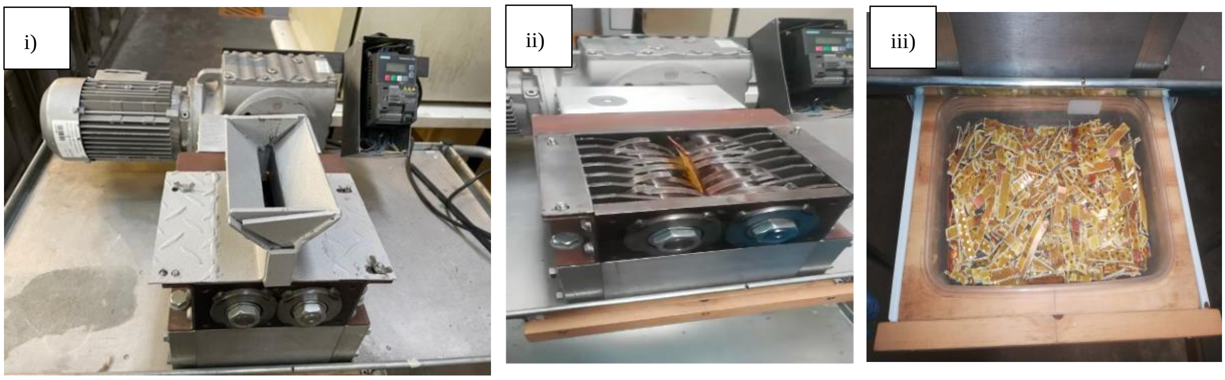


Figure 16 Industrial grab shredder i)External section; ii)Internal section; iii)Drawer with shredded boards

The PCBs were fed through the funnel chamber illustrated in Figure 16i), passed through the 14 blades illustrated in Figure 16ii) and thereafter collected in the tray illustrated in Figure 16iii). Once collected the shredded PCBs were re-fed into the chamber until they had passed through the blades a total of 6 times in the experiments where mechanical shredding was employed.

3.2.2 Solvent swelling and potassium permanganate oxidation

Solvent swelling was carried out in a 3 L round bottom flask with a detachable lid fitted with an overhead stirrer and a feedback temperature controller fitted with a thermocouple as illustrated in Figure 17. The same reaction vessel was utilized for potassium permanganate oxidation.

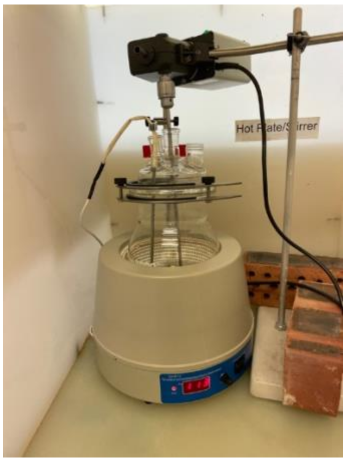


Figure 17 Solvent swelling reactor setup

3.2.3 Diagnostic Copper Leaching

Diagnostic leaching was carried out as an indicator of the extent of copper liberation from the preceding solvent pre-treatment processes. This was carried out in two column reactors 0.5 m in height and 0.09 m in diameter. Solution was fed into the column through a closed loop system using a peristaltic pump at a flowrate between 1-6 L/day. The pregnant leach solution flowed through an outlet at the bottom of the column as illustrated in Figure 18 and was continuously circulated through the column.

The procedure utilized for diagnostic leaching was as detailed below.

1. PCBs were added to the reactor column.
2. The lixiviant was continuously circulated through the column at a flowrate of 1 L/day in experiments 1-4 and 6 L/day in experiments 5-12.
3. The leaching was carried out for a minimum of 72 hours. Samples were collected at various time intervals and analyzed for pH and copper concentration as detailed in 3.3.2.

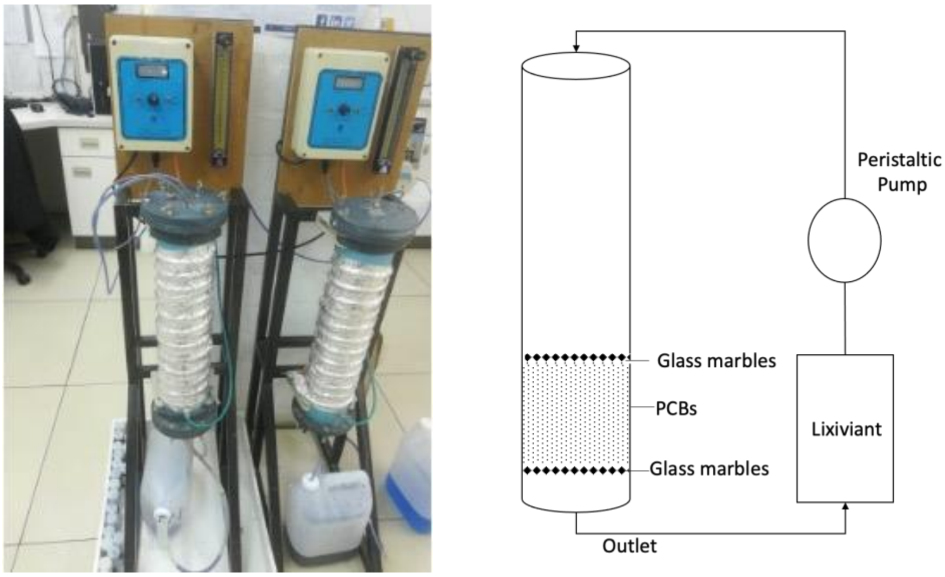


Figure 18 Leaching column configuration

No air was pumped into the column and the columns were operated at room temperature. The PCBs were loaded into the column as illustrated in Figure 18. 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 cupric ions was not considered a hinderance. However, the lixiviant was exposed to air in the receiving vessel thus allowing for oxidation of any accumulated cuprous ion when offloading the column.

3.3 Analytical Techniques

3.3.1 Waste etchant characterization and analysis

The copper content in the waste etchant samples collected from a local PCB manufacturer was determined by titration with EDTA as detailed in Appendix B. In addition, the ammonium chloride content was determined by chloride titration with silver nitrate using dichlorofluorescein indicator as adsorption indicator as further detailed in Appendix B. The chloride ion precipitates as silver chloride when silver nitrate is added as illustrated by Equation 9.

$$Ag^{+}{}_{(aq)} + Cl^{+}{}_{(aq)} \rightarrow AgCl_{(s)} \qquad \text{Equation 9}$$

The endpoint is determined when the additional silver ions left after precipitation react with the indicator from a fluorescent yellow colour to pink (Weckel, 1939).

3.3.2 Copper and metal ion determination during leaching

During diagnostic leaching, the collected samples were analysed for copper concentration using Atomic Absorption Spectroscopy (AAS). Figure 19 illustrates the Atomic absorption spectrophotometer used to analyse the copper concentration.

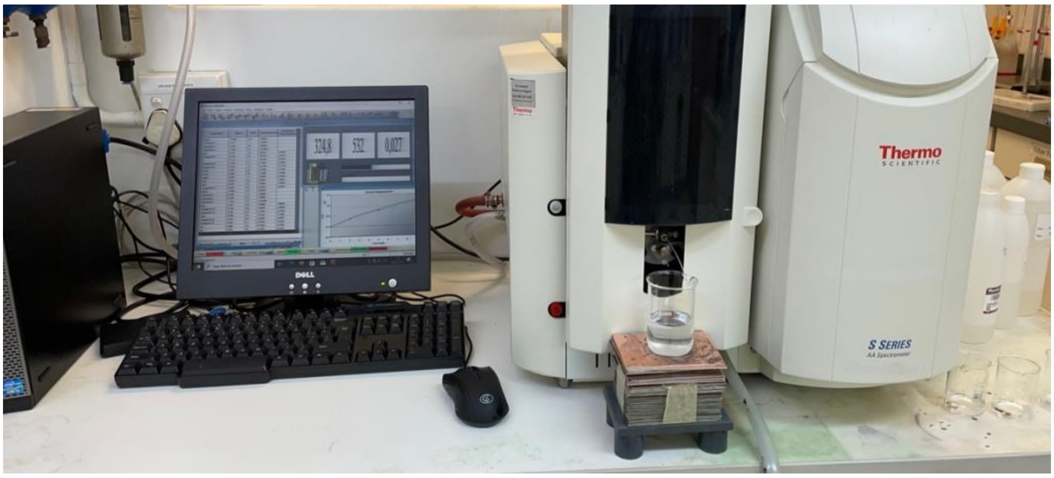


Figure 19 Atomic Absorption Spectrophotometer for copper analysis

The AAS was calibrated using standards 2,5 and 10ppm and a quality check was carried out by analysing the 10ppm standard three times and an average calculated. Similarly, all samples were analyzed three times and the average concentration reported. Given the high copper content of the synthetic and waste etchant lixiviants, the solutions were diluted by a factor of 10 000 to fall within the maximum working range of 0.03-10 ppm for copper analysis at 324.8nm (Agilent Technologies, 2021).

3.3.3 pH

The pH was monitored by measuring with a Hanna HI98190 benchtop pH meter calibrated for buffers 4, 7 and 10.

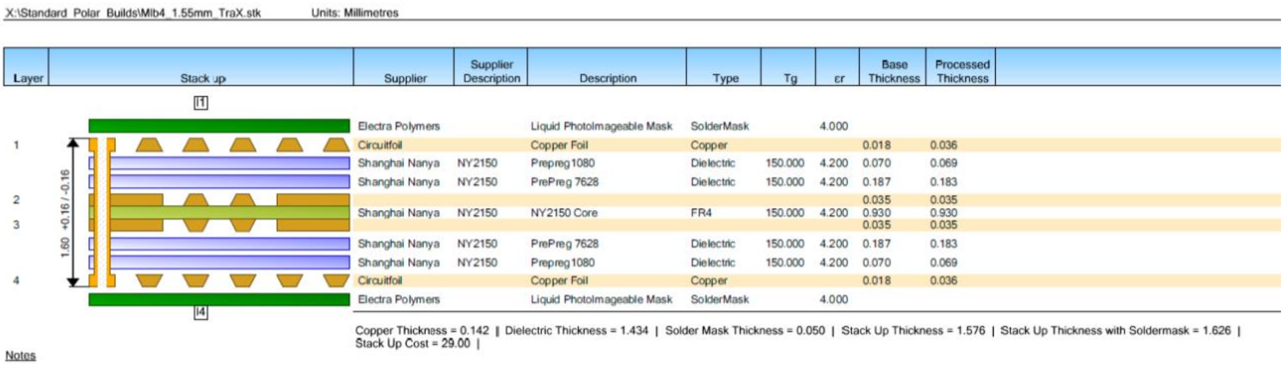
Samples were collected and measured during leaching and 25% Ammonium Hydroxide was added when necessary to maintain the pH between 8-10. When pH adjustment was required, this was achieved by adding the lixiviant to a beaker and adding 25% Ammonium Hydroxide while mixing with a magnetic stirrer and monitoring the pH.

3.4 Methods

The experimental procedure conducted in this study is as detailed in the relevant subsections below. Section 3.4.1 details the procedure used to determine the copper content of the custom-made PCBs. This is then followed in section 3.4.2 by a brief outline of the collection and analysis of a set of waste etchant samples from a local PCB manufacturer to characterize an example of a typical waste etchant stream from the PCB manufacturing process. This etchant was then tested for its ability to effectively leach copper from waste PCBs.

The main solvent swelling tests were carried out as detailed in sections 3.4.3 to 3.4.5. Solvent swelling performance was evaluated through determining the amount of copper extracted by means of diagnostic copper leaching. In addition, mechanical shredding was employed to determine the effect of combined mechanical and chemical pre-treatment on copper recovery as detailed in section 3.4.5.

3.4.1 Objective 1: Establishing the copper content of the custom-made PCBs



X:\Standard_Polar_Builds\Mlb4_1.55mm_TraX.stk Units: Millimetres

Layer	Stack up	Supplier	Supplier Description	Description	Type	Tg	εr	Base Thickness	Processed Thickness
		Electra Polymers		Liquid Photolmageable Mask	SolderMask		4.000		
1		Circuitfoil		Copper Foil	Copper			0.018	0.036
		Shanghai Nanya	NY2150	Prepreg 1080	Dielectric	150.000	4.200	0.070	0.069
		Shanghai Nanya	NY2150	PrePreg 7628	Dielectric	150.000	4.200	0.187	0.183
2								0.035	0.035
		Shanghai Nanya	NY2150	NY2150 Core	FR4	150.000	4.200	0.930	0.930
3								0.035	0.035
		Shanghai Nanya	NY2150	PrePreg 7628	Dielectric	150.000	4.200	0.187	0.183
		Shanghai Nanya	NY2150	Prepreg 1080	Dielectric	150.000	4.200	0.070	0.069
4		Circuitfoil		Copper Foil	Copper			0.018	0.036
		Electra Polymers		Liquid Photolmageable Mask	SolderMask		4.000		

Copper Thickness = 0.142 | Dielectric Thickness = 1.434 | Solder Mask Thickness = 0.050 | Stack Up Thickness = 1.576 | Stack Up Thickness with Soldermask = 1.626 | Stack Up Cost = 29.00 |

Notes

Figure 20 4-Layer PCB multilayer stack up as manufactured by Trax Interconnect (Trax Interconnect, 2016)

Figure 20 illustrates the cross-sectional build-up of the custom-made PCBs which details the sequence in which the conductive copper layers as well as the non-conductive layers are placed (Eurocircuits, 2021). The custom-made PCB makeup is as detailed in 3.1.2.

To determine the actual copper thickness of each layer, samples of the custom-made PCBs were taken from the representative areas illustrated in Figure 21. The board was cut using a coupon cutter which had dimensions 2 x 1.5 cm to fit into the microsection coupon holder. The microsection coupons were evaluated using a metallurgical Olympus microscope to determine the copper thickness of each layer of the PCB. The microscope magnification range was from 50X to 500X. All measurements were taken at a magnification of 200X and images for illustration were taken at the minimum magnification.

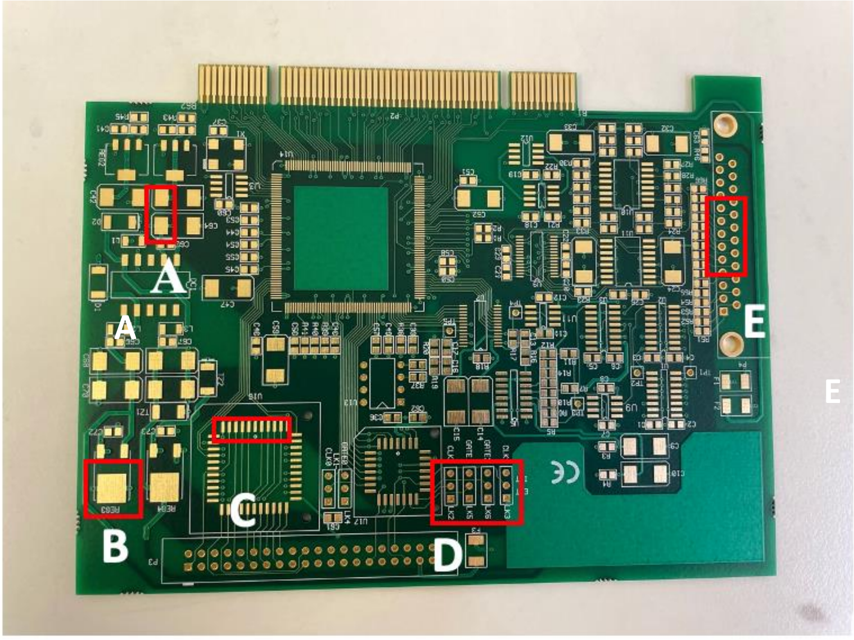
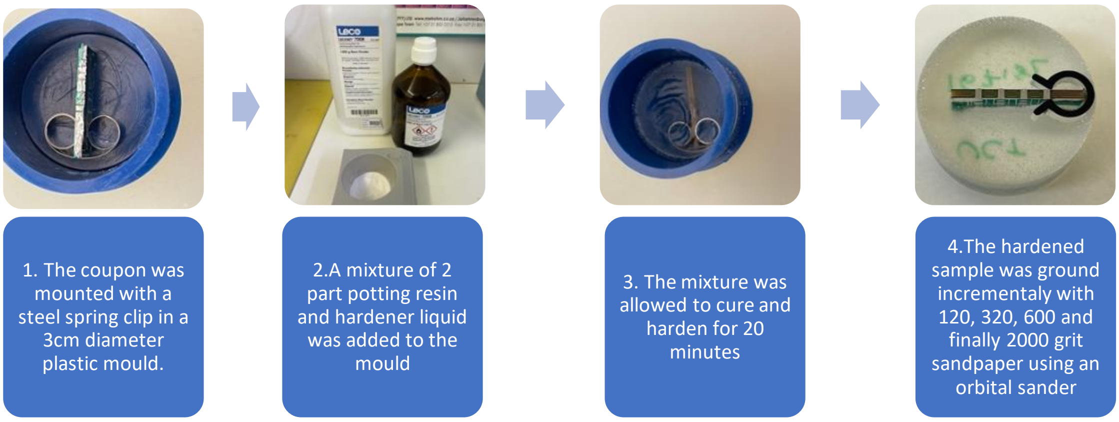


Figure 21 Areas sampled for microsection analysis

At least one coupon was taken from an area with plated through holes to determine the copper thickness in the drilled holes, the inner layer copper as well as the surface copper which comprises of tracks and pads to be soldered.

The method used for preparation of the microsections was as illustrated in Figure 22.



1. The coupon was mounted with a steel spring clip in a 3cm diameter plastic mould.

2.A mixture of 2 part potting resin and hardener liquid was added to the mould

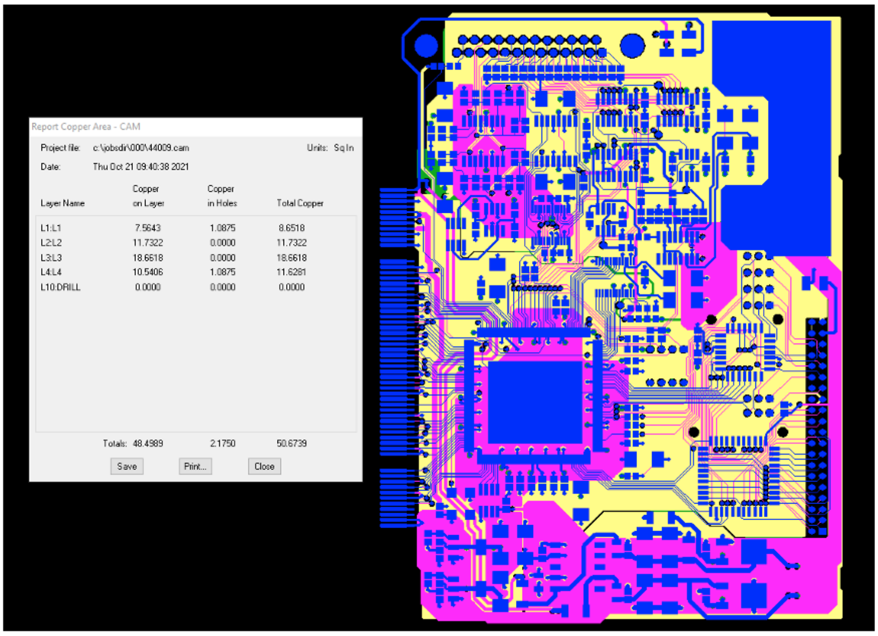
3. The mixture was allowed to cure and harden for 20 minutes

4.The hardened sample was ground incrementaly with 120, 320, 600 and finally 2000 grit sandpaper using an orbital sander

Figure 22 Micro sectioning method for copper evaluation

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 as illustrated by Figure 23.

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).



```
Project file:   c:\jobsdir\000\44009.cam                        Units:   Sq In
Date:           Thu Oct 21 09:40:38 2021

                      Copper          Copper
Layer Name            on Layer        in Holes        Total Copper

L1:L1                  7.5643          1.0875          8.6518
L2:L2                 11.7322          0.0000         11.7322
L3:L3                 18.6618          0.0000         18.6618
L4:L4                 10.5406          1.0875         11.6281
L10:DRILL              0.0000          0.0000          0.0000

             Totals:  48.4989          2.1750         50.6739
```

Layer No.	Layer Type	Key
1	Top Surface	🟦
2	Inner	🟩
3	Inner	🟨
4	Bottom Surface	🟪

Figure 23 CAM350 software copper area illustration

The results from the microsection analysis were compared to the results from the acid digestion characterization method carried out by (Maharaj, under examination.)

3.4.2 Objective 2: Waste Etchant Characterization

Samples of waste etchant were collected from a local PCB manufacturers chemical storage. The samples provided were a combination of etchant regenerated from their etchant regeneration plant, etchant contaminated with water from rinsing of the process tank and spent etchant directly from their etching line prior to etchant regeneration.

The parameters of interest were copper content, ammonium chloride content and pH which were analyzed as detailed in section 3.3.1.

3.4.3 Objective 3- Evaluation of combined solvent swelling pre-treatment and potassium permanganate oxidation configurations modelled after the desmear process.

Experiments 1-4 simulated the process sequence of the PCB manufacturing desmear process where solvent swelling is combined with subsequent treatment of the PCBs with alkaline potassium permanganate as detailed in section 2.2.1. The methodology and experimental conditions were as summarized in Appendix B and detailed in Figure 24. For solvent swelling, pure undiluted NMP or Solvent B was used. The potassium permanganate pre-treatment and neutralizing reagents were prepared as detailed in Appendix A.

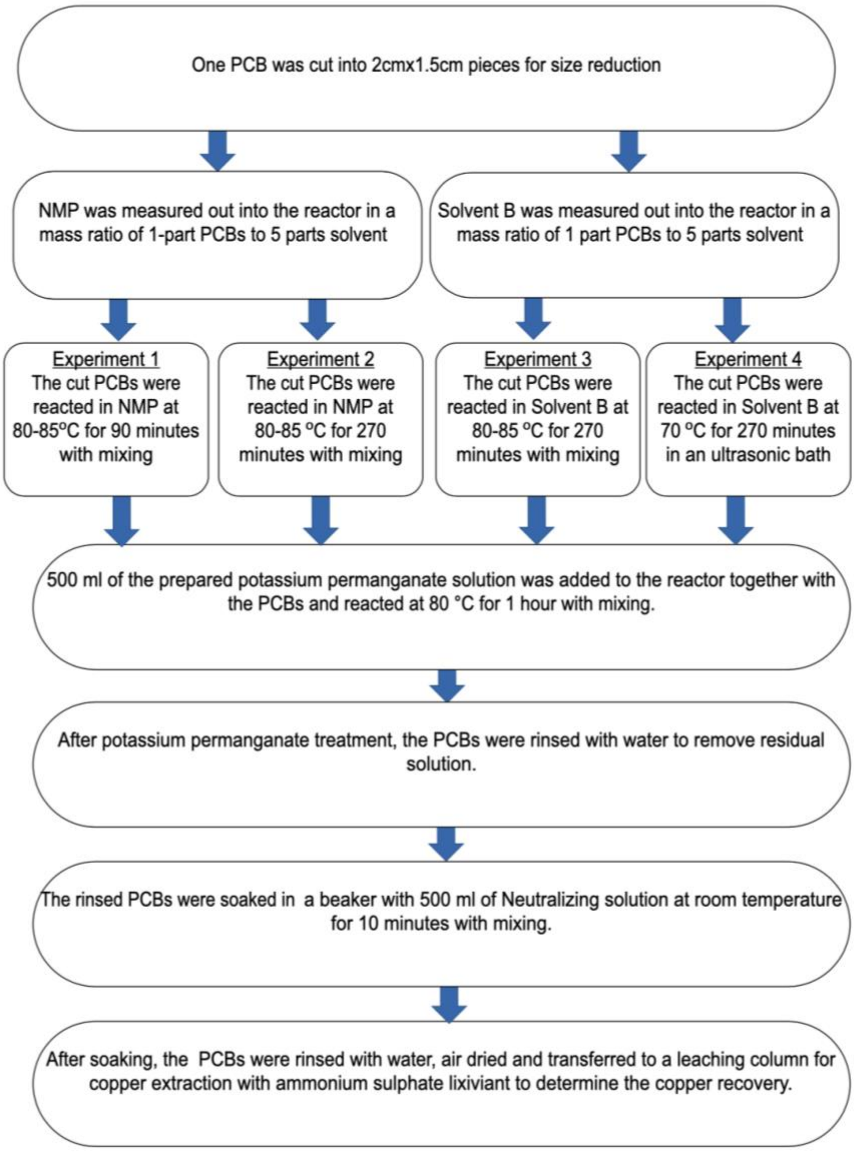


Figure 24 Methodology for experiments 1-4

3.4.4 Objective 4-Determining the effect of solvent swelling on copper recovery and comparing the performance of NMP vs Solvent B in exposing copper for access by lixiviant.

The key lixiviant used in this study was waste etchant sourced from a local PCB manufacturing factory. However, synthetic etchant was utilized to eliminate the influence of contaminants. As detailed in 3.1.1, the copper concentration of the synthetic etchant utilized was 50 g/L. To closely simulate the waste etchant utilized at the PCB manufacturing factory, a chloride to copper mass ratio of 1.2-1.5 was selected for preparation of the synthetic etchant. The synthetic etchant starting copper concentration used was lower than the maximum loading capacity of the etchant used at the factory as detailed in 2.2.2.

Prior to carrying out the tests in experiments 7 and 8 which focus on comparing NMP and Solvent B respectively, experiment 5 which focuses on untreated PCBs was carried out as a baseline study. The goal of this was to exclude the effects of background contaminants such as entrained organics from the integrated copper recovery plant detailed in 2.2.2, 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 on untreated PCBs for comparison with experiment 5. 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. The solder mask layer was removed by soaking the PCBs in sodium hydroxide to allow for access to the surface layer. The conditions for experiments 5-9 are summarized in Appendix B and detailed below.

3.4.4.1 Experiment 5-Untreated PCBs leached with synthetic etchant.

1. Three PCBs were cut into 2 x 1.5 cm pieces for size reduction.
2. The cut PCBs were soaked for 36 hours in 10 M Sodium Hydroxide in a w/w ratio of 1-part PCBs to 5 parts Sodium Hydroxide at room temperature for the removal of solder mask in order to expose the underlying surface copper.
3. The soaked PCBs were rinsed until clean and free of residual liquified solder mask after which the PCBs were transferred to a leaching column for copper leaching with synthetic etchant to determine the copper recovery.

3.4.4.2 Experiment 6-Untreated PCBs leached with waste etchant from PCB manufacturing

1. Three PCBs were cut into 2 x 1.5 cm pieces for size reduction.
2. The cut PCBs were soaked for 36 hours in 10 M Sodium Hydroxide in a w/w ratio of 1-part PCBs to 5 parts Sodium Hydroxide for the removal of solder mask in order to expose the underlying surface copper.
3. The soaked PCBs were rinsed until clean and free of residual liquified solder mask after which the PCBs were transferred to a leaching column and leached with waste etchant to determine the copper recovery.

To compare the performance of NMP vs Solvent B, experiments 7 and 8 were run to establish how much copper was liberated from the PCBs after pre-treatment with the respective solvents alone. As discussed in 3.1.2, the laminate material used to manufacture the PCBs was FR-4 with a Tg of 150 °C, therefore the solvent swelling temperature was increased to 150 °C. Similar to the literature studies detailed in 2.4, the pre-treatment was carried out with solvent swelling alone without the potassium permanganate oxidation carried out in experiments 1 to 4.

In order to evaluate the performance of these solvents, the pre-treated PCBs were leached in synthetic etchant and the amount of copper dissolved was used to indicate the effectiveness of each pre-treatment method.

3.4.4.3 Experiment 7- Solvent swelling with NMP and diagnostic leaching with synthetic etchant

1. Three PCBs were cut into 2 x 1.5 cm pieces for size reduction.
2. NMP was measured out and added to the reactor in a w/w ratio of 1-part PCBs to 5 parts solvent by mass.
3. The solvent was heated to 150 °C and the PCBs were charged to the reactor and reacted for 90min with agitation at 100 rpm.
4. After 90min, the solvent was drained, and the boards were rinsed with water and air dried.
5. The PCBs were then transferred to a leaching column for copper extraction with synthetic etchant to determine the copper liberated by the solvent swelling.

3.4.4.4 Experiment 8 -Solvent swelling with Solvent B and diagnostic leaching with synthetic etchant

1. Three PCBs were cut into 2 x1.5 cm pieces for size reduction.
2. Solvent B was measured out and added to the reactor in a w/w ratio of 1-part PCBs to 5 parts solvent by mass.
3. The solvent was heated to 150 ^{o}C and the PCBs were charged to the reactor and reacted for 90 min with agitation at 100 rpm.
4. After 90 min, the solvent was drained, and the boards were rinsed with water and air dried.
5. The PCBs were transferred to a leaching column for copper extraction with synthetic etchant to determine the copper liberated by solvent swelling.

3.4.4.5 Experiment 9- Solvent swelling with solvent B with diagnostic leaching using waste etchant from PCB manufacturing

To evaluate and compare the effect of using waste etchant vs synthetic etchant in leaching the inner layer copper from solvent swelled PCBs, samples were collected from the PCB etching process at a local factory. The composition of the collected samples for leaching was as detailed in Appendix A. This etchant sample was used for diagnostic leaching of PCBs that had undergone solvent swelling with solvent B as detailed below;

1. Three PCBs were cut into 2 x 1.5 cm pieces for size reduction.
2. Solvent B was measured out and added to the reactor in a w/w ratio of 1-part PCBs to 5 parts solvent.
3. The solvent was heated to 150 ^{o}C and the PCBs were charged to the reactor and reacted for 90 min with agitation at 100 rpm.
4. After 90 min, the solvent was drained and the boards were rinsed with water and air dried.
5. The PCBs were transferred to a leaching column and leached with the waste etchant sample to determine the copper recovery.

3.4.5 Objective 4: Evaluating the effect of combining solvent swelling with mechanical treatment by shredding using an industrial grab shredder.

To determine the effect of combining mechanical treatment with solvent swelling, a comparison was made between shredding prior to solvent swelling and shredding after solvent swelling as detailed below.

3.4.5.1 Experiment 10- Solvent swelling with Solvent B with shredding prior to swelling

1. Three PCBs were shredded in 6 passes through the industrial grab shredder for size reduction and delamination.
2. Solvent B was measured out and added to the reactor in a w/w ratio of 1-part PCBs to 5 parts solvent.
3. The solvent was heated to 150 °C and the shredded PCBs were charged to the reactor and reacted for 90 min with agitation at 100 rpm.
4. After 90 min, the solvent was drained and the boards were rinsed with water and air dried.
5. The shredded PCBs were transferred to a leaching column for copper extraction with synthetic etchant to determine the copper liberated.

3.4.5.2 Experiment 11- Solvent swell with Solvent B with shredding prior to leaching

1. Three PCBs were cut into 2 x 1.5 cm pieces for size reduction.
2. Solvent B was measured out and added to the reactor in a w/w ratio of 1-part PCBs to 5 parts solvent.
3. The solvent was heated to 150 °C and the cut PCBs were charged to the reactor and reacted for 90 min with agitation at 100 rpm.
4. After 90 min, the solvent was drained and the boards were rinsed with water and air dried.
5. The PCBs were then shredded 6 passes through the industrial grab shredder for further size reduction and delamination.
6. The shredded PCBs were transferred to a leaching column for copper extraction with synthetic etchant to determine the copper liberated.

4 Results and Discussion

The results from the experiments conducted in this study are outlined and discussed in this section. The key focus of this work was centred around determining the extent to which solvent swelling liberates copper for lixiviant access from the inner layers of multilayer PCBs as well as the potential for using waste etchant as lixiviant for PCB recycling.

Experiments were carried out based on the objectives set out in this study, the following section presents the results based on the objectives as detailed below;

Objective 1- Establish the copper content of the custom-made PCB used in the study.

- Section 4.1 Copper characterization of custom-made PCBs

Objective 2-Carry out preliminary laboratory investigations to characterize the waste etchant supplied by the PCB manufacturer.

- Section 4.2 Waste etchant characterization

Objective 3- Evaluate combined solvent swelling pre-treatment and oxidation configurations modelled after the desmear process.

- Section 4.3 Solvent swelling and oxidation with potassium permanganate

Objective 4-Determine the effect of solvent swelling on copper recovery and compare the performance of NMP vs Solvent B in exposing copper for access by lixiviant.

- Section 4.4.1 Baseline experimental results of untreated PCBs leached with synthetic etchant compared to leaching with waste etchant
- Section 4.4.2 Comparison of Solvent B and NMP performance in liberating copper
- Section 4.4.3 Evaluation of diagnostic leaching with waste etchant

Objective 5- Evaluate the effect of combining solvent swelling with mechanical treatment by shredding using an industrial grab shredder.

- Section 4.5 Combined solvent swelling and mechanical shredding results.

4.1 Characterization of custom-made PCBs

4.1.1 Microsection analysis

The test coupons A-E obtained from various areas on the PCB as illustrated in Figure 21 yielded visual results of the 4 copper layers in the PCB. Each coupon provided a view of at least two copper layers and the number of layers visible was dependent on the location of the coupon as illustrated in the examples of coupons D and B in Figure 25 and Figure 26.

Figure 25 Coupon D 50X magnification view of plated through hole

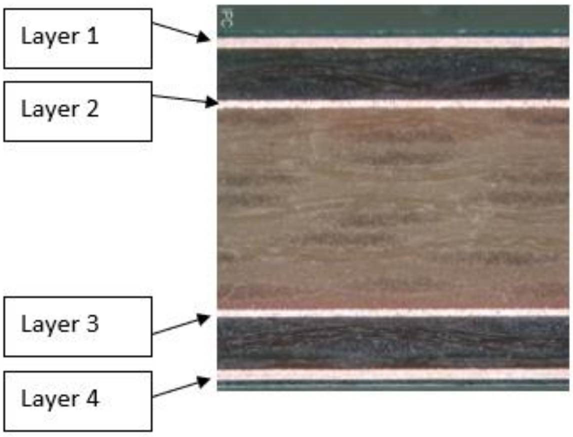


Figure 26 Coupon B 50X magnification view of internal and surface copper layers

The average copper thickness measured per layer across the five coupon samples as well as the theoretical copper thickness given in the design stack up in Figure 20 are as detailed in Table 11.

Table 11 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]	Theoretical Cu Thickness from design stack-up [µm]	Measured Cu thickness deviation from theoretical Cu thickness [%]
layer 1	40	50	45	40	35	**42**	**36**	**17%**
layer 2	33	32	-	32	30	**32**	**35**	**9%**
layer 3	33	32	35	32	-	**33**	**35**	**6%**
layer 4	50	40	-	50	50	**48**	**36**	**32%**
holes	25	-	-	35	-	**30**	**25**	**20%**
average								**17%**

On average, the measured copper thickness values deviate from the theoretical copper thickness given in the design measurements by ±17%. This deviation is expected within the manufacturing process as discussed in 2.2 and is in line with the standards set out by IPC. The resulting copper mass of the custom-made PCB was calculated to be 10.82 g, as given in Table 12 and further detailed in Appendix C. This was found to be comparable with wet chemical analysis of the same custom-made PCB completed by Maharaj., (under examination) through aqua regia digestion and ICP-MS analysis of resultant solutions which indicated each PCB to contain 11.8 g of copper.

Table 12 Calculated and theoretical PCB copper content in custom made PCBs

	Calculated copper mass [g]	**Theoretical Copper mass [g]**
layer 1	1.84	1.57
layer 2	2.15	2.37
layer 3	3.56	3.78
layer 4	2.89	2.19
holes	0.38	0.31
Total	**10.82 (+/-) 0.45g**	10.22

From the results of the current study, it was concluded that the calculated copper mass agrees with the theoretical design thickness within 6%, therefore assuming consistent manufacturing conditions, the design blueprint is an accurate tool for characterizing the copper content of the PCB. In the current study a consistent custom PCB design was utilized. In addition, it was beneficial that the design blueprint was readily available thus the copper content was easily determined both from the manufacturing blueprint as well as from the copper thickness measurements. In reality, this information would not be available and diverse types of PCBs with varying designs would be in the waste stream thus quantifying the copper content of a waste PCB stream prior to recycling is a significant challenge.

The results from the microsection analysis which provide a breakdown of the copper distribution are essential for the purposes of tracking the extent to which copper liberation from solvent swelling has taken place. In addition, the chemical characterization by Maharaj., (under examination) agrees with the microsection result with a minor deviation of +9%. Therefore, a copper content of 10.82 g per PCB was utilized to determine the copper liberation in this study. From the microsection analysis, the copper distribution throughout the PCB layers was determined as illustrated in Figure 27.

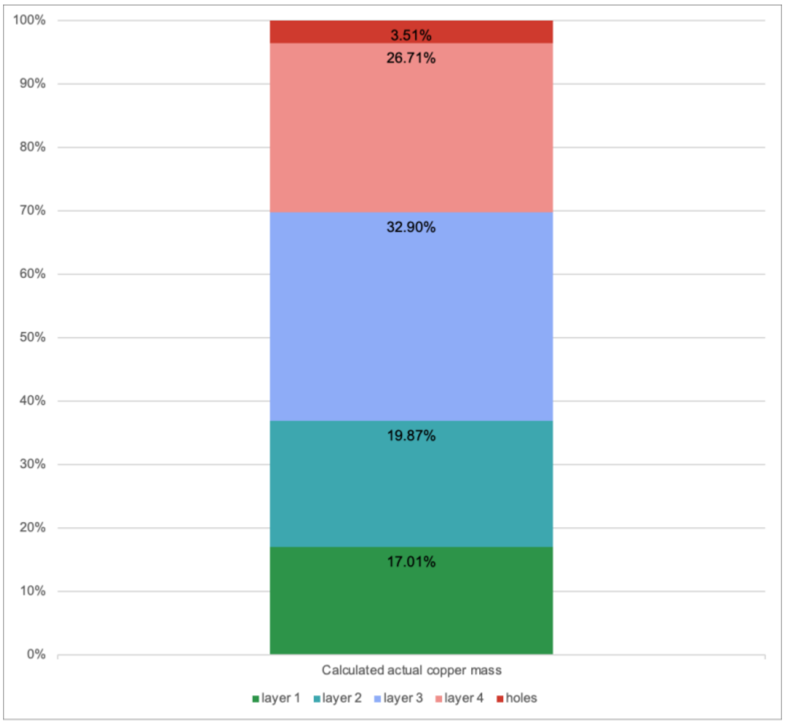


Figure 27 Copper distribution determined from microsection analysis

Layers 2 and 3 are the inner layer copper targeted for liberation in this study. From the copper distribution it was determined that these two layers constituted the majority of the copper content of the PCB with a total contribution of 52.8% as determined through copper thickness measurements from the microsection analysis and the copper area per layer as per the manufacturing blueprint in Figure 23. This leaves the balance of 47.2% to account for the surface copper comprising of layers 1 and 4, as well as the plated through holes as further detailed in Appendix C.

Upon visual observation of the microsection, the copper thickness of each layer was found to be uniform on a coupon as illustrated in Figure 26, however minor variations of a maximum of 10 µm were measured on the surface layers across coupons sampled from various areas on the PCB. This can be attributed to processing deviations from the copper plating process as detailed in section 2.2. This maximum deviation in thickness which is found on the surface copper corresponds to 1.05 g based on the total surface area given by the CAM350 software highlighted in Figure 23. Of the 47% surface copper comprising of layers 1, 4 and the holes, 31% of this surface copper area is covered by a nickel phosphorus and gold layer deposited by the ENIG process as further detailed in Appendix C.

4.2 Waste etchant characterization

Table 13 illustrates the results from the analysis of waste etchant samples collected from storage drums at a local PCB manufacturer in order of ascending copper concentration.

Table 13 Composition of waste etchant samples collected from a local PCB manufacturer

sample no.	Copper concentration	Ammonium Chloride concentration	Chloride concentration	Chloride : Copper ratio	pH
	[g/L]	[g/L]	[g/L]		
1	4.8	0	0	0	12.68
2	6.4	0	0	0	11.67
3	15.9	80.3	53	3.33	7.46
4	22.2	80.3	53	2.39	11.2
5	47.7	107.0	71	1.49	12.5
6	47.7	133.8	89	1.87	9.52
7	54.0	128.4	85	1.57	11.4
8	63.5	107.0	71	1.12	11.65
9	69.9	128.4	85	1.22	10.26
10	71.5	133.8	89	1.24	11.65
11	73.1	251.5	167	2.28	9.34
12	82.6	160.5	106	1.28	9.21
13	117.5	230.1	152	1.29	8.8
14	117.5	251.5	167	1.42	8.65
15	127.1	240.8	160	1.26	8.58
16	128.7	224.7	149	1.16	8.85
17	130.3	219.4	145	1.11	8.75
18	135.0	246.1	163	1.21	8.4
19	143.0	279.3	185	1.29	8.76
20	147.7	284	188	1.27	8.8

It was established from the samples that the copper concentration ranges from a minimum of 4.8 g/L to a maximum of 147 g/L. The results indicated a wide range in copper concentration which can be attributed to the waste etchant samples deriving from various points in the etching process outlined in Figure 8 as below;

1. Cu > 140 g/L, copper loaded etchant from etching process tank
2. 140 > Cu > 90 g/L regenerated etchant from copper recovery plant
3. 90 g/L > Copper loaded rinse water, regenerated rinse water and diluted etchant from cleaning of the etchant tank.

In addition to the copper concentration, the ammonium chloride content of the samples generally increased with increasing copper concentration. The ammonium chloride concentration in the etching process ranges from 260-300 g/L, with a chloride to copper mass ratio of 1.15-1.35 thus a decrease in ammonium chloride concentration below 260 g/L is another indication of dilution of the stream. Analysis of the pH indicates that some samples were outside the stability range of the cupric amine complex as given in Figure 9. This can be attributed to some samples originating from either rinsing of the etchant processing tank with water thus leading to pH below 8 as well as some samples originating from rinsing of the etchant tank with ammonia solution hence pH values above 10.5. On discussing with the PCB factory, this may arise from instances where maintenance of the etching line is required.

It was evident from the characterization that there is significant variation in the content of a typical PCB waste etchant stream. Thus when considering utilizing this stream for PCB recycling mixing of streams from various points in the etching process would be expected and chemical adjustments for pH and ammonium chloride would be required to maintain stability and a consistent feed concentration. In addition, considerations such as integrating the process with a copper recovery unit for example the Mecer system developed by Sigma Engineering AB., (n.d.) would aid in maintaining consistent operating conditions within the process. The waste etchant samples collected yielded an average copper concentration of 80g/L which is significantly high compared to the copper concentration of typical lixiviants as detailed in 2.3.2, highlighting that waste etchant is a particularly rich source of cupric ions therefore this stream has an excess amount of oxidant rendering it significantly beneficial for copper recovery from waste PCBs.

4.3 Solvent swelling and oxidation with potassium permanganate

Experiments 1-4 simulated the process sequence of the PCB manufacturing desmear process where solvent swelling is combined with subsequent treatment of the PCBs with alkaline potassium permanganate as detailed in section 2.2.1. Experiments 1 and 2 utilized NMP as the pre-treatment solvent and experiments 3 and 4 used Solvent B.

The maximum copper recovery out of all four experiments after 144 hours of leaching was 44.3% from PCBs that had undergone ultrasonic treatment with solvent B at 70 °C for 270 minutes in experiment 4 as illustrated in Figure 28. The remaining experiments 1-3 had recoveries ranging from 30.8% in experiment 2 to 33.2% in experiment 3 within this time frame.

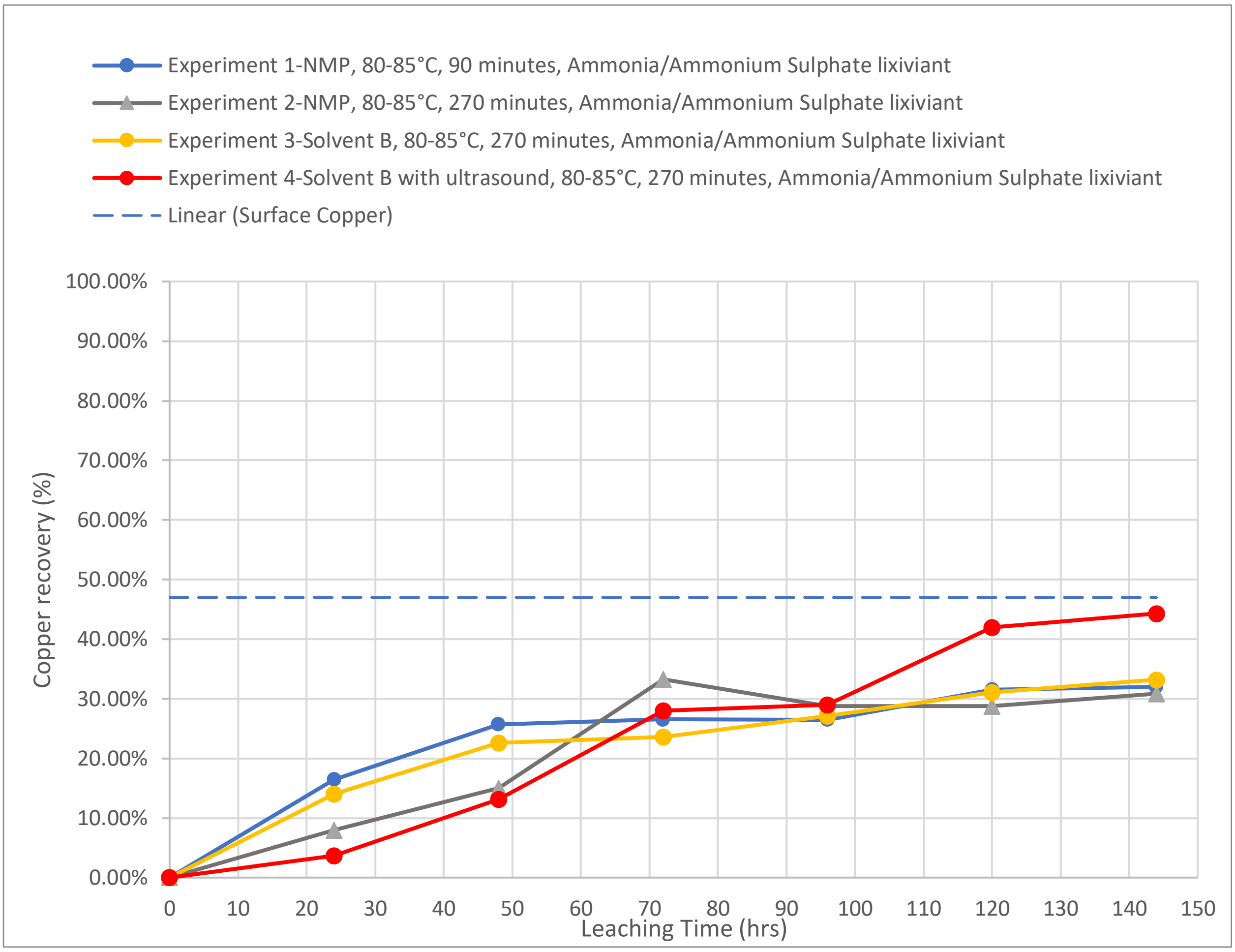


Figure 28 Copper extraction curves for experiments 1-4, solvent swelled, and potassium permanganate treated PCBs leached for 144 hours

A comparison between experiments 1 and 2 indicated that the increase in swelling time from 90 to 270 minutes using NMP as solvent at a temperature of 80-85 °C yielded no significant increases in copper liberation within the first 144 hours of leaching with an increase of only 1.2% from tripling the swelling time.

In comparison to experiment 2, experiment 3 which utilized Solvent B yielded a recovery of 33.2% which was once again a minor increase in recovery from the 30.8% in experiment 2. Overall, experiment 4 which ran for 270 minutes at 70 °C in an ultrasonic bath had the highest recovery at 44.3%, thus implying relatively more access to copper given that the leaching conditions were consistent for all 4 experiments. Monteiro et al. (2021) achieved delamination and separation of the copper foil from the fibreglass with ultrasonic NMP solvent swelling of 25 mm^2 PCB pieces at 60 °C with a reaction time of 25 hours. This temperature is considered low compared to conventional organic swelling temperatures of 135-160 °C (Kang et al., 2021), however, delamination was still possible to achieve due to the action of the ultrasound which accelerated the breaking of the internal van der Waals bonds of the BER (Tatariants et al., 2017). In the mentioned study by Monteiro et al. (2021), the degree of delamination and separation was comparable to thermostatic swelling at an elevated temperature of 153°C for 10 minutes, however the BER dissolution was higher for the heated thermostatic bath thus indicating better swelling at elevated temperatures. Despite this advantage, an energy consumption analysis further indicated that ultrasound had the benefit of a lower energy consumption at 18.65kWh compared to 45.49kWh for thermostatic (Monteiro et al., 2021).

Most of the studies detailed in literature (see Table 9) focused on the dissolution of BER in the organic solvent and the extent of metal liberation was measured by the extent of dissolution of BER as well as the ability to achieve complete separation of the copper foil from the fiberglass. Although complete delamination and separation is the target in these studies it is not necessarily a pre-requisite for lixiviant access to the inner layer copper. This is highlighted in this study by the results obtained by further leaching of the PCBs in experiments 3 and 4 where the recovery of copper increases beyond the 47% surface copper. By extending the leaching time to 456 hours, a maximum copper recovery of 62% was achieved as shown in Figure *29*. Despite the absence of any significant delamination or separation, the pre-treatment carried out in experiments 3 and 4 did result in swelling which created channels through which lixiviant could penetrate to facilitate copper extraction.

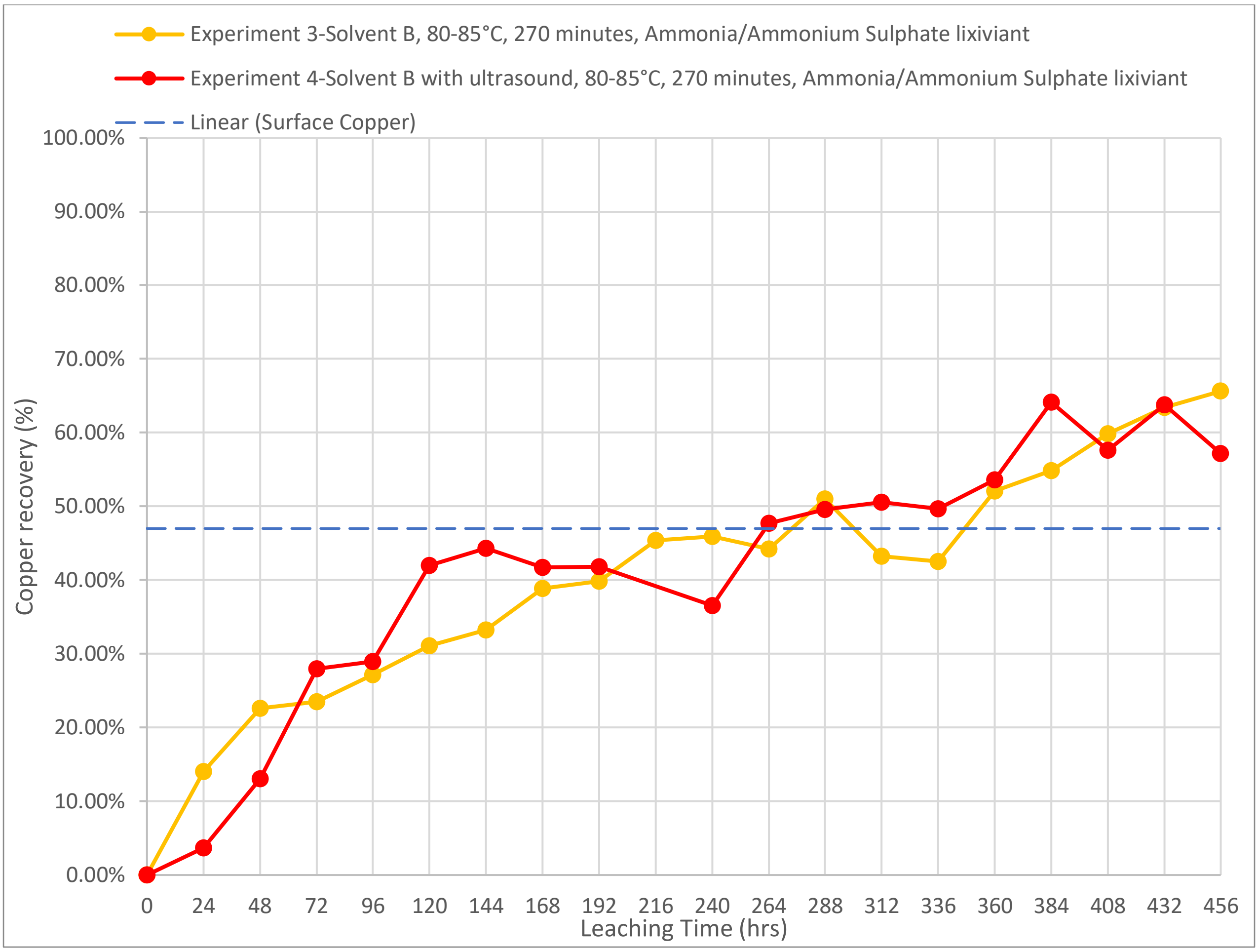


Figure 29 *Copper extraction curves with an extended leaching time of 456 hours for experiments 3 and 4*

The 57.2% recovery obtained from extending the leaching time of the PCBs swelled in the ultrasonic reactor at a low temperature in experiment 4 was comparable to the recovery of 65.6% yielded from a 15 °C increase in reaction temperature without ultrasound treatment in experiment 3.

In PCB manufacturing, solvent swelling is combined with potassium permanganate oxidation to remove minimal amounts of swelled resin smeared in the drilled holes as detailed in 2.2.1. During this process the solvent and oxidant processing parameters are carefully controlled with minimal dwell time to avoid damaging the laminate material whereas for PCB recycling the aim is to compromise the integrity of the laminate material and to dissolve as much of the resin as possible.

Figure 30 illustrates a cross sectional view of a PCB piece in experiment 4 after solvent swelling and oxidation, it can be seen that the structure of the PCB is intact, and no visible indication of delamination was observed .

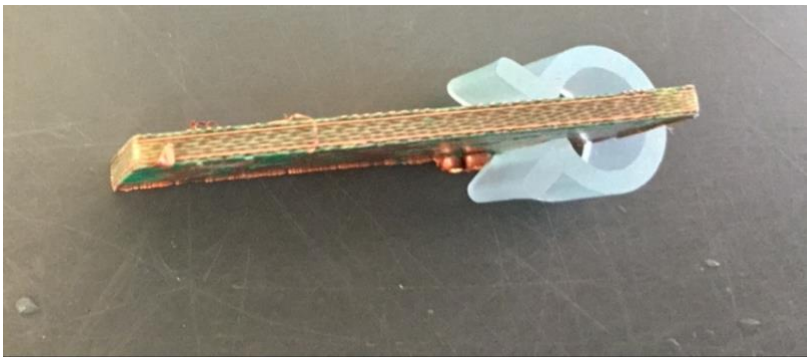


Figure 30 PCB piece from experiment 4 after swelling and oxidation, before leaching

Upon visual inspection of the PCBs after solvent swelling and potassium permanganate oxidation, the solder mask covering the underlaying surface copper had peeled off in all experiments during swelling and subsequent rinsing. Minimal amounts of solder mask remained on the non-conductive FR-4 material as illustrated by the green residue on the PCB pieces in the example of experiment 4, as can be seen in Figure 31. This remaining solder mask has no impact on leaching as it was located on the non-conductive areas that were free of copper. Analysis of the potassium permanganate residue indicated no copper dissolution in the alkaline potassium permanganate solution as shown in Table 14.

Figure 31 Solder mask layer on PCBs in experiment 4 after solvent swelling and potassium permanganate oxidation, before leaching

The remaining barrier to the lixiviant was the gold and nickel phosphorus layer as evident in Figure 31. This layer began to flake off as the leaching progressed over time. Gold was not expected to dissolve in the lixiviants used and thus it makes sense that the gold flakes remained as suspended solids. Gold deportment was outside of the scope of this study, so no further investigations were done on it. The flaking is thought to be due to the porous structure of the gold which allowed the lixiviant to diffuse through to the underlaying nickel phosphorus layer as mentioned in 3.1.2. Due to the selectivity of the ammonia lixiviant to nickel, the nickel phosphorus layer was leached thus allowing for access to the surface copper underneath the nickel and gold layer. Visual observation of residual boards after leaching in experiment 4 revealed trace amounts of gold flakes on the surface after leaching as well as trace amounts of copper. In addition, the remaining inner layer copper was visible through the laminate as seen by the brown coloured layer in Figure 32.

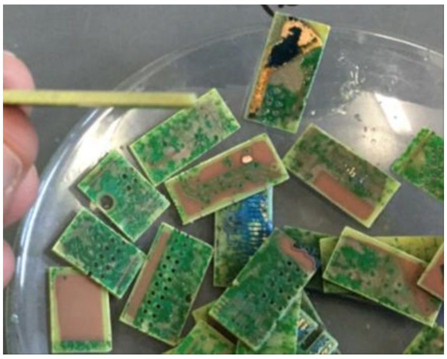


Figure 32 PCB pieces from experiment 4 after solvent swelling, potassium permanganate oxidation, and leaching

An accounting of copper losses from each step during solvent swelling for experiments 1-4 is detailed in Table 14 highlighting that the chemistry used in the solvent swelling, potassium permanganate oxidation and subsequent neutralization of manganese residue resulted in zero to minimal copper losses.

Table 14 Copper mass balance for experiments 1-4

Copper				
experiment no.	1	2	3	4
Copper extracted from leaching	32.0%	30.8%	65.6%	57.2%
Copper loss in solvent	No Cu detected	No Cu detected	0,005%	0,01%
Copper loss in potassium permanganate solution	No Cu detected	No Cu detected	No Cu detected	No Cu detected
Copper loss in Neutralizer	No Cu detected	No Cu detected	No Cu detected	No Cu detected
Calculated Unrecovered copper on PCBs	68.0%	69.2%	34.4%	42.8%

It was found that solvent swelling and potassium permanganate oxidation at low temperatures yielded a maximum copper liberation of 65.6% from PCBs that had undergone solvent swelling for 4.5 hours at a relatively low temperature characteristic of a typical desmear process. Although there is no data reported in literature regarding subsequent copper extraction from PCBs that had been pre-treated through solvent swelling, visual observations of the PCBs treated by this method revealed no delamination or separation of layers. However, despite the lack of visible delamination, access to the inner layer copper was successfully facilitated with an additional 18.6% of the total copper leached from the inner layers in this experiment. Thus, it can be concluded that this method is effective however when using ammonium sulphate with minimal initial copper concentration as lixiviant, extended leaching periods are required.

4.4 Solvent swelling

The key aspects of the experimental methodology were to determine the effect of solvent swelling as a pre-treatment method for copper recovery. Similar to experiments 1-4, column leaching was used as a means of determining the extent to which solvent swelling had achieved copper liberation. Swelling and subsequent diagnostic leaching tests were carried out twice for statistical analysis for experiment 9 and this was used as an indication of the repeatability of the process sequence used in all the experiments.

4.4.1 Baseline experimental results of untreated PCBs leached with synthetic etchant compared to leaching with waste etchant

A baseline study of untreated PCBs was carried out to determine two key factors, namely, the comparison in performance of waste etchant vs synthetic etchant, and as a control experiment for the solvent swelling tests as the PCBs had not undergone any pre-treatment that would render access to the inner layer copper.

In order to evaluate the performance of waste etchant vs synthetic etchant, column leaching was done on PCBs that were soaked in sodium hydroxide for the removal of solder mask to expose the surface copper layers, as detailed in 3.4.4.1 and 3.4.4.2 . The top and bottom layers of a PCB sample after solder mask removal are shown in Figure 33.

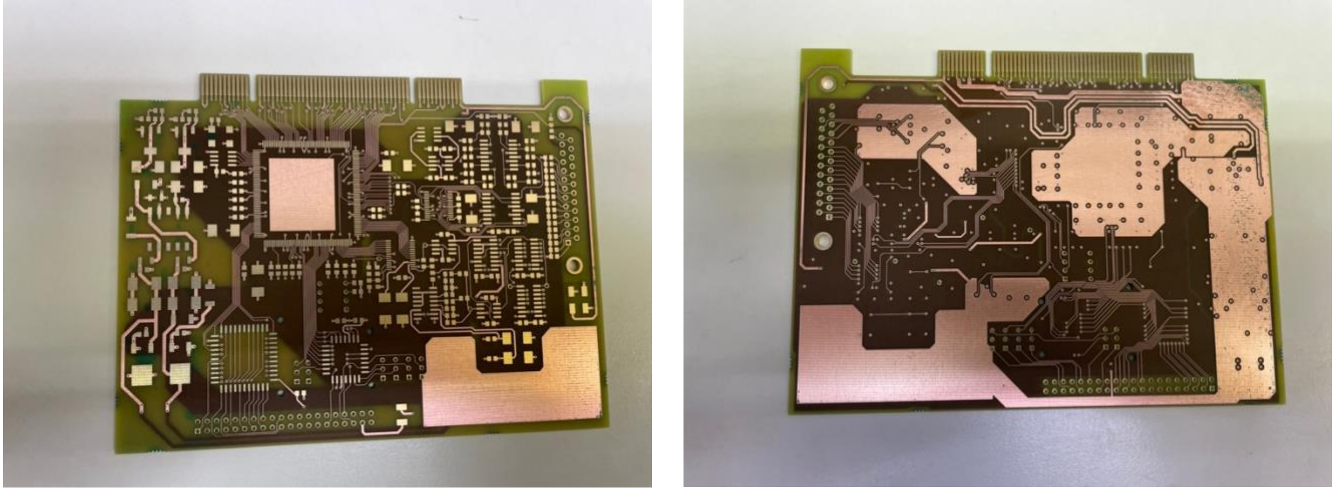


Figure 33 PCB after sodium hydroxide soak for solder mask removal

For the reasons outlined in section 2.3.2 the higher copper content (minimum 145 g/L) in waste etchant was expected to increase the leaching rate thus reducing the leaching time required for copper recovery. The synthetic etchant had a copper content of 50 g/L with an adjusted ammonium chloride concentration to maintain the chloride to copper mass ratio of the PCB etchant as recommended by the PCB manufacturer. The performance of the lixiviant was measured by the leaching time required to completely extract the surface copper. The main aim for removing the solder mask without exposing the inner layer copper was to determine the baseline performance of waste etchant and synthetic etchant without the influence of pre-treatment that would expose the inner layer copper. Figure 34 illustrates the leaching progress for experiments 5 and 6; it was established that the waste etchant achieved 100% recovery of the surface copper (47% of total copper) within the 1st hour of leaching and the synthetic etchant got close after 100 hours with full recovery of the surface copper firmly reached only after 244 hours.

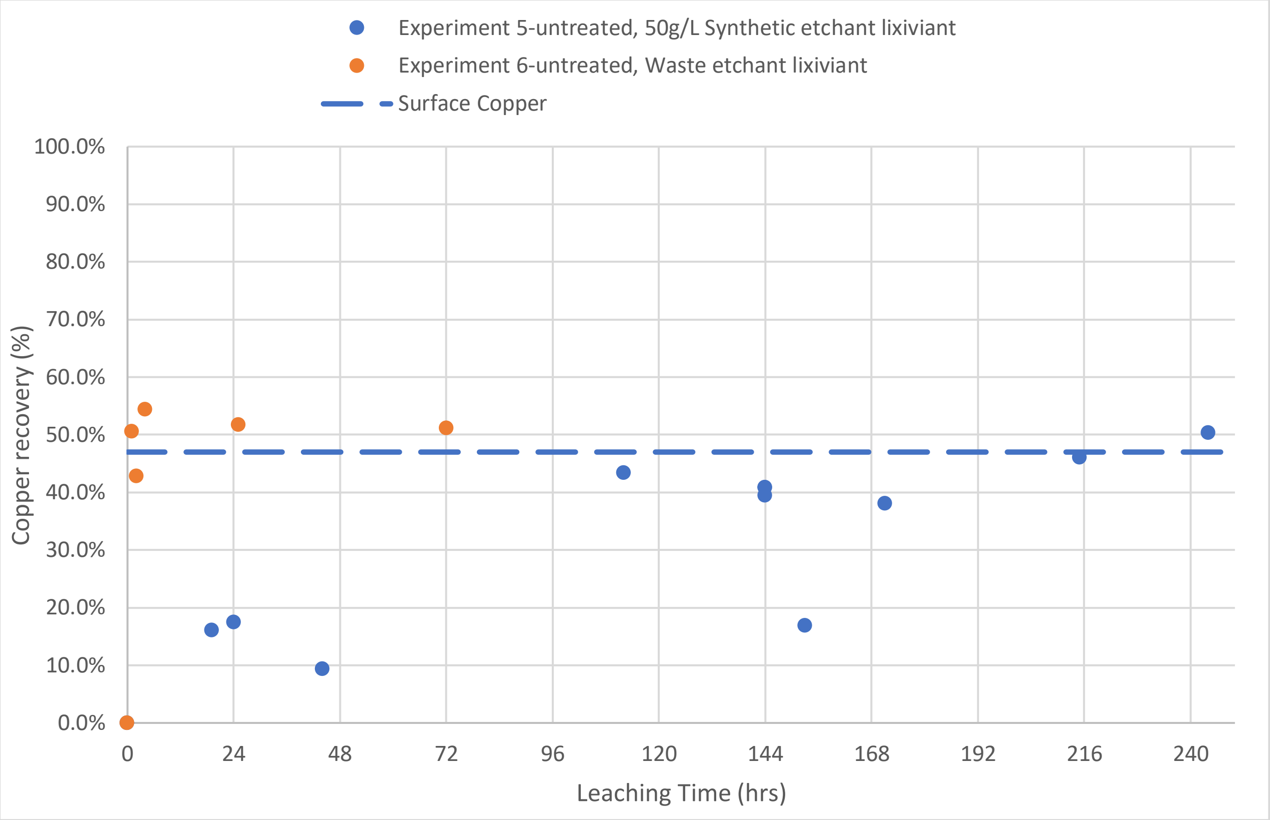


Figure 34 Copper extraction curves for untreated PCBs leached with synthetic etchant in experiment 5 and waste etchant in experiment 6

Both experiments had a recovery slightly above 47% despite no pre-treatment for inner layer liberation taking place. Washing of the column with water to remove entrained etchant and ammonia to dissolve any precipitated copper yielded an additional 5.5% recovery with waste etchant. Analysis of the leaching curve for experiment 6 highlights an initial drop in copper recovery from 50.6% after 1 hour to 42.9% after 2hrs, indicating possible precipitation within 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 as detailed in 2.3.3 and oxygen limitations were not considered a factor due to the excess supply of cupric ions which act as the oxidant for the leaching reaction, in addition the solution was exposed to air when offloading 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 35 shows the PCBs after leaching in experiments 6; it was noted that some of the residual PCBs showed a light blue precipitated copper residue after leaching thus indicating that precipitation did take place within the column.

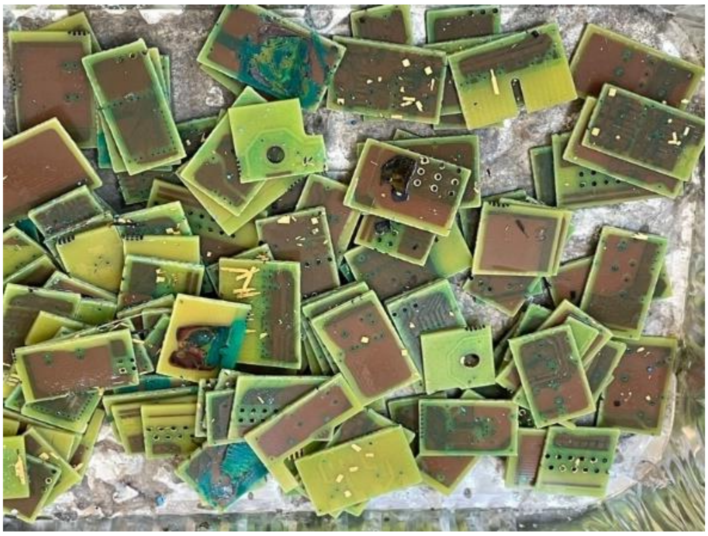


Figure 35 Untreated PCBs in experiment 6 after leaching with waste etchant

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 industrial pilot phase setup with low capital and operational costs as is characteristic of heap leaching (Fernando et al., 2019). 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. In the manufacturing environment the copper loading of the etchant is monitored and maintained within a set range. The etching system considered in this study had a maximum copper capacity of 150 g/L after which precipitation becomes a risk due to a drop in the chloride to copper ratio and pH. For this reason, the starting chloride to copper ratio was set at 1.5 to accommodate the sharp uptake of copper in the first few hours of leaching after which ammonium chloride was continuously added to the lixiviant to maintain the chloride to copper ratio within the limits advised by the PCB manufacturer. 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 lines as detailed in 2.2.2. 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 in 2.2.2.

4.4.2 Comparison of Solvent B and NMP performance in liberating copper

Figure 36 illustrates the leaching profile of PCBs that had been treated with Solvent B as detailed by experiment 7 and NMP as detailed by experiment 8.

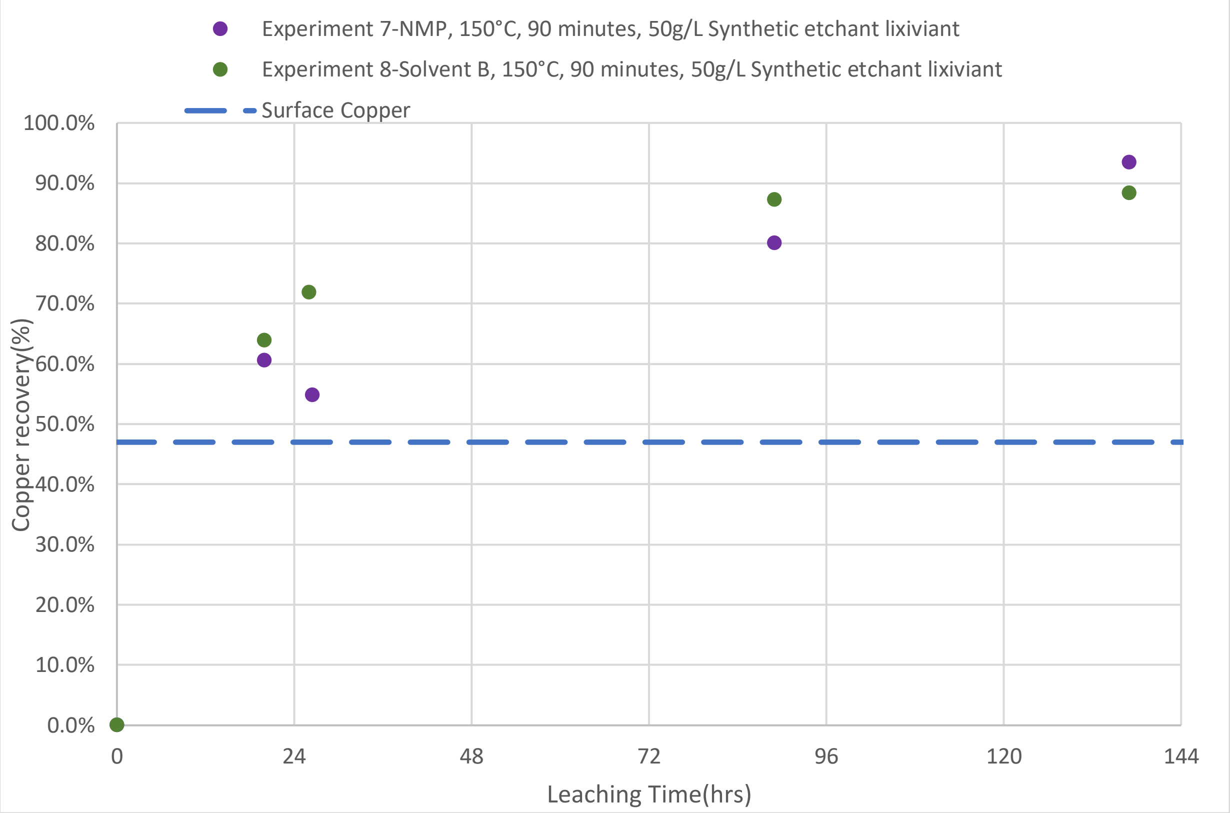


Figure 36 Comparison in performance of Solvent B in experiment 7 and NMP in experiment 8 at 150℃

The copper recovery from boards treated with NMP was 5% higher compared to boards treated with Solvent B. 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 37). This indicated that the swelling of the laminate material had progressed. There were no noticeable visual differences in the degree of delamination between experiments 7 and 8, partial delamination was observed in both instances.

Figure 37 i) Experiment 7 -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 benefits from using Solvent B given the marginally lower copper recovery as well as the increased cost from using a proprietary solvent vs NMP. 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 USD6.25/kg (ECHEMI, n.d.) which is around half the price of proprietary solvents used in the desmear process.

The benefit of using Solvent B in this study was its ease of access at the PCB factory where the experiments were conducted. In addition, a proprietary solvent such as Solvent B is often formulated with surfactants and multiple solvent combinations that are designed to optimize swelling of various types of laminates beyond FR-4 in the desmear process and may thus be beneficial to PCB recycling with varied 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 *38* illustrates residual pieces of PCBs after copper leaching. Some remaining inner layer copper was present as seen through the yellow laminate material.

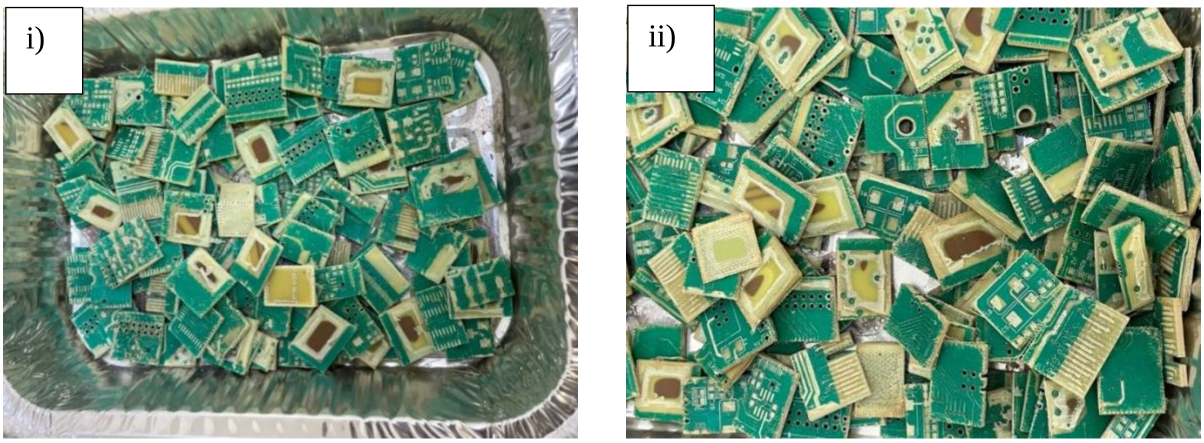


Figure 38 *i) Experiment 7-NMP swelled PCBs leached with synthetic etchant ii) Experiment 8-Solvent B swelled PCBs leached with synthetic etchant*

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 7 in Figure 39. 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.

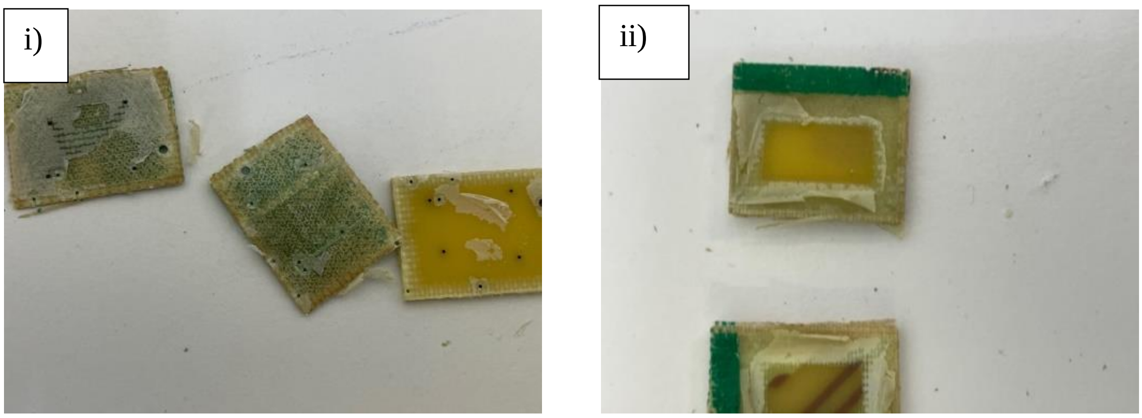


Figure 39i) Swelled PCBs with layers separated ii) residual copper trapped under pre-preg

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.

4.4.3 Evaluation of diagnostic leaching with waste etchant

One of the key questions of this study was to determine the suitability of using waste etchant for copper recovery in PCB recycling. As highlighted by the baseline leaching tests in 4.4.1, waste etchant outperformed synthetic etchant in its ability to leach copper from the surface of

PCBs in that the surface copper was completely leached within a much shorter time period of 1hr.

The leaching configuration in experiment 6 was repeated, however in experiment 9 solvent swelling pre-treatment with Solvent B at 150 °C as detailed in 3.4.4.5 was carried out to determine the performance of waste etchant in extracting the inner layer copper from PCBs. Within 72 hours, under the same leaching conditions the waste etchant was able to extract a maximum of 78% as highlighted in Figure 40. The error bars indicate a large spread in data as well as significant overlap within the first 24 hours of leaching thus indicating a large degree of variability within this period. It was thus concluded that the trend in the results obtained within this period was not statistically significant.

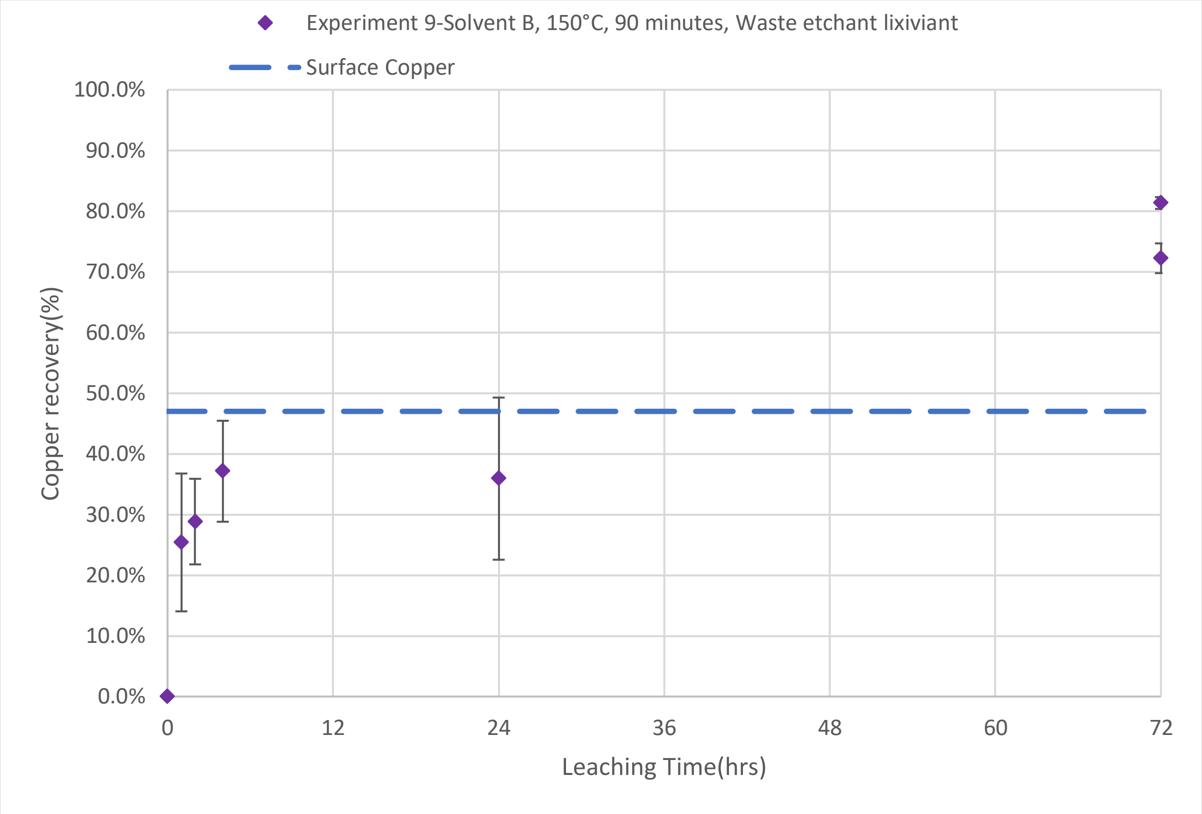


Figure 40 Copper extraction curve for solvent swelled PCBs leached with waste etchant in experiment 9

Comparing this leaching profile to that of experiment 6 as illustrated in Figure 41, it was observed that the copper recovery progressed slower within the first 24 hours of leaching in experiment 9 compared to experiment 6 where the surface copper had been completely recovered using the same waste etchant sample.

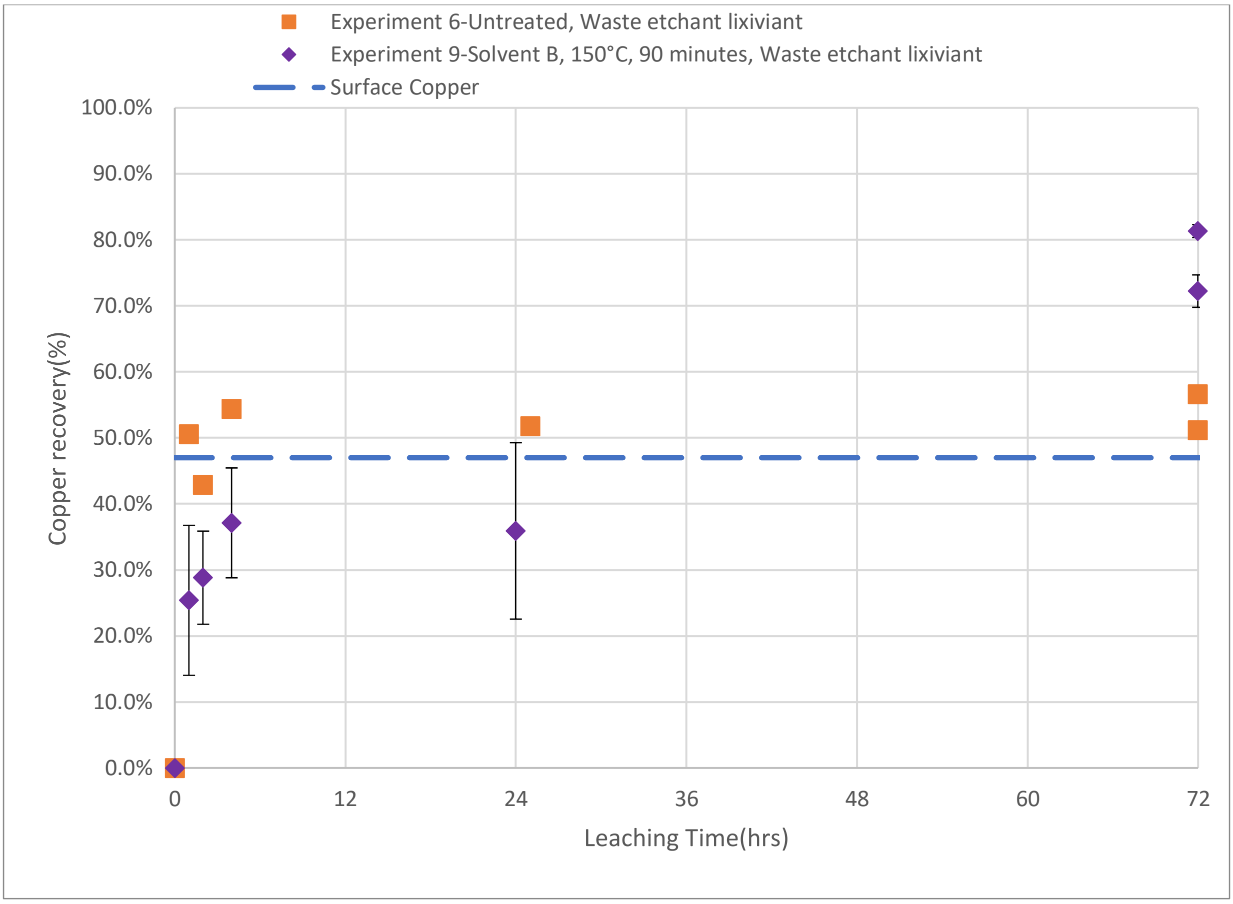


Figure 41 Comparison of waste etchant leaching profiles of untreated PCBs in experiment 6 and PCBs treated with solvent B at 150°C in experiment 9.

The slower progression may be attributed to the increased number and size of pores from solvent swelling of the PCBs, thus increasing the occurrence of channelling of the lixiviant leading to concentration gradients that may have resulted in precipitation within the column. After observing possible precipitation, the columns were washed with ammonia solution, which yielded an additional 9.1% extraction in experiment 9 and 5.5% in experiment 6. This further indicated that leaching in the columns resulted in local accumulation of lixiviant and its gradual supersaturation leading to precipitation.

Despite the concentration drop noted in the first 24 hours of leaching in experiment 9, a final copper recovery of 83.3% after 72 hours was obtained, indicating that delamination was achieved and waste etchant was able to recover 36.3% of total copper from the inner layers in addition to the 47% surface copper. The results obtained confirm that the solvent swelling method was successful in exposing the previously encapsulated copper by dissolving some of the BER in the pre-preg as illustrated in Figure 39ii). It is expected that the copper recovery would increase further were leaching allowed to progress for a longer period.

Figure 42 shows a comparison of the leaching progression of swelled PCBs leached with synthetic etchant with 50 g/L initial copper in experiment 8 to those leached with waste etchant with a starting concentration of 150 g/L in experiment 9. It was evident that the leaching of swelled boards progressed slower with waste etchant compared to synthetic etchant, but appears to ultimately reach the same extent.

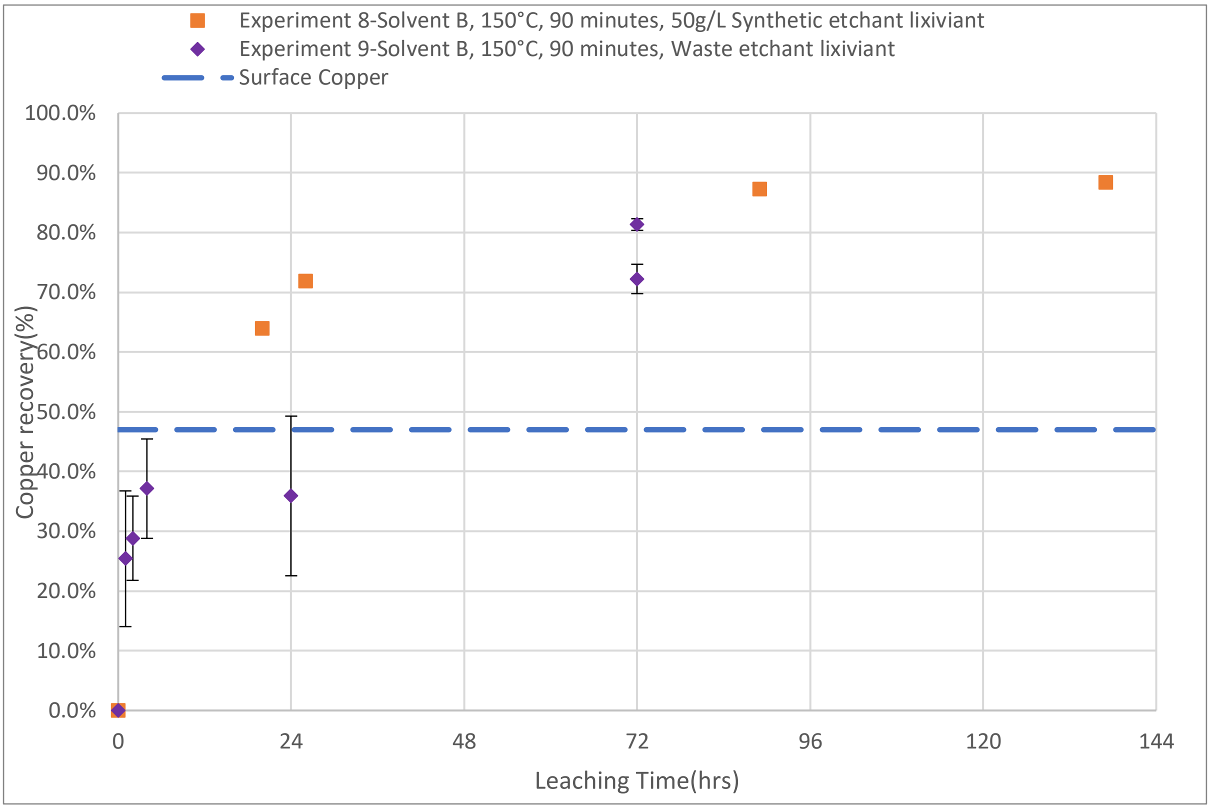


Figure 42 Comparison of PCBs treated with Solvent B at 150°C and thereafter leached with synthetic etchant in experiment 8 and waste etchant in experiment 9.

It can be concluded that waste etchant from PCB manufacturing is a suitable lixiviant for PCB recycling however there is a limit to the maximum copper loading of the etchant after which leaching begins to slow down and precipitation occurs. The degree of precipitation was observed to be lower with synthetic etchant with a lower starting copper concentration compared to waste etchant with a much higher copper concentration. As highlighted by the analysis of several waste etchant samples in section 4.2, the copper content of waste etchant streams from the PCB manufacturer varied between 4.8-147.7g/L making it possible to mix several waste etchant streams taken from various points in the etching system to attain an overall lower copper content prior to leaching, which would benefit the rate of extraction.

This would require the monitoring and adjustment of the ammonium chloride as well as the pH.

To close off the mass balance as well as to verify the copper extraction data, a select few of the residual boards from the solvent swelling experiments conducted were sent for milling followed by acid digestion and ICP analysis to determine the amount of copper remaining on the boards as detailed in Table 15.

Table 15 Copper extraction based on ICP analysis of milled and digested PCB residue after leaching vs AAS analysis of lixiviant samples

	residual PCBs after milling and aqua regia leaching	**lixiviant AAS analysis after leaching**	**deviation**
	Cu Recovery %	Cu Recovery %	
experiment 6	49.00%	56.60%	7.6%
experiment 7	96.30%	93.40%	-2.9%
experiment 8	97.90%	88.40%	-9.5%

From this it was concluded that the copper recovered from the pre-treatment steps used in this study reasonably corresponded to the copper left on the residual PCBs with a maximum deviation of 9.5% in experiment 8 as illustrated in Table 15. This may be attributed to error resulting from the high degree of dilution during AAS analysis as detailed in 3.3.2.

4.5 Combined solvent swelling and mechanical shredding

Physical pre-treatment methods have been explored in great detail in literature as outlined in 2.1.2.1. For physical pre-treatment methods, the amount of metal liberated is dependent on the particle size with a smaller particle size achieving greater metal liberation as detailed in 2.3.4.

In general, coarser fraction sizes achieved lower liberation and poor recoveries due to encapsulation of metals in the non-metallic materials. For example Prestele (2020) achieved 57.8% copper recovery from 6 pass shredding through an industrial grab shredder with a maximum particle size of 8 mm. It was noted in Prestele’s study that significant amounts of copper remained encapsulated in the non-metallic fraction.

Upon visual analysis of the residual PCB pieces post leaching in experiments 1-9 it was observed that the remaining amount of copper was encapsulated underneath the pre-preg that had not been completely dissolved by solvent swelling. It was postulated that combining solvent swelling with mechanical shredding would aid in further delamination. Hence experiment 10 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 11 was carried out to determine the extent to which delamination was aided by shredding the boards after swelling. Figure 43 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.

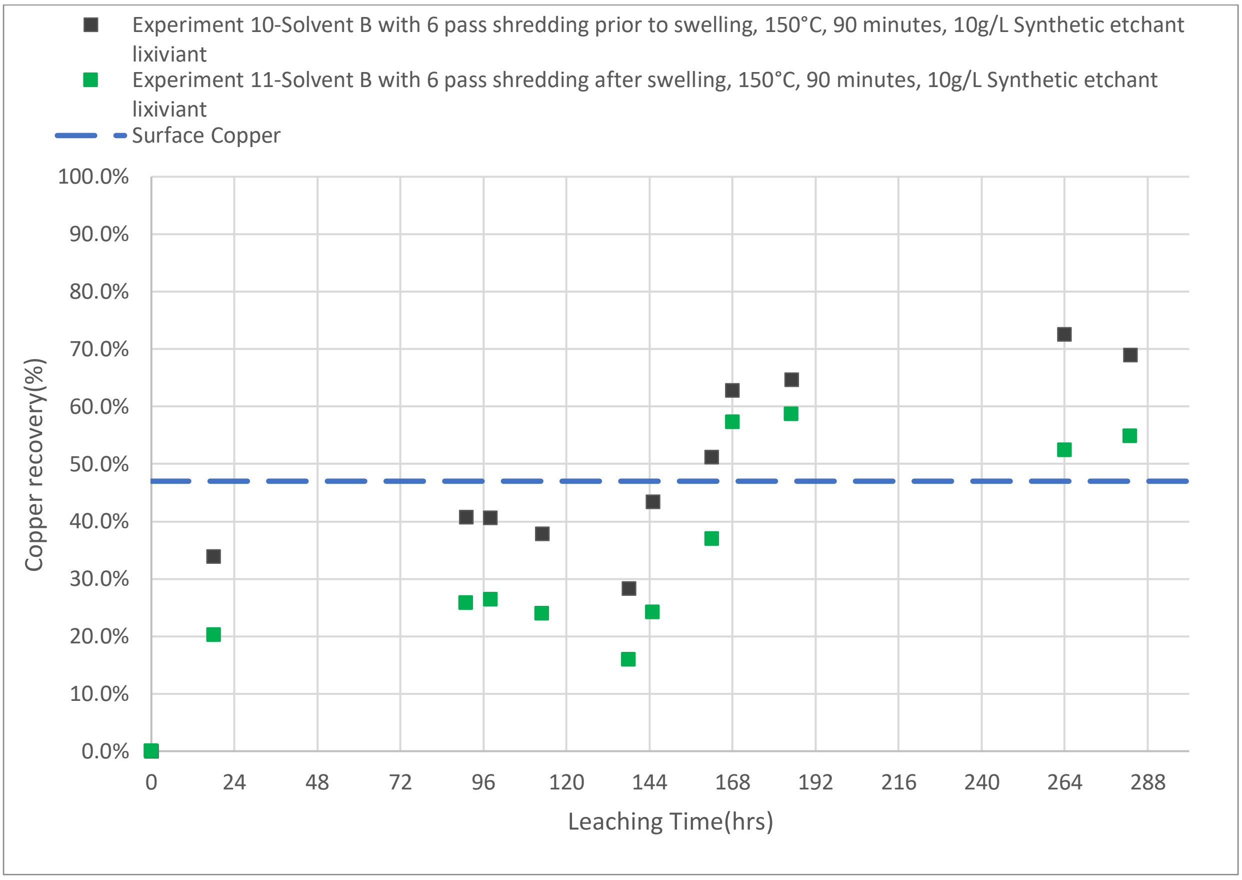


Figure 43 Copper extraction curves for PCBs shredded prior to solvent swelling in experiment 10 and after solvent swelling in experiment 11.

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 and this highlighted 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 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 hence the 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 Conclusion

The overall objective of this study was to evaluate solvent swelling as an effective pre-treatment for copper recovery in PCB recycling. In addition, a key aspect was exploring the use of 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%.

Three lixiviants were utilized in this study namely ammonia/ammonium sulphate, waste etchant and synthetic etchant. Of the three, ammonium sulphate with initial copper concentration of 100 ppm was significantly outperformed in leaching rate by waste etchant and synthetic etchant which required shorter leaching times to recover the readily accessible surface copper. Waste etchant was concluded to be a suitable lixiviant, however, 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. It was established 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. In addition, mixing of waste etchant streams could prove beneficial in diluting the copper concentration to increase the copper loading capacity of waste etchant; however, further studies into the maximum copper carrying capacity are recommended.

The maximum copper recovery was obtained from PCBs swelled with NMP at 150 °C for 90 minutes. Combining swelling with potassium permanganate oxidation yielded some copper extraction from the inner layers, however single step swelling at a higher temperature for a shorter time produced higher metal liberation and was thus the most optimal method. Pure

NMP was found to outperform the proprietary NMP-based solvent with regards to copper recovery and operating cost for an industrial process. 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.

Table 16 illustrates a summary of the copper recovery from all the leaching experiments conducted in this study.

Table 16 Summary of experimental results (solvent swelling combined with potassium permanganate treatment for experiments 1-4)

	Solvent Swelling Pre-Treatment			**Column Leaching**		
Experiment no	**Organic Solvent**	**Temperature**	**Time**	**Lixiviant**	**Time(hrs)**	**Copper recovery (%)**
1	NMP	80-85 °C	90 minutes	Ammonia/Ammonium sulphate	144	32%
2	NMP	80-85 °C	270 minutes	Ammonia/Ammonium sulphate	144	30.8%
3	Solvent B	80-85 °C	270 minutes	Ammonia/Ammonium sulphate	456	65.6%
4	Solvent B ultrasound	70 °C	270 minutes	Ammonia/Ammonium sulphate	456	57.2%
5	Untreated	-	-	Synthetic etchant	244	50.3%
6	Untreated	-	-	Waste etchant	72	51.1%
7	NMP	150 °C	90minutes	Synthetic etchant-50g/L	137	93.4%
8	Solvent B	150 °C	90minutes	Synthetic etchant-50g/L	137	88.4%
9	Solvent B	150 °C	90minutes	Waste etchant	72	81.3%
10	Solvent B	150 °C	90minutes	Synthetic etchant-10g/L	283	68.9%
11	Solvent B	150 °C	90minutes	Synthetic etchant-10g/L	283	54.9%

Overall, solvent swelling with NMP and NMP based proprietary solvent was found to be a viable method to consider for implementation in a hydrometallurgical copper extraction process. This process would be ideal to integrate with a PCB manufacturing factory due to the availability of solvent, waste etchant as well as solvent extraction and electrowinning copper recovery equipment and infrastructure thus promoting resource efficiency. Further investigations into the techno-economic viability of this process are recommended.

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7 Appendices

7.1 Appendix A

Ammonium Sulphate lixiviant preparation

Previous work by Chirume (2019) utilized ammonia/ammonium sulphate lixiviant for diagnostic copper leaching to evaluate copper liberated by various pre-treatment methods using the same custom-made PCBs used in this study. For continuity with the work completed in the research group, the lixiviant for experiments 1-4 was prepared as below (Chirume, 2019);

1. 500 ml of De-ionized water was measured out using a measuring cylinder and poured into a 2 L volumetric flask.
2. 528.56 g of Ammonium Sulphate was weighed and added to the de-ionized water and dissolved using a magnetic stirrer.
3. 597 ml of Ammonium Hydroxide was measured out using a measuring cylinder and added to the solution followed by 0.784 g of Copper Sulphate.
4. De-ionized water was added to the 2 L volumetric flask to top up to final volume while stirring with a magnetic stirrer until all the copper sulphate was dissolved.

Synthetic etchant preparation-50g/L copper concentration

Utilizing the reagents in 3.1.1, 50g/L synthetic etchant was prepared as follows.

1. 500 ml of De-ionized water was measured out using a 1 L measuring cylinder and poured into a 2 L beaker.
2. 200 g of Ammonium Chloride was weighed and added to the de-ionized water and dissolved using a magnetic stirrer.
3. 500 ml of Ammonium Hydroxide was added to the solution.
4. 100 g of copper foil was weighed and added to the beaker in small amounts at a time and the copper foil was left to dissolve. Prior to copper foil addition, 10 ml of 50% Hydrogen Peroxide was added to the solution to facilitate the dissolution of the copper foil.
5. Once the copper was dissolved, the pH of the solution was measured, and additional ammonium hydroxide was added to bring the pH between 8.5-10
6. The solution was transferred to a 2 L volumetric flask and topped up to the final volume with de-ionized water with mixing as illustrated in Figure 43.

Synthetic etchant preparation-10g/L copper concentration

Utilizing the reagents in 3.1.1, 10g/L synthetic etchant was prepared as follows.

1. 500 ml of De-ionized water was measured out using a 1 L measuring cylinder and poured into a 2 L beaker.
2. 40 g of Ammonium Chloride was weighed and added to the de-ionized water and dissolved using a magnetic stirrer.
3. 150 ml of Ammonium Hydroxide was added to the solution.
4. 20 g of copper foil was weighed and added to the beaker in small amounts at a time. Prior to copper foil addition, 10 ml of 50% Hydrogen Peroxide was added to the solution to facilitate the dissolution of the copper foil
5. Once the copper was dissolved, the pH of the solution was measured and additional ammonium hydroxide was added to bring the pH between 8.5-10
6. The solution was transferred to a 2 L volumetric flask and topped up to the final volume with de-ionized water with mixing as illustrated in Figure 44.

Figure 44 Lixiviant preparation

Waste Etchant for leaching

Table 17 Waste etchant composition range

Waste etchant sample	
Copper concentration	145-150 g/L
Chloride concentration	175-180 g/L

Potassium Permanganate solution preparation

Utilizing the reagents in 3.1.1, the potassium permanganate solution utilized in experiments 1-4 was prepared as follows.

1. 107 g of Sodium Hydroxide pellets were weighed and dissolved in 100 ml of deionized water before being transferred to a 500 ml volumetric flask.
2. 30 g of Potassium Permanganate was weighed and dissolved in the sodium hydroxide solution.

   The solution was topped up to a final volume of 500 ml while stirring with a magnetic stirrer.

Neutralizing solution preparation

Utilizing the reagents in 3.1.1, the neutralizing solution utilized in experiments 1-4 was prepared as follows.

1. Using a measuring cylinder, 35 ml of 98% sulphuric acid was added into a 500 ml volumetric flask containing 100 ml of deionized water.
2. 75 ml of Neutralizer solution was measured using a measuring cylinder and added to the solution while mixing.
3. Deionized water was added, bringing the contents to a final volume of 500 ml while mixing the solution with a magnetic stirrer.

7.2 Appendix B

Copper determination by titration for waste etchant characterization

The copper in the waste etchant samples collected from a local PCB manufacturer was analysed as follows.

1. 10 mL of the etchant solution was transferred to a 500 ml volumetric flask using a pipette
2. To prevent copper precipitation, 10ml of 25% ammonia was added to the flask prior to dilution to the 500ml mark with de-ionized water.
3. Using a pipette, 20 ml of the diluted sample was measured into an Erlenmeyer flask and the sample was diluted with 100 ml of de-ionized water. A few drops of ammonia were added to the solution while visually ensuring a clear blue colour and no precipitation.
4. 1g murexide indicator was added to the diluted sample which was titrated with 0.1 M EDTA until a colour change from green to deep violet.
5. The titre was measured, recorded, and used to calculate the copper concentration.

Ammonium Chloride Determination by titration

The ammonium chloride in the waste etchant sample was analysed by chloride titration with silver nitrate using dichlorofluorescein indicator as adsorption indicator. The chloride ion precipitates as silver chloride as silver nitrate is added as illustrated by Equation 9.

$$Ag^{+}{}_{(aq)} + Cl^{+}{}_{(aq)} \rightarrow AgCl_{(s)} \qquad \text{Equation 9}$$

The endpoint is determined when the additional silver ions left after precipitation react with the indicator to from a fluorescent yellow colour to pink (Weckel, 1939).

1. 10 mL of the etchant solution was transferred to a 500 ml volumetric flask using a pipette.
2. The flask was topped up to final volume using de-ionized water.
3. Using a pipette, 5 ml of the diluted sample was measured into an Erlenmeyer flask and diluted to 100 ml with de-ionized water.
4. 15 ml of pH 4 buffer solution was added followed by 6 drops of dichlorofluorescein indicator and titrated with 0.1 M Silver Nitrate until a permanent colour change from fluorescent yellow to pink.

The titre was measured, recorded, and used to calculate the ammonium chloride concentration.

Table 18 Experimental method parameters for experiments 1-4

Experiment no.	**Pre-treatment method**	**Solvent Swelling Conditions**		**Lixiviant**
		Solvent Temperature	Swelling Time	
1	Solvent swelling with NMP followed by oxidation with potassium permanganate at 80°C for 1 hour	80-85 °C	90 minutes	Ammonia-Ammonium sulphate
2	Solvent swelling with NMP followed by oxidation with potassium permanganate at 80°C for 1 hour	80-85 °C	270 minutes	Ammonia/Ammonium sulphate
3	Solvent swelling with Solvent B followed by oxidation with potassium permanganate at 80°C for 1 hour	80-85°C	270 minutes	Ammonia/Ammonium sulphate
4	Ultrasonic Solvent swelling with Solvent B followed by oxidation with potassium permanganate at 80°C for 1 hour	70°C	270 minutes	Ammonia/Ammonium sulphate

Table 19 Experimental method parameters for experiments 5-11

Experiment no	Pre-treatment method	Solvent Swelling Conditions		Lixiviant
		Solvent Temperature	**Swelling Time**	
5	Untreated	-	-	50g/L Synthetic etchant
6	Untreated	-	-	Waste etchant
7	Solvent swelling with NMP	150°C	90 minutes	50g/L Synthetic etchant
8	Solvent swelling with Solvent B	150°C	90 minutes	50g/L Synthetic etchant
9	Solvent swelling with Solvent B	150°C	90 minutes	50g/L Synthetic etchant
10	Solvent swelling with Solvent B with shredding prior to swelling	150°C	90 minutes	10g/L Synthetic etchant
11	Solvent swelling with Solvent B with shredding prior to leaching	150°C	90 minutes	10g/L Synthetic etchant

7.3 Appendix C

Table 20 Theoretical copper thickness determined from manufacturing build up

	Copper thickness [µm]	**Mass [g]**	**Copper distribution**
layer 1	36	1.57	15.4%
layer 2	35	2.37	23.2%
layer 3	35	3.78	37.0%
layer 4	36	2.19	21.4%
holes	25	0.31	3.0%
total		10.22	1

Table 21 Actual measured Copper thickness for each layer and calculated copper mass per layer

	copper thickness measurements [µm]					**Standard deviation [µm]**	**Standard error [µm]**	**Standard error mass[g]**	**Copper mass [g]**	**% Copper distribution**
	A	**B**	**C**	**D**	**E**					
layer 1	**40**	50	45	40	35	5.7	2.55	0.111	1.84	17.0%
layer 2	**33**	32	-	32	30	1.26	0.63	0.043	2.15	19.9%
layer 3	**33**	32	35	32	-	1.41	0.71	0.076	3.56	32.9%
layer 4	**50**	40	-	50	50	5	2.5	0.152	2.89	26.7%
holes	**25**	-	-	35	-	7.07	5	0.063	0.38	3.5%
Total								0.446	10.82	100.0%

Table 22 Calculated copper distribution

	Calculated copper distribution
layer 1	17.01%
layer 2	19.87%
layer 3	32.90%
layer 4	26.71%
holes	3.51%
Total	**100%**

Table 23 Calculated theoretical copper distribution

	Theoretical copper distribution
layer 1	15.38%
layer 2	23.21%
layer 3	36.92%
layer 4	21.45%
holes	3.04%

Table 24 Gold surface area distribution on the PCB surface-calculated from manufacturing blueprint

	copper area [m^2]	**gold area [m^2]**
layer 1	0.005	0.002
layer 2	0.008	-
layer 3	0.012	-
layer 4	0.007	0.001
holes	0.001	0.001
Total surface area	0.032	0.004
% gold surface area	-	30.77%

7.4 Appendix D

Table 25 Methods 1-4 experimental data

Method 1				
No. of boards	1	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]]	pH	Cu recovered [g]	Cu recovery[%]
0	0	10.65	0	0.0%
1	24	10.61	1.8	16.5%
2	48	10.57	2.8	25.7%
3	72	10.48	2.9	26.5%
4	96	10.37	2.9	26.5%
5	120	10.54	3.4	31.5%
6	144	10.54	3.5	32.0%
Method 2				
No. of boards	1	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery[%]

0	0	10.65	0	0.0%
1	24	10.55	0.9	8.0%
2	48	10.59	1.6	15.0%
3	72	10.69	3.6	33.3%
4	96	10.58	3.1	28.8%
5	120	10.49	3.1	28.7%
6	144	10.45	3.3	30.8%
Method 3				
No. of boards	**1**	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]]	pH	Cu recovered [g]	Cu recovery[%]
0	0	10.64	0	0.0%
1	24	10.53	1.5	14.0%
2	48	10.4	2.5	22.7%
3	72	10.29	2.5	23.5%
4	96	10.36	2.9	27.1%
5	120		3.4	31.1%
6	144	10.51	3.6	33.2%
7	168	10.3	4.2	38.9%
8	192	10.34	4.3	39.9%
10	216	10.19	4.9	45.4%
11	240	10.26	5.0	45.9%
12	264	10.28	4.8	44.3%
13	288	10.16	5.5	51.0%
14	312	10.29	4.7	43.2%
15	336	10.34	4.6	42.5%
16	360	10	5.6	52.1%
17	384	9.94	5.9	54.9%
18	408	10.58	6.5	59.9%
19	432	10.24	6.9	63.4%
20	456	10.45	7.1	65.6%
Method 4				
No. of boards	**1**	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery[%]
0	0	10.51	0	0.0%
1	24	10.45	0.4	3.7%

2	48	10.45	1.4	13.1%
3	72	10.23	3.0	28.0%
4	96	10.38	3.1	29.0%
5	120	10.38	4.5	42.0%
6	144	10.45	4.8	44.3%
7	168	10.35	4.5	41.7%
8	192	10.35	4.5	41.8%
10	240	10.22	4.0	36.5%
11	264	10.22	5.2	47.7%
12	288	10.25	5.4	49.6%
13	312	10.25	5.5	50.6%
14	336	10.22	5.4	49.7%
15	360	10.33	5.8	53.6%
16	384	10.34	6.9	64.1%
17	408	10.1	6.2	57.6%
18	432	10.1	6.9	63.8%
19	456	10.22	6.2	57.2%

Table 26 Methods 5-8 experimental data

Method 5				
No. of boards	**3**	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery[%]
0	0	10	0	0.0%
1	19	10	5.2	16.1%
2	24	10	5.7	17.5%
3	44	9.05	3.0	9.3%
4	112	9.78	14.1	43.4%
5	144	10.09	12.8	39.5%
6	144	-	13.2	40.8%
7	144	-	13.2	40.8%
8	153	10.2	5.5	16.9%
9	171	10.21	12.4	38.1%
10	215	10.2	15.0	46.1%
11	244	10.2	16.3	50.3%
Method 6				
No. of boards	**3**	**Cu content per board**		**10,82g**

sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery[%]
0	0	8.83	0	0.0%
1	1	8.84	16.4	50.6%
2	2	8.77	13.9	42.9%
3	4	8.62	17.6	54.4%
4	25	8.58	16.8	51.8%
5	72	-	16.6	51.1%
5	72		18.4	56.6%
Method 7				
No. of boards	**3**	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery[%]
0	0	10.2	0	0.0%
1	20	10.2	19.7	60.6%
2	26.5	10.2	17.8	54.9%
3	89	10.05	26.0	80.0%
4	137	10.2	30.3	93.4%
Method 8				
No. of boards	**3**	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery[%]
0	0	10.2	0	0.0%
1	20	10.2	20.8	63.9%
2	26	10.2	23.3	71.9%
3	89	10.05	28.3	87.3%
4	137	10.2	28.7	88.4%

Table 27 Method 9 experimental data

Method 9									
No. of boards	**3**	**Cu content per board**		**10.82g**					
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]		Cu recovery[%]		Average Cu recovery	Standard deviation	Standard error
0	0	8.83	0	0.0	0.0%	0.0%	0.0%	0%	0%
1	1	8.78	15.6	0.9	48.1%	2.7%	25.4%	16%	11%

2	2	8.81	13.9	4.8	42.9%	14.7%	28.8%	10%	7%
3	4	8.55	17.5	6.6	53.8%	20.5%	37.1%	12%	8%
4	24	8.62	20.3	3.0	62.6%	9.2%	35.9%	19%	13%
5	72	-	21.9	25.0	67.3%	77.1%	72.2%	3%	2%
wash	72	-	27.0	25.8	83.3%	79.4%	81.3%	1%	1%

Table 28 Method 10-11 experimental data

Method 10				
No. of boards	3	Cu content per board		10.82g
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery(%)
0	0	10	0	0.0%
1	18	10.47	11.0	33.9%
2	91	10.42	13.2	40.8%
3	98	10.26	13.2	40.6%
4	113	10.37	12.3	37.8%
5	138	10.66	9.2	28.3%
6	145	10.31	14.1	43.4%
7	162	10.45	16.6	51.2%
8	168	10.26	20.4	62.9%
9	185	10.15	21.0	64.6%
10	264	-	23.6	72.6%
11	283	10.2	22.4	68.9%
Method 11				
No. of boards	**3**	**Cu content per board**		**10.82g**
sample no.	Elapsed time[hrs]	pH	Cu recovered [g]	Cu recovery[%]
0	0	10	0	0.0%
1	18	10.38	6.6	20.3%
2	91	10.4	8.4	25.9%
3	98	10.22	8.6	26.5%
4	113	10.28	7.8	23.9%

5	138	10.63	5.2	16.0%
6	145	10.65	7.9	24.3%
7	162	10.24	12.0	36.9%
8	168	10.27	18.6	57.3%
9	185	10.26	19.1	58.7%
10	264	-	17.0	52.4%
11	283	10.25	17.8	54.9%